CHAPTER-VII
Synthesis and EPR studies of a dinickel complex
\([\text{Ni}_2(\text{L})_2(\text{OCIO}_3)_2] [\text{L} = \text{Hsalamp}]\)

VII.1 INTRODUCTION

The Ni(II) complex \([\text{Ni}_2(\text{Dabox})_2(\text{H}_2\text{O})_2]_2\): H$_2$Dabox = 2,6-bis(acetoxyimato)4-tert-butylphenol [1] is shown to possess moderate ferromagnetic interaction of 2$J$ = 5.1 cm$^{-1}$. The UV-Visible spectral bands are of energy similar to those of well characterised square-pyramidal high-spin Ni(II) complexes [2,3]. Biological activity of complexes derived from hydrazones has been widely studied and contrasted, acting in processes such as antibacterial, antitumoral, antiviral, antimalarial and antituberculosis effects [4]. The antitumoral and antiviral activities of lots of complexes derived from hydrazones such as thiosemicarbazones have also been reported [5-8]. Often these compounds show an N,N,S-coordinating pattern; however, there is very little information about O,N,O- or N,N,O coordinated hydrazone compounds in the literature. The Ni(II) complex with dianionic N,N,O tridentate Schiff’s base 6-amino-5-formyl-1,3-dimethyl uracil-benzoyl hydrazone [9] seems to possess some structural features related to the thiosemicarbazones complexes with biological activity. Single crystal X-ray diffraction studies on two nickel complexes with SalX ligands (X=NH,NCH$_3$) have shown the metal environments to be intermediate between square pyramidal and trigonal-bipyramidal geometries [10,11], while other studies have shown that Zn(cbpN).H$_2$O, Zn(mbpN).H$_2$O, Ni(mbpN) and Cu(mbpN) are all five coordinate with the central donor atom coordinated to the metal atom [12,13]. The zinc complexes have trigonal bipyramidal geometry, while the copper and nickel complexes have a distorted square pyramidal geometry.

Nickel(II), d$^8$ ion being a non-Krammer’s ion, EPR spectra can be observable, generally, at low temperatures. However, very few reports have been reported in the literature about the study of this d$^8$ ion at room temperatures. Most of the reported work concerns the study of this ion at 77 K or 4 K [14-26]. The g value will be isotropic and close to 2.2. In general, if the zero-field splitting (D) is zero, a single EPR line is observed. However, in most of the systems, D will be non-zero and hence more than one line is observed. In a recently communicated paper dealing with nickel(II) doped in hexaimidazole zinc(II)dichloride tetrahydrate [27], a maximum of two resonance lines, which completely
merged to a single line or sometimes go out of the reach of our X-band magnetic field region, during crystal rotations, are observed. Hence, it is concluded that the system is having a large zero-field splitting, compared to X-band energy. There are a few extra resonance lines, which have arisen from forbidden transitions. Generally, when the zero-field splitting is large, forbidden transitions are expected [26]. The EPR spectral parameters of Nickel(II) in [Ni(C3H4N2)3(NO3)] having trigonal symmetry are determined from powder and single crystal measurements [14] as \( g = 2.185, D = 0.882 \text{ cm}^{-1} \) and \( E = 0 \). The single-ion spin Hamiltonian parameters are determined for zinc fluoroborate hexahydrate doped with nickel(II) and compared with those obtained for the nickel fluoroborate hexahydrate [15]. The EPR studies are carried out for several concentrations (\( x = 0.005 \) to \( 1 \)) from room to liquid helium temperatures. However, for temperatures between 4.2 and 1.5 K and for low doping, the parameters are constant with \( g_\parallel = 2.229(6), g_\perp = 2.261(25) \) and \( D = -0.1219(8) \text{ cm}^{-1} \). In contrast, for nickel fluoroborate, the values are same, with weak temperature dependent, attributed to a ferromagnetic interaction. At high temperature, these parameters are remarkably concentration dependent. The study of line width dependence as a function of concentration has indicated that the nickel(II) ions have randomly occupied zinc site. \( d^8 \) ion in trigonal field is studied very extensively using \( \text{Al}_2\text{O}_3 \) [28,29] as the host lattice and the calculated \( g_\parallel, g_\perp \) and \( D \) are 2.1948(10), 2.1853(10) and \(-1.312 \text{ mT} \) respectively. Single crystal EPR studies of nickel(II) in hexakis(pyrazole) complexes of zinc(II) and cadmium(II) are also reported [30]. Nickel(II) is used to study phase transitions in \( \text{RbCaF}_3 \) single crystals at 25 K [31].

VII.2. PREPARATION OF COMPLEX

The nickel complex is prepared by taking two equivalents of the ligand (2.12 g, 0.01 moles) with two equivalent of nickel perchlorate (3.6571 g, 0.01 moles) in dry methanol. Initially, the ligand \( \text{Hsalamp} \) is first dissolved in methanol, where the colour of the solution is yellow. To this, methanolic solution of nickel perchlorate is added, wherein change in colour is observed from yellow to light green. The whole solution is then kept under reflux for 8 hours (around 300 K). Slow evaporation of this solution resulted in the formation of a pale greenish yellow coloured powder. Scheme-VII.1 gives the systematic procedure for the preparation of the nickel complex, the structure of which is confirmed by EPR studies (see below).
Scheme VII.1

$$2 \text{OH}$$

$$2 \text{Ni(ClO}_4\text{)}_2$$

Reflux in MeOH (6 hrs)

$$\text{CH}_3$$
The analytical data for the complex is as follows: Molecular formula \( \text{Ni}_2\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_{10}\text{Cl}_2 \). Calculated (Found): % C = 42.2(42.1), %H = 2.98(2.9), %N = 7.5(7.5), %Ni = 15.9(15.8). The melting of the complex is found to be 385° K.

VII.3. IR SPECTRA

The IR spectrum of the nickel complex, recorded in KBr pellet, in the range 500-4000 cm\(^{-1}\) is shown in Figure VII.1. The spectrum contains a peak at 1439 cm\(^{-1}\), which is assigned for the stretching vibrations of the aromatic skeleton [32]. As mentioned in literature [33], the presence of peaks around 1110, 1070, 1055, 630 and 620 cm\(^{-1}\) (\(\nu(\text{ClO}_4)\)) illustrate the coordinated perchlorate ion. Similar types of peaks are also observed in our complex around 1150, 1093 and 621 cm\(^{-1}\), confirming the presence of coordinated perchlorate ion. The C=N stretching frequency observed at about 1607 cm\(^{-1}\) confirms the participation of the nitrogen in the complex formation [32]. As discussed earlier, here also the shifting of frequencies between the pure ligand and complex are noticed, confirming the formation of the complex. The molar conductance for the complex measured in methanol solvent (in units of \(\Lambda_m / S \text{cm}^2 \text{ mol}^{-1}\)) is 230, which indicates that the complex is ionic and bivalent type[33]. In the solvent, the complex undergoes the dissociation indicating the nature of the complex to be 1:2 electrolyte [34].

VII.4. ELECTRONIC SPECTRA

Electronic spectrum of the nickel complex recorded in methanol solvent is given in Figure VII.2. It contains the d-d bands at 998, 660, a shoulder at 741 and a charge transfer band around 400 nm. The calculated absorbance values are 9340, 15290 and 22020 (\(\epsilon_{\text{max}}/\text{Lmol}^{-1}\text{cm}^{-1}\)). It is reported that in the visible-near-infrared spectrum of a nickel complex in dichloromethane solvent, bands observed near 1150, 950 and 600 nm confirm that the geometry around the metal ion is distorted square pyramidal [35]. However, for a nickel complex having six imidazole units, in a nearly octahedral fashion, three strong bands and a weak band are reported at 957, 591, 365 and 731 nm respectively [27].

VII.5. EPR STUDIES

As good single crystals suitable for EPR studies are obtained, crystal rotations have been done in the three orthogonal planes. As mentioned in the Chapter V, here also, no a
Fig. VII.1. IR spectrum of the dinickel complex [Ni$_2$(Hsalamp)$_2$(OCIO$_3$)$_2$] in the region 500-4000 cm$^{-1}$. Instrument: ABB Bomem MB104
Fig. VII.2. UV-Visible spectrum of the dinickel complex in methanol solvent indicating the d-d band and charge-transfer bands.
priori knowledge of the structure of the complex is known. Hence, a good single crystal with properly identifiable axes is chosen. The longest axis of the crystal is chosen as a-axis. b-axis is chosen in a big plane having a-axis and perpendicular to it. The third orthogonal axis is chosen as c-axis. The credibility of the axes will be known after comparing the results between the powder and single crystal work.

The crystal with ab plane is mounted on a goniometer for EPR rotations. In this plane, a single line is observed throughout the crystal rotation. However, the resonance lines show g anisotropy. This immediately concludes that the zero field splitting (D) is very small in this plane and close to zero. If D is not zero, a pair of lines, separated by 2D, are expected. On the other hand, if D is large, a single line is observed at a position corresponding to one of the two transitions and the g value of the line is far away from 2.2. A typical EPR spectrum obtained when the applied magnetic field is parallel to crystal b-axis is given in Figure VII.3. The crystal rotations are done for every ten degrees and the isofrequency plot is given in Figure VII.4. Later on, the crystal is mounted along the b axis, i.e., ac plane and the crystal rotations are done. Here, the EPR spectra at two different orientations are given in Figure VII.5 (a & b). Here, one noticed a splitting of resonance lines, indicating the non-zero value of D in this plane. The road map in the ac plane is given in Figure VII.6. Figures VII.7 (a & b) and VII.8 respectively correspond to EPR spectra at two different orientations in bc plane and the roadmap in the bc plane. As mentioned in Chapters II and V, Schonland [36] and EPR-NMR programs [37] are used to obtain the g and D matrices. The results are tabulated in Table VII.1.

Here also, similar to single crystal work done on copper complexes with Hsalamp (Chapter V), the direction cosines of the g and D tensors do not match that well. However, a close look at them indicates that the g and D are along a particular axis, say a, b or c. This is not so in the case of Chapter V complexes. In addition in a Ni(II) work done in our laboratory, in which it is doped into a hexaimidazole zinc(II) dichloride tetrahydrate lattice, the D tensor behaved almost similarly. Hence, we can say that the choice of our coordinate system is not that bad. However, powder work, as mentioned below confirmed our results. Table VII. 2 contains spin Hamiltonian data for a few nickel(II) complexes known in literature.
Fig. VII.3. Single crystal EPR spectrum of the dinickel complex at room temperature in the ab plane at $\theta = 90^\circ$ corresponding to B parallel to crystal b-axis. $\nu = 9.09134$ GHz.
Fig. VII.4. Isofrequency plot for the dinickel complex at room temperature in the ab plane, showing only a single resonance. $\nu = 9.09134 \text{ GHz}$.
Fig. VII.5(a & b). Single crystal EPR spectra of the dinickel complex in the ac plane at $\theta = 0^\circ$ and $40^\circ$. $\nu = 9.09060$ GHz.
Fig. VII.6. Isofrequency plot for the dinickel complex at room temperature in the ac plane. Here, one can notice splitting of the lines as $\theta$ varies. $\nu = 9.09060 \text{ GHz}$. 
Fig. VII.7(a & b). Single crystal EPR spectra of the dinickel complex in the bc plane at θ = 120° and 90°.

ν = 9.09248 GHz.
Fig. VII.8. Isofrequency plot for the dinickel complex, \([\text{Ni}_2(\text{Hsalamp})_2(\text{OCIO}_3)_2]\), at room temperature in the bc plane. \(v = 9.09248\ \text{GHz}\).
Table VII. 1. Principal values of g and zero-filed (D) tensors and their direction cosines in an orthorhombic framework.

<table>
<thead>
<tr>
<th>g matrix</th>
<th>Eigenvalues</th>
<th>Eigenvectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.219 -0.008 -0.002</td>
<td>2.377</td>
<td>-0.050 -0.999 -0.007</td>
</tr>
<tr>
<td>2.344 0.094</td>
<td>2.219</td>
<td>0.944 -0.045 -0.327</td>
</tr>
<tr>
<td>2.104</td>
<td>2.071</td>
<td>0.326 -0.023 0.945</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>D matrix (mT)</th>
<th>Eigenvalues (mT)</th>
<th>Eigenvectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.45 -0.61 -3.46</td>
<td>9.7</td>
<td>0.531 0.837 -0.129</td>
</tr>
<tr>
<td>-6.43 -10.2</td>
<td>4.2</td>
<td>0.438 -0.402 -0.804</td>
</tr>
<tr>
<td>0.98</td>
<td>-13.9</td>
<td>-0.725 0.370 -0.581</td>
</tr>
</tbody>
</table>

Table VII. 2. Spin Hamiltonian parameters for Nickel(II) in a few host lattices

<table>
<thead>
<tr>
<th>Host Lattice</th>
<th>g values</th>
<th>D (mT)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHIN</td>
<td>2.185</td>
<td>882.0</td>
<td>14</td>
</tr>
<tr>
<td>NFHH</td>
<td>2.229, 2.261</td>
<td>-129.8</td>
<td>15</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.1948, 2.1853</td>
<td>-1.312</td>
<td>28,29</td>
</tr>
<tr>
<td>RbCaF₃</td>
<td>2.30, 2.29, 2.32, 2.32</td>
<td>30.7**, 9.9***</td>
<td>31</td>
</tr>
<tr>
<td>HZDT</td>
<td>2.3691, 2.2105, 1.9405</td>
<td>244.07, 24.98, -269.05</td>
<td>27</td>
</tr>
<tr>
<td>Ni Complex</td>
<td>2.377, 2.219, 2.071</td>
<td>9.7, 4.2, -13.9</td>
<td>Present Study</td>
</tr>
</tbody>
</table>

NHIN- Nickel hexaimidazole nitrate

NFHH – Nickel fluoroborate hexahydrate

HPZ – Hexakis pyrazole zinc(II)

HPC - Hexakis pyrazole cadmium(II)

HZDT – Hexaimidazole zinc(II)dichloride tetrahydrate

** in units of GHz, two phases at 25 K.
The powder EPR spectrum of the complex recorded at room temperature is shown in Figure VII.9. As the D value obtained from single crystal rotation is close to 21 mT, the resolution into two components due to zero field splitting could not be seen, due to broadness of the spectrum. Using the program EPR-NMR [37], the powder spectrum is simulated using the data given in Table VII.1 and the agreement is very good between experimental and theoretical spectra.

However, the presence of two nickel ions, as mentioned by elemental analysis can not be confirmed with our EPR studies. One can argue that due to the similar geometric configurations of the two complexes, both give rise to identical EPR spectra and hence have identical spin Hamiltonian parameters. Even if a small difference in spin Hamiltonian parameters exists, it cannot be seen due to high broadness of the EPR resonance lines. Cooling the sample to 77K does not decrease the line width appreciably. Also, another suggestion that D in all these complexes is too large and the second resonance observed at some orientations may be due to the other nickel ion. To confirm this, one has to study the system at Q-band frequencies and if possible at low temperatures. This is not be done due to lack of facilities at our department. Moreover, if the two nickel atoms are interacting, one would expect the total spin to be 2 and hence, needs very low temperatures to observe the EPR spectrum, as the total spin is even. Hence, the suggestion of interaction between the two nickel ions is ruled out, even though the distance between them is comparable to that of copper atoms (assuming identical structures for copper and nickel complexes, Cu-Cu distance are 2.8324 Å). In the case of copper, the proper overlapping of orbital is permitted resulting in an exchange interaction, which is not so in the case of nickel complexes. Hence, further work at Q-band frequencies followed by single crystal X-ray work will really help to completely understand the system.

VII.6. OPTICAL STUDIES

A detailed understanding of paramagnetic resonance spectrum requires the knowledge of the position of the excited levels, for the ground state is ever a pure state. The spin orbital coupling causes other orbital arising from the same parent to inter-mix. In general, there have been few measurements of both the optical and the paramagnetic resonance spectra for the same crystal. Most authors generally assume that the optical spectrum obtained from the solution does not differ appreciably from that in the crystal or
Fig. VII.9. EPR powder spectrum of the dinickel complex \([\text{Ni}_2(\text{Hsalamp})_2(\text{OCIO}_3)_2]\), at room temperature. 
\[ \nu = 9.41912 \text{ GHz}. \]
powder. This is approximately true for the optical-transition taking place in a time short compared with the collision frequency in a liquid. One has to consider the number of orbital levels into which each ionic level is split. This depends on the symmetry of the complex. Since the optical transition shows broad bands in iron group, the effect of splitting caused by lower symmetry is neglected. Lower symmetry shifts the center of gravity of spacing of the excited levels somewhat, however the shift is neglected.

The Ni(II) d⁸ gives rise to the free ion terms ³F, ³P, ¹D, ¹G and ¹S, the ground state being ³F in octahedral symmetry. These terms split or transform as follows.

\[
\begin{align*}
³F & \rightarrow ³A₂g(F) + ³T₂g(F) + ³T₁g(F) \\
³P & \rightarrow ³T₁g(P) \\
¹D & \rightarrow ¹E₂(D) + ¹T₂g(D) \\
¹G & \rightarrow ¹A₁g(G) + ¹T₁g(G) + ¹T₂g(G) + ¹E₂(G) \\
¹S & \rightarrow ¹A₁g(S)
\end{align*}
\]

A simplified version of Tanabe-Sugano diagram for a d⁸ is given in Fig. VII.10 and allowed three transitions are marked in Fig. VII.11. The three spin allowed transitions are:

\[
\begin{align*}
³A₂g(F) & \rightarrow ³T₂g(F) \\
³A₂g(F) & \rightarrow ³T₁g(F) \\
³A₂g(F) & \rightarrow ³T₁g(P)
\end{align*}
\]

Expected bands for Ni(II) doped are three intense bands and two weak bands. The intense bands correspond to the spin allowed transitions and the weak bands correspond to the spin forbidden transitions. These weak bands are

\[
\begin{align*}
³A₂g(F) & \rightarrow ¹E₂(D) \\
³A₂g(F) & \rightarrow ¹T₂g(D)
\end{align*}
\]
Figure VII.10. A simplified version of Tanabe-Sugano diagram for a $d^8$ system
Figure VII 11. Tanabe-Sugano diagram representing the spin-allowed transition
The finely powdered sample of the nickel complex is dissolved in ethanol and the spectrum is recorded from 200 to 1300 nm. Fig. VII. 2. gives the optical spectrum of the nickel complex in the above solvent ethanol. We have observed three strong peaks at 400, 660 and 998 nm and the assignments are:

\[ ^3\text{A}_{2g}(F) \rightarrow ^3\text{T}_{2g}(F) \rightarrow 998 \text{ nm} = 10020 \text{ cm}^{-1} \]

\[ ^3\text{A}_{2g}(F) \rightarrow ^3\text{T}_{1g}(F) \rightarrow 660 \text{ nm} = 15151 \text{ cm}^{-1} \]

\[ ^3\text{A}_{2g}(F) \rightarrow ^3\text{T}_{1g}(P) \rightarrow 400 \text{ nm} = 25000 \text{ cm}^{-1} \]

A weak band at 741 nm is assigned to the forbidden transition from \(^3\text{A}_{2g}(F)\) to \(^1\text{E}_g(D)\).

From the normal procedure, the crystal field splitting value (Dq) and the inter electron repulsion parameters B and C (Racah parameters) have been calculated. The final parameters are

\[ \text{Dq} = 1019 \text{ cm}^{-1} \text{ and } B = 698 \text{ cm}^{-1}. \]

B for a free Ni(II) ion is 1080 cm\(^{-1}\), which indicates a reduction about 35% from the free ion value. Another weak band, corresponding to the transition from \(^3\text{A}_{2g}(F)\) to \(^1\text{T}_{2g}(D)\), expected at 428 nm (calculated from the theoretical calculations), can not be seen in this case due to its very low intensity.

The optical data and EPR data are correlated and the individual spin orbital coupling parameter (\(\lambda\)) is calculated using the formula

\[ g = 2.0023 - 8\lambda/\Delta \]

\[ 2.222 = 2.0023 - 8\lambda/10190 \]

\[ \lambda = 279.8 \text{ cm}^{-1} \]

The \(\lambda\) value for free Ni(II) ion is found to be 324 cm\(^{-1}\). A reduction of 14 % is obtained, which corresponds to percentage of covalent bonding. It is slightly higher than the corresponding values in Ni(II)-imidazole bond, Mn(II)-imidazole and Cu(II)-imidazole bonds.
The total spin-orbit coupling parameter ($\xi$) is calculated using the formula

$$\lambda = \pm \frac{\xi}{2S} : (S = 1 \text{ for Ni(II)})$$

$$\xi = -559.6 \text{ cm}^{-1}$$

where the $+$ sign is required for a shell that is less than half-filled and the $-$ sign for a shell that is more than half-filled.

The Racah parameter $B$ and $C$ have also been calculated theoretically by equating formulae given below which gives the energy of different terms

$$^3A_2g(F) = 0$$

$$^3T_{2g}(F) = 10Dq$$

$$^3T_{1g}(F) = \frac{1}{2} [(15B + 30Dq) - ((9B - 10Dq)^2 + 144B^2)^{1/2}]$$

$$^1E_g(D) = \frac{1}{2} [(17B + 4C + 20Dq) - ((B + 20Dq)^2 + 48B^2)^{1/2}]$$

$$^1T_{2g}(D) = \frac{1}{2} [(17B + 4C + 30Dq) - ((B + 10Dq)^2 + 48B^2)^{1/2}]$$

$$^3T_{1g}(P) = \frac{1}{2} [(15B + 30Dq) + ((9B - 10Dq)^2 + 144B^2)^{1/2}]$$

The $B$ value obtained is 640 cm$^{-1}$ from the above equation is found to be very close to the $B$ value, calculated using Tanabe-Sugano diagram[38]. Hence, the consistence in the values obtained from different sources. The calculated $C$ value is 4202 cm$^{-1}$. The $B'/B$ and $C'/C$ values are 0.62 and 0.86 respectively and are not very close due to some interaction from the other nickel atom. The ratios are expected to be equal, since reduction should be the same whether the transition is between states of same spin multiplicity or different multiplicity. Here $B'$ and $C'$ are inter electron repulsion parameters for free Ni(II) ion. From the optical results, one can say that the symmetry around the metal ion is nearly octahedral on this time scale. However, on EPR time scale the symmetry is proved to be orthorhombic, as mentioned earlier.
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