Chapter 4
ROOM TEMPERATURE EPR STUDIES OF Ni(II) ION IN A PARAMAGNETIC HOST LATTICE: A CASE OF LARGE D

Introduction:

Imidazole, an organic base, is a biologically important compound, which is often seen to bond with many proteins, enzymes and histidine ligands, behaves as a proton donor as well as acceptor and hence it takes part in many catalytic processes (e.g., enzyme reaction of chymotrypsin, in which the imidazole in histidine unit behaves as proton donor and in enzyme-tryosine-ATP complex reaction). In addition, Ni(II) ion is also required for biosynthesis of the enzyme Urease, which occur in many plants and other cells [1]. In methanogenic bacteria factor F430, Ni(II) is coordinated with four pyrrol nitrogens. Two other Ni(II) enzymes are also known, hydrogenase and carbon monoxide dehydrogenase. Study of imidazole complexes are of much interest because of the role played by the imidazole molecule in the binding of metals in proteins [2]. Hence the attempt has been made to incorporate Ni(II) ion into the lattice, hexa(1-imidazole) cobalt(II) dichloride tetrahydrate where the cobalt ion is surrounded by six imidazole units in distorted octahedron and mono crystal EPR and optical studies are done to understand the symmetry around the metal ion, chemical bonding and covalency of metal-ligand bond, etc.

Nickel(II) is a non Kramers ion with d⁸ electronic configuration. EPR resonance lines are generally observed below 77 K [3,4] and EPR studies have been carried out on nickel ion in various oxidation states also [5-10]. However, very few systems have been reported in literature, where the fine structure of Ni(II) is observed.
at ambient temperature. The single crystal EPR study of magnetically concentrated Ni(C₃H₆N₂)₆(NO₃)₂ [11] shows axially symmetric spin-Hamiltonian with $E = 0$, $D = 882$ mT and $g = 2.185$. Single crystal EPR study of Ni(II) ion in hexakis pyrazole complexes of zinc and cadmium [12] have been reported at Q-band. In case of Ni(II) doped in hexaimidazole zinc(II) dichloride tetrahydrate [13] at X-band frequency gives rise rhombic spin Hamiltonian and has been confirmed through optical absorption spectrum also [14]. In addition, the host lattice has given interesting results, when doped with Cu(II). As the host lattice behaves like diamagnetic at room temperature, single crystal EPR studies have been carried out, as if the dopant is present in a diamagnetic host. In addition, superhypefine from the ligand nitrogen nuclei have been observed, even at room temperature, as discussed in detail in Chapter 3. Hence, the host lattice has been selected for a non-Kramers ion. In this chapter, the results obtained from EPR and optical studies on Ni(II) ion in Hexaimidazole Cobalt(II) dichloride tetrahydrate have been presented. Moreover, these results are correlated with optical data to obtain various bonding parameters.

Experimental:

Single crystal of Ni(II) doped hexaimidazole cobalt dichloride tetrahydrate (abbreviated as HCDT) has been grown at ambient temperature by slow evaporation of aqueous imidazole and cobaltous chloride in the ratio of 6.1 to which dil HCl (to maintain neutral pH) and 0.05% of nickel(II) chloride by weight are added. The Ni(II) doped HCDT is crystallized out in 15 days. Crystal rotations have been done along the three orthogonal axes, namely $b$, $a^*$ and $c^*$ in JEOL JES TE100 ESR.
spectrometer working at X-band frequency. Here, b is the crystallographic b-axis, a* is perpendicular to b in ab plane and c* is perpendicular to both b and a*. Optical spectrum has been recorded using Beckman Coulter DU 530 spectrophotometer.

Crystal structure:

The IR spectrum and powder X-ray data of HCDT is almost identical with that of HZDT (hexaimidazole zinc(II) dichloride tetrahydrate) system. Hence, the crystal structure of isomorphous HZDT is assumed for HCDT lattice, in explaining the EPR analysis, since the crystal structures of HCDT is not available. HZDT belongs to triclinic crystal group with unit cell dimensions a = 1.07, b = 0.94 and c = 0.84 nm; α = 120, β = 97, γ = 98° and Z=1 [15]. In the lattice, the metal ion is in distorted octahedral environment. The detail discussion on the crystal structure of HZDT is given in Chapter 3.

Results and discussion:

EPR studies.

A single crystal of fine shape and optimum size has been selected for EPR measurements. A few representative single crystal EPR spectra of Ni(II)/HCDT, when the crystal is rotated along c*-axis are given in Figure 4.1. It is clear from these spectra that a single strong line is observed throughout the rotations, which is highly anisotropic. Another broad line, which is almost invariant is seen near the DPPH line (strong and sharp line at the centre of the spectrum). In order to get spin Hamiltonian parameters, single crystal rotations are done along three orthogonal axis namely
Figure 4.1 Single crystal EPR spectra of Ni(II)/HCDT, when the crystal is rotated along crystallographic c*-axis. In the EPR spectrum, starting field is 0 mT and end field is 650 mT. Frequency = 9 09362 GHz.
a*, b and c* respectively. One isofrequency plot, when the crystal rotation is done in a*b plane is given Figure 4.2. Since, Ni(II) ion is having $t_{2g}^6e_g^2$ electronic configuration (S = 1) in an octahedral symmetry, it gives rise to two allowed EPR resonances. These two transitions are attributed to $|-1\rangle \leftrightarrow |0\rangle$ and $|0\rangle \leftrightarrow |+1\rangle$. A weak resonance also be observed in some cases, due to the forbidden transition $\Delta M_s = \pm 2$, i.e., $|-1\rangle \leftrightarrow |+1\rangle$. This line will generally appear at half-field position, i.e., around $g = 4$. However, as mentioned before, in the present study, during single crystal rotation of Ni(II)/HCDT at room temperature (300 K) in X-band frequency, a maximum of two resonances at few orientations and only one resonance at most other orientations corresponding to $|-1\rangle \leftrightarrow |0\rangle$ is observed. This kind of observation suggest that only one type Ni(II) ion with a large ZFS value is present. It also indicates that the X-band energy is insufficient to observe the other allowed transition, i.e., $|0\rangle \leftrightarrow |+1\rangle$ and the forbidden transition $\Delta M_s = \pm 2$ corresponding to $|-1\rangle \leftrightarrow |+1\rangle$, which is seen in an earlier case, when Ni(II) is doped into HZDT lattice [13]. As the number of resonances is only one, the isofrequency plot for all the three mutually orthogonal planes is drawn in one figure and is given in Figure 4.3.

Before proceeding to analyze the single crystal EPR data, an attempt has been made to study the powder spectrum, since it may give some idea about the nature of spin Hamiltonian parameters. The EPR spectrum of the polycrystalline sample of Ni(II)/HCDT is recorded and given in Figure 4.4. It consists of a broad line and a sharp line ($\sim 610$ mT), near the end of our X-band field. This immediately suggests that the system, under study, has a very large zero field splitting (ZFS) value. Due to this very large ZFS, the other resonance is not noticed. The approximate ZFS value (D) has
Figure 4.2: Isofrequency plot for Ni(II)/HCDT when the crystal is rotated along \(a^*\)-axis. Open circles corresponds to experimental values, whereas solid line corresponds to theoretical values. Frequency = 9 09236 GHz.
Figure 4.3  Resultant isofrequency plot in all three planes for Ni(II)/HCDT at room temperature. Open circles corresponds to experimental values, whereas solid line corresponds to theoretical values.
Figure 4.4  Polycrystalline EPR spectrum of Ni(II)/HCDT recorded at room temperature. Frequency = 9 39822 GHz
been evaluated from the powder spectrum, assuming that the impurity is in an axially symmetric environment. In other words, D is calculated from the expression by assuming $E = 0$ and $g = 2.2$ (normal g value observed for Ni(II) ion) [11],

$$B = [B_0(B_0 + D)]^{1/2}$$

here $B_0 = hν/βg$. A $D$ value of $\sim 910$ mT is deduced from the above expression. This value will help us to analyse the single crystal data.

From the information gained from polycrystalline EPR spectrum, single crystal EPR resonance field positions have been fitted with EPR-NMR program to obtain proper spin Hamiltonian parameters using the spin Hamiltonian

$$\mathcal{H}' = β B \cdot g S + S \cdot D \cdot S$$  \[4.1\]

In first term, $B$ is $(1 \times 3)$ matrix, $g$ is $(3 \times 3)$ matrix, $S$ is $(3 \times 1)$ matrix. In second term, $S$ is $(1 \times 3)$ matrix, $D$ is $(3 \times 3)$ matrix, $S$ is $(3 \times 1)$ matrix.

As the number of resonance lines is only one, a new procedure has been adopted, as discussed in one of our previous communications [13]. The procedure adapted in trial and error method is as follows. Initially, all the three $g$ values namely $g_{xx}$, $g_{yy}$ and $g_{zz}$ are assumed to be 2.2 (normal g value observed for Ni(II) ion). We also assumed that the orthogonal Cartesian framework XYZ coincides with the crystallographic $a^*b^*c^*$ framework. For example, if the crystal rotation is done in $b^*c^*$ plane, $D_{yy}$, $D_{tz}$ and $D_{yz}$ components of $D$ have been optimized. With this new $D$ values, the second isofrequency plot is used to get another set of three new $D$ values. With this set of new $D$ values, the third isofrequency plot has been used to get one more set of three $D$ values. Out of these nine $D$ values, $D_{xx}$, $D_{yy}$ and $D_{zz}$ appear twice. The average of these two values is taken and the whole procedure is repeated, until a good agreement is obtained between two successive iterations. Once the approximate $D$ matrix is obtained, then the data in all the three planes is combined and all the
elements of D (of course, five elements only) have been optimized. The same
procedure is repeated by adjusting the g values namely $g_{xx}$, $g_{yy}$ and $g_{zz}$. The spin
Hamiltonian parameters, thus obtained are given in the Table 4.1. For comparison, the
direction cosines of metal-nitrogen bonds have also been given in the table. It is clear
from the table, that the direction cosines of one of the g values, $g_{zz} (=2.392)$ is found to
be aligned along $N_1$-$Zn$-$N_4$ direction, the angle of deviation between them is only $2.5^\circ$.
This immediately suggests the accuracy of our calculations and also indicate that the
impurity Ni(II) ion has occupied the substitutional position in place of the host ion
Co(II) in the lattice. The orthorhombic nature of the g values indicates that the
symmetry around the central Ni(II) ion is lower than axial. A similar observation can
also be obtained from the D matrix. It is generally observed that the direction cosines
of the D matrix do not coincide with the direction cosines of the g matrix. A similar
observation is noticed here also. One of the eigen values of D matrix, i.e., 734.1 mT,
corresponds to $D_{zz}$. This gives rise to a D value of around 1100 mT. The D value
obtained from powder spectrum is around 910 mT. This difference can be attributed to
non availability of all resonances in crystal/powder spectra and the assumption of g. A
Q-band work is a must to confirm these results. Moreover, the eigen values of D
indicate that axial symmetry is not retained. The parameter E, which measures the
deviation from axial symmetry, is 27.6 mT.

With the data given in Table 4.1, the isofrequency plots are simulated in all the
three planes. The resultant isofrequency plot in all three planes is also given in
Figure 4.3. In the figure, the circles denote experimental points, whereas the solid line
corresponds to theoretical curve. The agreement is satisfactory.
Table 4.1: Spin Hamiltonian parameter obtained for Ni(II) ion in cobalt hexaimidazole dichloride tetrahydrate from single crystal analysis.

<table>
<thead>
<tr>
<th></th>
<th>Eigen Values</th>
<th>Direction cosines</th>
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<tr>
<td></td>
<td></td>
<td>a*</td>
</tr>
<tr>
<td><strong>g matrix</strong></td>
<td></td>
<td>2.392</td>
</tr>
<tr>
<td>2.276</td>
<td>0.069</td>
<td></td>
</tr>
<tr>
<td>2.181</td>
<td>-0.131</td>
<td></td>
</tr>
<tr>
<td>2.185</td>
<td></td>
<td>2.198</td>
</tr>
<tr>
<td><strong>D matrix (mT)</strong></td>
<td></td>
<td>2.051</td>
</tr>
<tr>
<td>-68.7</td>
<td>-351.3</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>-373.1</td>
<td></td>
</tr>
<tr>
<td>64.5</td>
<td></td>
<td>3.741</td>
</tr>
<tr>
<td><strong>N1-Zn-N4</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>N2-Zn-N5</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>N3-Zn-N6</strong></td>
<td></td>
<td>0.493</td>
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<tr>
<td></td>
<td></td>
<td>0.416</td>
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<tr>
<td></td>
<td></td>
<td>0.803</td>
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As mentioned earlier, a single resonance has been obtained in most of the single crystal rotations. During the cooling of the sample, an increase in D value is noticed. Hence, variable temperature studies could not be carried out at X-band frequencies. Work with Q-band frequency at different temperatures may give an idea about relaxation mechanism, if a change in line width is noticed. Lack of this facility makes the above conclusions as tentative.

**Optical studies**

The optical studies of Ni(II) ion has been carried out by a number of authors [14, 16-19]. Since the EPR study shows rhombic symmetry for the metal ion, optical spectrum has been recorded to verify the electronic structure around Ni(II) ion. Figure 4.5 gives the optical spectrum of Ni(II)/HCDT in methanol solvent at room temperature. It consists of four peaks, situated at 26588 (376 nm), 15919 (628 nm), 13565 (737 nm), 9967 cm⁻¹ (1003 nm) respectively. Out of these four peaks, the three intense peaks at 26588, 15919 and 9967 cm⁻¹ can be assigned to spin allowed transitions $^3\text{A}_2\text{g}(F) \rightarrow ^3\text{T}_{1g}(P)$, $^3\text{A}_2\text{g}(F) \rightarrow ^3\text{T}_{1g}(F)$ and $^3\text{A}_2\text{g}(F) \rightarrow ^3\text{T}_{2g}(F)$ respectively as shown in Figure 4.6 and the weak transition at 13565 cm⁻¹ can be attributed to the spin forbidden transition $^3\text{A}_2\text{g}(F) \rightarrow ^1\text{E}_g(D)$.

The theoretical calculation yields, the crystal field splitting parameter Dq as 995 cm⁻¹ and the inter electron repulsion parameters B and C are estimated as 855 cm⁻¹ and 13565 cm⁻¹ respectively. The peak head positions are also calculated and given the Table 4.2. The evaluated B value is 79% of the free Ni(II) ion (1084 cm⁻¹). The ratio of B, C with the inter electron repulsion parameters of free Ni(II) ion are found to
Figure 4.5: Room temperature optical absorption spectrum of Ni(II)/HCDT dissolved in methanol solvent.
Figure 4.6. A simplified Tanabe-Sugano diagram representing the spin allowed transitions.
Table 4.2: Peak head position calculated from optical absorption spectrum of Ni(II)/HCDT.

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Observed</th>
<th></th>
<th>Calculated</th>
<th></th>
<th>Deconvoluted</th>
<th></th>
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<tr>
<td></td>
<td>(cm(^{-1}))</td>
<td>(nm)</td>
<td>(cm(^{-1}))</td>
<td>(nm)</td>
<td>(cm(^{-1}))</td>
<td>(nm)</td>
</tr>
<tr>
<td>(3^3A_{2g}(F) \rightarrow 3^3T_{1g}(P))</td>
<td>26588</td>
<td>376</td>
<td>26596</td>
<td>375.9</td>
<td>26462</td>
<td>378</td>
</tr>
<tr>
<td>(3^3A_{2g}(F) \rightarrow 1^1T_{1g}(D))</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>23310</td>
<td>429.4</td>
</tr>
<tr>
<td>(3^3A_{2g}(F) \rightarrow 3^3T_{1g}(F))</td>
<td>15919</td>
<td>628</td>
<td>16085</td>
<td>621.7</td>
<td>16425</td>
<td>608.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14892</td>
<td>671.6</td>
</tr>
<tr>
<td>(3^3A_{2g}(F) \rightarrow 1^1E_{g}(D))</td>
<td>13565</td>
<td>737</td>
<td>13576</td>
<td>736.6</td>
<td>13533</td>
<td>738.9</td>
</tr>
<tr>
<td>(3^3A_{2g}(F) \rightarrow 3^3T_{2g}(F))</td>
<td>9967</td>
<td>1003</td>
<td>9950</td>
<td>1005</td>
<td>10098</td>
<td>990.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9389</td>
<td>1065</td>
</tr>
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</table>
0.79 and 0.74 respectively. EPR and optical data are correlated to get spin-orbital coupling parameter (λ) using the expression

\[ g_{\text{so}} = 2.0023 - 8\lambda /\Delta \]  

where \( \Delta \) is the crystal field splitting parameter (10Dq). A value of -263 cm\(^{-1}\) has been evaluated for \( \lambda \). The reduction of spin-orbital interaction parameter from the free ion value yields the covalency of metal-ligand bonds. In the present case, the covalency of metal-ligand bond is found to be 19%. The total spin-orbital repulsion parameter (\( \xi \)) has been calculated from expression \( \lambda = \pm \xi/2S \), \( S = 1 \), here positive sign will be given for less than half filled orbital and negative sign will be given to more than half filled orbital. In this study, the total spin-orbital interaction parameter has been calculated to be -527 cm\(^{-1}\).

The absorption band corresponding to \( ^3A_g(F) \rightarrow ^3T_{1g}(F) \) and \( ^3A_g(F) \rightarrow ^3T_{2g}(F) \) are very broad; the local site symmetry of Ni(II) ion in the lattice is ambiguous. Hence the spectrum has been deconvoluted using a program PeakFit v4.11 (SYSTAT Software Inc.) to identify the hidden peaks. The deconvoluted spectrum is presented in Figure 4.7, in which a maximum of seven transitions are observed. The transitions corresponding to \( ^3A_g(F) \rightarrow ^3T_{1g}(F) \) and \( ^3A_g(F) \rightarrow ^3T_{2g}(F) \) at 13565 and 9967 cm\(^{-1}\) are further split into doublets headed at 16425, 14892 and 10098, 9389 cm\(^{-1}\) respectively supporting that the system has trigonal or tetragonal distorted octahedral symmetry. If the symmetry is lowered from octahedral, then due to spin-orbital interaction, the transitions \( ^3A_g(F) \rightarrow ^3T_{1g}(F) \) and \( ^3A_g(F) \rightarrow ^3T_{2g}(F) \) will split into a quartet. However, it is not so in the present case; hence it can be neglected. In addition, a weak transition at 23310 cm\(^{-1}\) has been identified, which can be attributed to
Figure 4.7 Deconvoluted optical absorption spectrum of Ni(II)/HCDT. Here broken line corresponds to the experimental spectrum and continuous line corresponds to the simulated spectrum.
\(^3A_{2g}(F) \rightarrow ^1T_{1g}(D)\). This transition has been hidden under the \(^3A_{2g}(F) \rightarrow ^3T_{1g}(P)\) transition due to its low intensity. The terms namely \(T_{1g}\) and \(T_{2g}\) are split into \(A_2 + E\) and \(B_2 + E\) in the case of tetragonal distortion and \(A_2 + E\) and \(A_1 + E\) components in case of trigonal distortion. Hence, in both the cases, the transitions corresponding to \(^3A_{2g}(F) \rightarrow ^3T_{1g}(P)\), \(^3A_{2g}(F) \rightarrow ^3T_{1g}(F)\) and \(^3A_{2g}(F) \rightarrow ^3T_{2g}(F)\) will be split in doublets. However, the Eg term splits in to \(A_1 + B\), if there is tetragonal distortion. So the transition due to \(^3A_{2g}(F) \rightarrow ^1E_g(D)\) will be seen as doublets. Since, the transition corresponding to \(^3A_{2g}(F) \rightarrow ^1E_g(D)\) observed as singlet, one can evidently say that the system has undergone trigonal distortion rather than tetragonal distortion supporting the EPR data.
Conclusions:

Single crystal EPR studies of a non-Kramers ion in a paramagnetic host have been undertaken. The interesting observation being that the EPR spectra are observed, even at room temperature. A very few systems are known having room temperature EPR spectra. In addition, the analysis has been complicated due to the presence of only one allowed transition. The large zero field splitting term has been analyzed and the g tensor indicates rhombic nature for the symmetry, an observation also stemmed from D matrix. The optical spectrum has been completely analyzed and various parameters have been calculated. Further work at Q-band frequency will really throw considerable light on this system and the current predictions.
References:


