CHAPTER VI

Synthesis, Characterization and Structural Assessment of Ni(II) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Introduction

The first two chapters describe the synthesis and characterization of monometallic and homobimetallic Mo(VI) complexes of the title dihydrazone respectively, while the third chapter describes the synthesis and characterization of zinc complexes of the same ligand. Nickel is another metal ion from the first transition series which has been selected for the synthesis of its complexes with the title dihydrazone and their characterization. Its selection is based on the consideration that a nickel or cobalt promoted molybdenum catalyst is important in industrial catalysis; particularly in the hydrosulfurization process [5] whereby organo sulfur compounds in petroleum feed stocks are heterogeneously desulfurized with dihydrogen. Moreover nickel is also present in six types of metalloenzymes namely ureases, hydrogenases, methyl coenzyme M reductase, carbon monoxide dehydrogenase, acetyl coenzyme A synthase and nickel superoxide dismutases [1]. Urease, the only nickel containing metallohydrolase catalyses the hydrolysis of urea to ammonia and carbon dioxide [2]. The microbial urease from klebsiella aerogenes has been found to contain two nickel(II) ions which are 3.5 Å apart within the dinuclear active site [2]. Further nickel occurs in heterobimetallic enzymes such as jack bean urease [3] and hydrogenase enzyme [4] in which nickel is present in combination with iron.

In addition nickel plays a prominent role in several areas of material chemistry. Some topical interplay between nickel coordination chemistry and material science exists in the use of Ni-containing alkoxides for the synthesis of ceramic materials by MOCUD and sol-gel processes, in the preparation of nanoscopic dendrimers incorporating Ni, the construction of 3D hybrid inorganic-organic porous materials with Ni coordination units and the fabrication of supported Ni catalysts and Ni nano-structures through nanotechnology and paramagnetic high magnetism, culminating in the recent discovery of the first single molecule magnets based on Ni(II) centres [6].

A survey of literature reveals that few complexes of Ni(II) ion with the dihydrazone ligand derived from the condensation of salicylaldehyde and related o-hydroxy aromatic
aldehydes and ketones with malonoyl dihydrazine and other acyl dihydrazines, aroyl dihydrazines and pyridoyl dihydrazines have been reported [7, 8, 9, 10], yet it has failed to locate any study on metal complexes of the dihydrazone ligand containing succinoyl fragment and bulky naphthyl fragment in its molecular skeleton.

In view of such an importance of nickel and its relation to hetero molybdenum systems and the fact that the previous chapters describe the synthesis and characterization of zinc and molybdenum complexes derived from the title dihydrazone ligand, it was of interest to study the monometallic and the homobimetallic Ni(II) complexes with the title ligand which might serve as precursors in the synthesis of heterobimetallic systems comprising of nickel and molybdenum. Accordingly, the synthesis and characterization of monometallic and homobimetallic Ni(II) complexes with the title dihydrazone by various methods in methanol are described in this chapter. The composition of the isolated complexes has been judged mainly from the analytical data. The structures of the complexes have been discussed with the help of molar conductance, magnetic moment, electronic and infrared spectral data.

**Preparation of the complexes:**

1. **Preparation of \([\text{Ni}(\text{H}_2\text{nsh})(\text{H}_2\text{O})_2]\) (6.1)**

Succinoyl dihydrazine (0.90 g, 6.16 mmol) was dissolved in hot methanol-water mixture (50 mL, 90:10). A solution of Ni(OAc)$_2$.4H$_2$O (1.50 g, 6.02 mmol) in methanol (50 mL) was added to the above solution accompanied by gentle stirring for a period of 10 minutes. The resulting solution was refluxed for 15 minutes. To this was added a hot solution of 2-hydroxy-1-naphthaldehyde (2.70 g, 15.70 mmol) in methanol (100 mL). The reaction mixture was refluxed for 1 hour which precipitated a yellow-brown compound. The complex, thus, obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether and dried over anhydrous CaCl$_2$. Yield: 0.72 g.

2. **Preparation of \([\text{Ni}(\text{H}_2\text{nsh})(\text{A})_2]\) (where \(A = \text{pyridine (py, 6.2)}; \ 2\text{-picoline (2-pic, 6.3)}; \ 3\text{-picoline (3-pic, 6.4)}; \ 4\text{-picoline (4-pic, 6.5).}}\)

The complex \([\text{Ni}(\text{H}_2\text{nsh})(\text{H}_2\text{O})_2]\) (6.1) (1.00 g, 1.86 mmol) was suspended in methanol (100 mL) accompanied by gentle stirring for 10 minutes at 50-60°C. To this suspension, pyridine (1.50 mL, 18.10 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture was refluxed for 3 hours which precipitated the light brown compound.
The compound, thus, obtained was filtered, washed repeatedly with hot methanol and then
with ether and dried over anhydrous CaCl\(_2\). Yield: 0.70 g

The complexes (6.3), (6.4) and (6.5) were also prepared in the same manner using 2-
picoline, 3-picoline and 4-picoline instead of pyridine and maintaining the metal:base ratio
at 1:10 respectively. Yield: 0.75 g (6.3); 0.77g (6.4); 0.78g (6.5).

3. **Preparation of \([\text{Ni}_2(\text{nsh})(\text{H}_2\text{O})_4]\) (6.6)**

The dihydrazone (H\(_4\)nsh) (1.00g, 2.20 mmol) was suspended in methanol (100 mL) and
stirred for 30 minutes at 60 °C. To this was added a solution of Ni(OAc)\(_2\).4H\(_2\)O (1.65 g,
6.63 mmol) in methanol (50 mL) maintaining the molar ratio at 1:3. The reaction mixture
was refluxed for 3 hours, which precipitated a brown compound. The compound, thus,
obtained was filtered while hot, washed repeatedly with hot methanol and finally with
ether and dried over anhydrous CaCl\(_2\). Yield: 0.65 g.

4. **Preparation of \([\text{Ni}_2(\text{nsh})(\text{A})_4]\) (where A = pyridine (py, 6.7); 2-picoline(2-pic,
6.8); 3-picoline(3-pic, 6.9); 4-picoline (4-pic, 6.10)**

The complex \([\text{Ni}_2(\text{nsh})(\text{H}_2\text{O})_2]\) (6.6) (1.00 g, 1.55 mmol) was suspended in methanol (100
mL) by gentle heating at 60° C. To this suspension, pyridine (1.24 mL, 15.42 mmol) was
added maintaining the molar ratio at 1:10. The reaction mixture was refluxed for 2 hours.
The resulting precipitate was isolated in the usual way. The complexes (6.7) to (6.10)
were also synthesized by essentially following the above procedure using 2-picoline, 3-
picoline and 4-picoline instead of pyridine maintaining the metal: base molar ratio at 1:10,
respectively. Yield: 0.61g (6.7); 0.65 g (6.8); 0.67 g (6.9); 0.64 g (6.10).

**Results and Discussion**

The complexes described in the present chapter together with their molecular formula,
colour, decomposition point, percentage yield, analytical data, magnetic moment and
molar conductance data are set out in Table 6.1. The electronic spectral data for the
complexes have been shown in Table 6.2. The composition of the complexes has been
deduced on the basis of elemental analyses as given below.

\[
\begin{align*}
[\text{Ni}(\text{H}_2\text{nsh})(\text{A})_2] & \quad (A = \text{H}_2\text{O} \ (6.1), \text{py} \ (6.2), \text{2-pic} \ (6.3), \text{3-pic} \ (6.4) \text{ and 4-pic} \ (6.5)) \\
[\text{Ni}_2(\text{nsh})(\text{A})_4] & \quad (A = \text{H}_2\text{O} \ (6.6), \text{py} \ (6.7), \text{2-pic} \ (6.8), \text{3-pic} \ (6.9) \text{ and 4-pic} \ (6.10))
\end{align*}
\]
The complexes are brown, yellow, light brown and dark yellow in colour. All of the complexes are air stable and decompose above 300 °C without melting. All of the complexes are insoluble in water and common organic solvents such as ethanol, methanol, chloroform, benzene, hexane, and ether. However, all of the complexes are soluble in DMF and DMSO.

**Thermal studies**

The detailed weight loss studies of the complexes have been carried out in the temperature range 80–250 °C and the vapours evolved have been identified by passing through a trap containing anhydrous copper sulfate and a test tube containing sodium hydroxide solution and chloroform [11]. There was no weight loss observed in the temperature range 80–120 °C in any of the complexes ruling out the possibility of presence of water molecules in the lattice structure of the complexes. However, the complexes (6.1) and (6.6) showed weight loss corresponding to two and four water molecules respectively at 180°C suggesting the presence of two and four water molecules in the first coordination sphere around the metal centre in these complexes. On the other hand, the complexes (6.2) to (6.5) and (6.7) to (6.10) showed weight loss corresponding to two and four pyridine/2-picoline/3-picoline/4-picoline molecules in the temperature range 200–240°C. The expulsion of these neutral electron donor molecules at such a high temperature indicates that they are coordinated to the metal centre. Further, in the complexes (6.2) and (6.7) the vapours evolved in the temperature range 200–240 °C turned the solution of chloroform and sodium hydroxide red. This confirmed that the vapours from these complexes originated from pyridine [12]. Similarly, the vapours evolved from the complexes (6.4), (6.5), (6.9) and (6.10) in this temperature range turned the colour of cyanogen bromide solution to green-violet and blue respectively on treatment with phloroglucinol solution. This further confirmed the presence of 3-picoline molecules in the complexes (6.4) and (6.9) and 4-picoline molecules in the complexes (6.5) and (6.10), respectively.

**Molar Conductance**

The molar conductance values of the complexes (6.1) to (6.10) in DMSO solution at 10⁻³ M dilution falls in the range 2.62–3.13 ohm⁻¹ cm² mol⁻¹ suggesting that they are non-electrolytes in this solvent [13].
Magnetic Moment

The \( \mu_B \) (BM) values for the complexes (6.1) to (6.10) are set out in Table 6.1. The effective electronic configuration of nickel(II) is \( 3d^8 \) and exhibits a magnetic moment higher than that expected for two unpaired electrons in an octahedral and a tetrahedral environment, whereas diamagnetism of the nickel(II) complexes lead to square planar stereochemistry. The effective magnetic moment reported for a high-spin octahedral Ni(II) complexes is in the range 3.00–3.50 BM, while for the tetrahedral complexes it ranges from 3.5 to 4.0 BM. The reason for this deviation is attributed to arise from spin-orbit coupling which causes an orbital contribution in the quenched \( ^3A_{2g} \) ground state of Ni(II) ion in an octahedral environment and not due to contribution from the orbital angular momentum of the electrons because the orbital angular momentum do not affect the \( ^3A_{2g} \) state. On the contrary, in case of a tetrahedral Ni(II) complex, the orbital angular momentum contributes strongly to the magnetic moment leading to magnetic moment values as high as 4.0 BM. The paramagnetism of the nickel (II) complexes (6.1) to (6.5) rules out the possibility of square planar structure and tetrahedral structure can be discarded on the basis of the magnitude of the magnetic moment. The complexes (6.1) to (6.5) have magnetic moment values in the region 2.87–3.45 BM which is typical of an octahedral Ni(II) compound [14].

In the homobimetallic Ni(II) complexes (6.6) to (6.10), two Ni(II) ions are present for each ligand molecule and the resulting complexes have magnetic moment values in the region 1.14–1.73 BM i.e. 0.5–0.87 BM per metal(II) ion. Such low values of magnetic moment in the complexes (6.6) to (6.10) certainly rules out low-spin square planar stereochemistry for the complexes. But these values are considerably less than the values reported for spin free nickel (II) complexes indicating a strong metal-metal interaction in the structural unit. Anomalous magnetic moment values in the solid state have been explained on the basis of absorption spectra by proposing a mixed octahedral and square planar stereochemistry in the solid state due to molecular association [15], but the electronic absorption spectra of the complexes described in this chapter are consistent with the tetragonally distorted octahedral stereochemistry. Since, the hydrazine bridges do not cause any lowering of the magnetic moment [16], therefore, it is still reasonable to believe that the lowering of the magnetic moment is due to the presence of oxo-bridged structure and as a result of this Ni(II) complexes attain a tetragonally distorted octahedral stereochemistry.
Electronic Spectra

The electronic spectra of the ligand and its Ni(II) complexes were recorded in DMF solution because of poor solubility of the ligand and the complexes in common organic solvents. The important electronic spectral bands for the dihydrazone ligand (H₄nsh) and the monometallic and homobimetallic Ni(II) complexes along with their molar extinction coefficient are presented in Table 6.2. The electronic spectra for the complexes (6.1), (6.2), (6.4), (6.6), (6.7) and (6.8) have been shown in Fig. (6.1) to (6.6).

The free ligand H₄nsh exhibits a couple of bands in the region 317 nm and 363 nm. The band at 317 nm is assigned to intraligand $\pi-\pi^*$ transition while the band at 363 nm is assigned to $n-\pi^*$ transition [17].

The electronic spectra of the complexes exhibit two to four bands in the region 300–450 nm. The bands appearing in the region 319–370 nm are attributed to arise due to intraligand transitions which exhibit red shift on complexation. The red shift of the ligand bands gives good evidence of chelation of dihydrazone to the metal centre. All of the complexes show new bands in the region 410–440 nm which has very high molar extinction coefficient. In view of very high molar extinction coefficient of this band, it is assigned to have its origin in the ligand-to-metal charge transfer transition. This band arises most probably from charge-transfer transition from naphtholate oxygen atoms to the metal centre [18]. This ligand-to-metal charge-transfer band is strongly influenced by the chemical nature of the ligand within a given stereochemistry and is responsible for the appearance of orange colour of the complexes.

In an octahedral environment, Ni(II) complexes exhibit three bands which are assigned to $^3A_{2g} \rightarrow ^3T_{2g} (F)$, $(v_1)$; $^3A_{2g} \rightarrow ^3T_{1g} (F)$, $(v_2)$ and $^3A_{2g} \rightarrow ^3T_{1g} (P)$, $(v_3)$ transitions, respectively. Since the transition $^3A_{2g} \rightarrow ^3T_{1g} (P)$, $(v_3)$ generally occurs in the region 330–400 nm in which the bands due to organic fraction of the complexes arise as well, hence, this region is not useful from the point of view of drawing any conclusion about the stereochemistry around the Ni(II) centre. However, the first two low energy bands observed in the region 500–900 nm in all of the complexes are characteristic of nickel(II) in octahedral environment. The octahedral geometry of Ni(II) complexes is further supported by the value of $v_2/v_1$ ratio which lie in the region 1.498–1.504 [19].

Various ligand field parameters (Table 6.3) viz. Racah inter-electronic repulsion parameter (B), ligand field splitting energy (10Dq), covalency factor ($\beta$) and ligand field stabilization energy (LFSE) have been calculated for the Ni(II) complexes.
The ligand field splitting energy (10Dq) and the Racah inter-electronic repulsion parameter (B) were calculated by the equations given by Lever [20].

\[{^3A_2g} \rightarrow {^3T_2g} (F), (v_1) = 10Dq\]

\[{^3A_2g} \rightarrow {^3T_1g} (F), (v_2) = 7.5B + 15Dq - \frac{1}{2}(225B^2 + 100Dq^2 - 180DqB)^{\frac{1}{2}}\]

\[{^3A_2g} \rightarrow {^3T_1g} (P), (v_3) = 7.5B + 15Dq + \frac{1}{2}(225B^2 + 100Dq^2 - 180DqB)^{\frac{1}{2}}\]

The Racah interelectronic repulsion parameter (B) was also calculated by the following equation [21] and the values obtained were found to be same as calculated from the equations given by Lever.

\[B_{\text{Complex}} = \frac{(2v_1^2 + v_2^2 - 3v_1v_2)}{(15v_2 - 27v_1)}\]

The covalency factor (β) was obtained by the following equation:

\[\beta = \frac{B}{B'} \text{ (B' is the free ion value = 1038 cm}^{-1}[22])\]

The ligand field stabilization energy (LFSE) is expressed by the equation:

\[\text{LFSE} = 12Dq\]

The percentage lowering of energy of ‘P’ state in the complexes as compared to its value in the free gaseous ion (β°) is obtained by the equation:

\[\beta^\circ = 100 - (\beta \times 100)\]

The energy of first transition for the complexes (6.1) to (6.10) lie in the range 11765–11876 cm\(^{-1}\)which is equal to 10Dq. The evaluation of Racah inter-electronic repulsion parameter ‘B’ from the expression of \(v_1\) gave values which lie in the range 645–662. These values are very low as compared to the free ion value (1038 cm\(^{-1}\)). This indicates that all of the complexes have considerable covalent character. The nephelauxetic ratio, \(\beta\), for the complexes lie in the range 0.62–0.64. The obtained \(\beta\) value being less than unity suggests the presence of considerable amount of covalent character in the metal–ligand bonds. The percentage lowering of energy of ‘P’ state in the complexes as compared to its value in the free gaseous ion i.e. \(\beta^\circ\) lie in the range 36.32–37.95% which shows a high degree of covalency.

The \(v_2/v_1\) values for tetragonal complexes are found significantly higher than the usual range for octahedral complexes and sometimes greater than the theoretical limit of 1.80 for octahedral symmetry. The interaction between \(^3T_{1g} (P)\) and \(^3T_{1g} (F)\) states [23] gradually
lowers the ratio of $v_2/v_1$ from the theoretical value of 1.80 to 1.50–1.70 and values in the range 1.60–1.70 are common for nickel(II) complexes of octahedral symmetry. In the present complexes the $v_2/v_1$ values lie in the range 1.49–1.50 which are slightly lower than the lower limit of usual octahedral complexes but are within the range reported for octahedral nickel(II) complexes [24]. These low values indicate a strong interaction between $^3T_{1g}$ (P) and $^3T_{1g}$ (F) states of the complexed nickel(II) ion. The value of ligand field stabilization energy for the complexes lie in the range 40.42 – 40.80 kcal mol$^{-1}$.

**Infrared Spectra**

Some of the structurally significant infrared (IR) spectral bands for the free dihydrazone ($H_{2}nsh$) and the nickel (II) complexes are listed in Table 6.4. The IR spectra of the complexes (6.2), (6.3), (6.6) and (6.10) are shown in Fig. (6.7) to (6.10) as representative examples.

A comparison of the IR spectra of the nickel (II) complexes with that of the uncoordinated dihydrazone ($H_{2}nsh$) suggests that the dihydrazone is coordinated to the metal centre in enol form in all of the complexes.

The uncoordinated dihydrazone shows a medium intensity broad band centered at 3423 cm$^{-1}$ and a medium intensity band at 3244 cm$^{-1}$. The band at 3423 cm$^{-1}$ has been assigned to $\nu$(OH) vibration of 2-hydroxy-1-naphthaldehyde part of the dihydrazone, while the band at 3244 cm$^{-1}$ is assigned to arise from secondary -NH group. The IR spectra of the complexes show a weak to medium intensity band in the region 3000–3500 cm$^{-1}$. This band is attributed to arise due to stretching vibrations of water molecules absorbed by KBr during pellet preparation. However, these bands appear to have contribution from coordinated water molecules in the complexes (6.1) and (6.6). The band in the region 3000–3500 cm$^{-1}$ in the complexes (6.1) to (6.5) also appears to have contribution from the stretching vibration of coordinated naphtholic –OH group. Further, the spectral features of the complexes (6.6) to (6.10) conspicuously indicate the coordination of naphtholic –OH group via deprotonation to the metal centre in these complexes.

None of the complexes shows the band characteristic of $\nu$NH vibration. This suggests the destruction of –NH group as a result of enolization of the ligand in the complexes and its coordination to the metal centre in the enol form.

The $\nu$(C=O) stretching vibration appears as a very strong band at 1672 cm$^{-1}$ in the infrared spectrum of the uncoordinated dihydrazone. In the infrared spectra of all the complexes,
the amide I band disappears indicating destruction of amide structure of the ligand in these complexes.

The $\nu(C=\text{N})$ band appears as a couple of bands in the region 1622–1602 cm$^{-1}$ in the IR spectra of the complexes similar to that in the uncoordinated dihydrazone. This band registers an average downward shift of 2–3 cm$^{-1}$ indicating coordination of dihydrazone through azomethine nitrogen atom to the metal centre [25]. This downward shift of $\nu(C=\text{N})$ band is attributed to the drainage of electron density from azomethine nitrogen atom to the metal centre. The existence of two $\nu(C=\text{N})$ band in the complexes shows that the two azomethine nitrogen groups are inequivalent suggesting that the strength of the two $\text{M}\rightarrow\text{N}$ bands are not the same. Further, the difference between the two $\nu(C=\text{N})$ stretching frequencies are of the order of 13–18 cm$^{-1}$ which falls in the range in which groups existing in the anti-cis configuration have been reported to absorb [26]. This suggests that the dihydrazone exist in the anti-cis configuration in these complexes.

A band of medium intensity observed at 1540 cm$^{-1}$ in the infrared spectra of the free dihydrazone is attributed to arise due to joint contribution of amide II ($\nu(C-N) + \nu(NH) + \nu(C--O)$ (naphtholic)). This band splits into two bands in the IR spectra of the complexes and appears around 1540 cm$^{-1}$ and 1508 cm$^{-1}$, respectively. The position of the band at 1540 cm$^{-1}$ remains almost unchanged in the complexes as compared to that in the free ligand. However, the intensity of this band is considerably increased in the complexes comparatively. This may be related to bonding between the naphtholate oxygen atom and metal centre. A weak but intense band at 1508 cm$^{-1}$ in the IR spectra of the complexes is attributed to arise due to stretching vibration of newly created NCO$^-$ group produced as a result of enolization of the ligand [25].

The medium intensity band at 1281 cm$^{-1}$ due to $\nu(C--O)$ shifts to higher frequency by 21 cm$^{-1}$ in the complexes (6.1) to (6.5) and appears at $\sim$ 1303 cm$^{-1}$ as a medium intensity band. On the other hand this band splits into two bands in the complexes (6.6) to (6.10). One of the bands remains almost at the same position in the complexes as compared to that in the free ligand while the other band shifts to higher position by $\sim$21 cm$^{-1}$ and appears around 1303 cm$^{-1}$ as a medium intensity band. Such a feature associated with $\nu(C--O)$ band indicates bonding through C--O oxygen atoms to the metal centre [25].

The naphthyl ring shows a weak absorption at about 1600 cm$^{-1}$. In the present ligand and as well as in the complexes, the band due to naphthyl ring does not show its independent existence, most probably, because of its overlapping with either $\nu(>\text{C}=\text{N}--\text{N}=\text{C}<)$ band or
amide II band or $\nu$(C - O) (naphtholic) band. The band at 1467 cm$^{-1}$ in the free ligand is characteristic of substitution at $\alpha$-position of naphthalene ring.

It has been found that the $\nu$(N–N) band appears in the region 1040–970 cm$^{-1}$ in the metal complexes derived from N,N-diacyl hydrazines [27]. Eliminating the bands due to C–H in-plane deformation in the region 1050–900 cm$^{-1}$, a weak band at 1029 cm$^{-1}$ in the present ligand has been assigned to $\nu$(N–N). This band shifts to higher frequency by 14–27 cm$^{-1}$ in all of the metal complexes. This indicates the involvement of nitrogen atom of N–N group in coordination to the metal centre [28]. The complexes (6.6) to (6.10) show an additional band in the region 861-897 cm$^{-1}$ and is assigned to have contribution from the band arising from the tetraatomic species $\left[\overset{\infty}{\longrightarrow}\right]$ resulted from the involvement of naphtholate oxygen atoms in bridge formation [29].

The complexes (6.2) to (6.5) and (6.7) to (6.10) show a new but very weak intensity band in the region 1076–1045 cm$^{-1}$. This band is assigned to ring breathing mode of pyridine, 2-picoline, 3-picoline and 4-picoline molecules. The presence of this band in the IR spectra of the complexes (6.2) to (6.5) and (6.7) to (6.10) indicates coordination of pyridine, 2-picoline, 3-picoline and 4-picoline to the metal centre [30].

The antisymmetric and symmetric -OH stretching modes of lattice water appear in the region 3500–3000 cm$^{-1}$, while the H – O – H bending mode appears in the region 1630 – 1610 cm$^{-1}$. Coordinated water molecules besides showing the above two bands also show wagging and rocking modes in the region 900–750 cm$^{-1}$ which are activated by coordination to the metal centre [31].

Since there is no detectable change in the IR spectra of the complexes (6.2) to (6.5) and (6.7) to (6.10) in the above ranges as compared to IR spectrum of the ligand, where modes of lattice and coordinated water should appear and since, there is no loss of water molecules at 110°C, it is suggested that there are neither lattice water nor coordinated water molecules in these complexes. On the other hand the complexes (6.1) and (6.6) show a new band of medium intensity at 687 cm$^{-1}$ and 630 cm$^{-1}$ respectively. These bands are assigned to rocking mode of coordinated water molecules in these complexes.

**Conclusion**

In this chapter, monometallic and homobimetallic Ni(II) complexes derived from the dihydrazine ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone have been described. In all of the complexes, the dihydrazine is present in *anti-cis* configuration in enol form.
The monometallic complexes (6.1) to (6.5) possess μ_{eff} value in the range 2.85–3.45 BM consistent with their octahedral stereochemistry. These values rule out the possibility of any metal-metal interaction between metal atoms in the structural unit of the complexes. The dihydrazone (H
\textit{msh}) coordinates to the metal centre as a dibasic tetradentate ligand in enol form through azomethine nitrogen atoms and deprotonated naphtholic oxygen atoms. In these complexes, the dihydrazone donor atoms are arranged around the Ni(II) centre in the equatorial position while the axial positions are occupied by the co-ligands H₂O/pyridine/2-picoline/3-picoline/4-picoline molecules.

In the homobimetallic complexes (6.6) to (6.10), the magnetic moment values lie in the region 1.14–1.73 BM i.e. 0.57–0.87 per Ni(II) ion which are less than the values reported for spin free Ni(II) complexes indicating a strong metal-metal interaction in these complexes. Electronic spectral studies suggest that all of the homobimetallic complexes have distorted octahedral stereochemistry.

In these complexes the ligand coordinates to the metal centre as a tetrabasic hexadentate ligand. One of the Ni(II) centre is present in N₂O₂ coordination sphere and other Ni(II) centre is bonded to it through naphtholate oxygen atoms via oxo-bridging. Magnetic moment values for these complexes lying in the region 1.14–1.73 BM i.e. 0.57–0.87 BM per Ni(II) ion are less than the values reported for spin free Ni(II) complexes indicating a strong metal-metal interaction in these complexes.

The tentative structures for the complexes have been shown in Fig.6.11 and 6.12.
Fig. 6.1. Electronic spectrum of \([\text{Ni(H}_2\text{sh)}\text{(H}_2\text{O)}_2]\) (6.1) in DMF.
Fig. 6.2. Electronic spectrum of \([\text{Ni(H}_2\text{nsH)(py)}_2]\) (6.2) in DMF.
Fig. 6.3. Electronic spectrum of [Ni(H₂nsh)(3-pic)₂] (6.4) in DMF.
Fig. 6.4. Electronic spectrum of \([\text{Ni}_2(\text{nsh})(\text{H}_2\text{O})_4]\) (6.6) in DMF.
Fig. 6.5. Electronic spectrum of \([\text{Ni}_2(\text{nsh})(\text{py})_4]\) (6.7) in DMF.
Fig. 6.6. Electronic spectrum of [Ni$_2$(nsh)(2-pic)$_4$] (6.8) in DMF
Spectrum Name: mc-61.sp

Instrument Model: Spectrum BX Series

Resolution: 4 cm⁻¹

Fig. 6.7. Infrared spectrum of [Ni(H₂nsh)(py)₂] (6.2) in KBr.
Fig. 6.8. Infrared spectrum of [Ni(H2nsh)(2-pic)2] (6.3) in KBr.
Fig. 6.9. Infrared spectrum of [Ni₂(H₂nsh)(H₂O)₄] (6.6) in KBr.
Fig. 6.10. Infrared spectrum of [Ni₂(H₂nsh)(4-pic)₄] (6.10) in KBr.
<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Complex and Colour</th>
<th>D.P (°C)</th>
<th>Yield(%)</th>
<th>Analysis: Found (Calc.) (%)</th>
<th>Molar Conductance ($\lambda M$) Ohm$^{-1}$ cm$^{2}$ mol$^{-1}$</th>
<th>Magnetic Moment $\mu_B$ (BM)</th>
</tr>
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<tbody>
<tr>
<td>6.1</td>
<td>[Ni(H$_2$nsn)(H$_2$O)$_2$] Brown</td>
<td>&gt;300</td>
<td>70.00</td>
<td>Ni 10.54 (10.73) C 56.94 (57.07) H 4.39 (4.42) N 10.14 (10.24)</td>
<td>3.13</td>
<td>2.87</td>
</tr>
<tr>
<td>6.2</td>
<td>[Ni(H$_2$nsn)(py)$_2$] Brown</td>
<td>&gt;300</td>
<td>68.00</td>
<td>Ni 8.54 (8.77) C 63.74 (64.60) H 4.51 (4.52) N 12.23 (12.55)</td>
<td>2.81</td>
<td>3.45</td>
</tr>
<tr>
<td>6.3</td>
<td>[Ni(H$_2$nsn)(2-pic)$_2$] Yellow</td>
<td>&gt;300</td>
<td>65.00</td>
<td>Ni 8.04 (8.41) C 64.94 (65.44) H 4.89 (4.91) N 11.94 (12.05)</td>
<td>2.62</td>
<td>2.98</td>
</tr>
<tr>
<td>6.4</td>
<td>[Ni(H$_2$nsn)(3-pic)$_2$] Brown</td>
<td>&gt;300</td>
<td>63.00</td>
<td>Ni 8.09 (8.41) C 65.04 (65.44) H 4.90 (4.91) N 11.96 (12.05)</td>
<td>2.91</td>
<td>3.09</td>
</tr>
<tr>
<td>6.5</td>
<td>[Ni(H$_2$nsn)(4-pic)$_2$] Dark Brown</td>
<td>&gt;300</td>
<td>65.00</td>
<td>Ni 8.11 (8.41) C 65.03 (65.44) H 4.89 (4.91) N 11.98 (12.05)</td>
<td>2.85</td>
<td>3.30</td>
</tr>
<tr>
<td>6.6</td>
<td>[Ni$_2$(nsn)(H$_2$O)$_4$] Brown</td>
<td>&gt;300</td>
<td>69.00</td>
<td>Ni 17.94 (18.34) C 48.64 (48.80) H 4.03 (4.10) N 8.64 (8.75)</td>
<td>2.97</td>
<td>1.73</td>
</tr>
<tr>
<td>6.8</td>
<td>[Ni$_2$(nsn)(2-pic)$_4$] Brown</td>
<td>&gt;300</td>
<td>65.00</td>
<td>Ni 12.17 (12.47) C 63.94 (63.87) H 4.89 (4.93) N 11.84 (11.92)</td>
<td>2.72</td>
<td>1.54</td>
</tr>
<tr>
<td>6.9</td>
<td>[Ni$_2$(nsn)(3-pic)$_4$] Brown</td>
<td>&gt;300</td>
<td>64.00</td>
<td>Ni 12.24 (12.47) C 63.74 (63.87) H 4.88 (4.93) N 11.81 (11.92)</td>
<td>2.64</td>
<td>1.39</td>
</tr>
<tr>
<td>6.10</td>
<td>[Ni$_2$(nsn)(4-pic)$_4$] Light Brown</td>
<td>&gt;300</td>
<td>65.00</td>
<td>Ni 12.06 (12.47) C 63.91 (63.87) H 4.89 (4.93) N 11.87 (11.92)</td>
<td>2.81</td>
<td>1.29</td>
</tr>
</tbody>
</table>
Table 6.2: Electronic spectral data for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its Ni(II) complexes

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Ligand/ Complex</th>
<th>Electronic spectral bands $\lambda_{\text{max}}$ (nm) (e$_{\text{max}}$ (dm$^3$mol$^{-1}$cm$^{-1}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_{2}$nsh</td>
<td></td>
<td>317 (5480), 363 (5420)</td>
</tr>
<tr>
<td>6.1</td>
<td>[Ni(H$<em>{2}$nsh)(H$</em>{2}$O)$_{2}$]</td>
<td>319 (2755), 364 (1815), 410 (1733), 564 (80), 845(37)</td>
</tr>
<tr>
<td>6.2</td>
<td>[Ni(H$<em>{2}$nsh)(py)$</em>{2}$]</td>
<td>319 (3938), 364 (2579), 413 (2214), 562 (80), 842(36)</td>
</tr>
<tr>
<td>6.3</td>
<td>[Ni(H$<em>{2}$nsh)(2-pic)$</em>{2}$]</td>
<td>319 (1428), 366 (1265), 411 (1777), 429 (1386), 564 (37), 847(33)</td>
</tr>
<tr>
<td>6.4</td>
<td>[Ni(H$<em>{2}$nsh)(3-pic)$</em>{2}$]</td>
<td>319 (3930), 366 (2534), 410 (2216), 563 (80), 846(37)</td>
</tr>
<tr>
<td>6.5</td>
<td>[Ni(H$<em>{2}$nsh)(4-pic)$</em>{2}$]</td>
<td>319 (1838), 362 (1131), 409 (1047), 561 (80), 842(36)</td>
</tr>
<tr>
<td>6.6</td>
<td>[Ni$<em>{2}$(nsh)(H$</em>{2}$O)$_{4}$]</td>
<td>325 (6874), 369 (6653), 420 (8649), 562 (50), 843 (29)</td>
</tr>
<tr>
<td>6.7</td>
<td>[Ni$<em>{2}$(nsh)(py)$</em>{4}$]</td>
<td>326 (3345), 368 (3442), 421(5091), 564 (81), 848 (35)</td>
</tr>
<tr>
<td>6.8</td>
<td>[Ni$<em>{2}$(nsh)(2-pic)$</em>{4}$]</td>
<td>326 (2987), 421(4006), 565 (79), 849 (29)</td>
</tr>
<tr>
<td>6.9</td>
<td>[Ni$<em>{2}$(nsh)(3-pic)$</em>{4}$]</td>
<td>326 (5030), 421(7445), 568 (79), 850 (29)</td>
</tr>
<tr>
<td>6.10</td>
<td>[Ni$<em>{2}$(nsh)(4-pic)$</em>{4}$]</td>
<td>348 (5058), 420 (7123) 563 (79), 844 (29)</td>
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</tbody>
</table>
Table 6.3: Ligand field parameters for Ni(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Complex</th>
<th>$\lambda_{A_{2g}}$ (nm)</th>
<th>$\lambda_{T_{2g}}$ (F) (v$_1$) (cm$^{-1}$)</th>
<th>$\lambda_{A_{2g}}$ (nm)</th>
<th>$\lambda_{T_{1g}}$ (F) (v$_2$) (cm$^{-1}$)</th>
<th>$\Delta q$ (cm$^{-1}$)</th>
<th>$\nu_2/\nu_1$</th>
<th>B (cm$^{-1}$)</th>
<th>$\beta$ (%)</th>
<th>$\beta^\circ$ (%)</th>
<th>LFSE (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>[Ni(H$_2$nhH$_2$O)$_2$]</td>
<td>845</td>
<td>11834</td>
<td>564</td>
<td>17730</td>
<td>1183.4</td>
<td>1.498</td>
<td>653.57</td>
<td>0.6278</td>
<td>37.22</td>
<td>40.66</td>
</tr>
<tr>
<td>6.2</td>
<td>[Ni(H$_2$nh)(py)$_2$]</td>
<td>842</td>
<td>11876</td>
<td>562</td>
<td>17794</td>
<td>1187.6</td>
<td>1.4983</td>
<td>656.09</td>
<td>0.6302</td>
<td>36.98</td>
<td>40.80</td>
</tr>
<tr>
<td>6.3</td>
<td>[Ni(H$_2$nh)(2-pic)$_2$]</td>
<td>847</td>
<td>11806</td>
<td>564</td>
<td>17730</td>
<td>1180.6</td>
<td>1.5017</td>
<td>659.79</td>
<td>0.6338</td>
<td>36.62</td>
<td>40.56</td>
</tr>
<tr>
<td>6.4</td>
<td>[Ni(H$_2$nh)(3-pic)$_2$]</td>
<td>846</td>
<td>11820</td>
<td>563</td>
<td>17762</td>
<td>1182</td>
<td>1.5027</td>
<td>662.63</td>
<td>0.6365</td>
<td>36.35</td>
<td>40.61</td>
</tr>
<tr>
<td>6.5</td>
<td>[Ni(H$_2$nh)(4-pic)$_2$]</td>
<td>842</td>
<td>11876</td>
<td>561</td>
<td>17825</td>
<td>1187.6</td>
<td>1.5009</td>
<td>661.81</td>
<td>0.6357</td>
<td>36.43</td>
<td>40.80</td>
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<tr>
<td>6.6</td>
<td>[Ni$_2$(nhH$_2$O)$_4$]</td>
<td>843</td>
<td>11862</td>
<td>562</td>
<td>17794</td>
<td>1186.2</td>
<td>1.5001</td>
<td>659.18</td>
<td>0.6332</td>
<td>36.68</td>
<td>40.75</td>
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<tr>
<td>6.7</td>
<td>[Ni$_2$(nh)(py)$_4$]</td>
<td>848</td>
<td>11792</td>
<td>564</td>
<td>17730</td>
<td>1179.2</td>
<td>1.5035</td>
<td>662.95</td>
<td>0.6368</td>
<td>36.32</td>
<td>40.51</td>
</tr>
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<td>6.8</td>
<td>[Ni$_2$(nh)(2-pic)$_4$]</td>
<td>849</td>
<td>11779</td>
<td>565</td>
<td>17699</td>
<td>1177.9</td>
<td>1.5025</td>
<td>660.07</td>
<td>0.6341</td>
<td>36.59</td>
<td>40.47</td>
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<tr>
<td>6.9</td>
<td>[Ni$_2$(nh)(3-pic)$_4$]</td>
<td>850</td>
<td>11765</td>
<td>566</td>
<td>17606</td>
<td>1176.5</td>
<td>1.4964</td>
<td>645.98</td>
<td>0.6205</td>
<td>37.95</td>
<td>40.42</td>
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<tr>
<td>6.10</td>
<td>[Ni$_2$(nh)(4-pic)$_4$]</td>
<td>844</td>
<td>11848</td>
<td>563</td>
<td>17762</td>
<td>1184.8</td>
<td>1.4991</td>
<td>656.37</td>
<td>0.6302</td>
<td>36.98</td>
<td>40.70</td>
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</table>
Table 6.4: Structurally significant Infrared (IR) bands (in cm\(^{-1}\)) for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its Ni(II) complexes.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Ligand/Complex</th>
<th>(v(\text{OH} + \text{NH}))</th>
<th>(v(\text{C} = \text{O}))</th>
<th>(v(\text{C} = \text{N}))</th>
<th>Amide II + (v(\text{C} = \text{O})) (naphthalonic)</th>
<th>(v(\text{NCO}^-))</th>
<th>(v(\text{C} = \text{O}))</th>
<th>(v(\text{N} = \text{N}))</th>
<th>Other bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>[Ni(H(_2\text{nsh})(\text{H}_2\text{O})_2])</td>
<td>3410 m 3291 m</td>
<td>1672 vs 1633 vs</td>
<td>1540 m</td>
<td>1281 m</td>
<td>1029 w</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>6.2</td>
<td>[Ni(H(_2\text{nsh})(\text{py})_2])</td>
<td>3419 m 3286 m</td>
<td>1618 s 1604 m</td>
<td>1540 s</td>
<td>1507 w</td>
<td>1303 m 1282 w</td>
<td>1038 w</td>
<td>---</td>
<td>521 w 1052 w</td>
</tr>
<tr>
<td>6.3</td>
<td>[Ni(H(_2\text{nsh})(2\text{-pic})_2])</td>
<td>3421 m</td>
<td>1617 s 1602 m</td>
<td>1540 s</td>
<td>1508 w</td>
<td>1303 m 1282 w</td>
<td>1038 w</td>
<td>---</td>
<td>521 w 1053 w</td>
</tr>
<tr>
<td>6.4</td>
<td>[Ni(H(_2\text{nsh})(3\text{-pic})_2])</td>
<td>3420 m</td>
<td>1616 s 1602 m</td>
<td>1540 s</td>
<td>1506 w</td>
<td>1303 m 1038 w</td>
<td>---</td>
<td>521 w 1070 w</td>
<td></td>
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<tr>
<td>6.5</td>
<td>[Ni(H(_2\text{nsh})(4\text{-pic})_2])</td>
<td>3435 s</td>
<td>1617 s 1604 m</td>
<td>1540 m</td>
<td>1508 w 1303 m 1036 w</td>
<td>---</td>
<td>522 w 1045 w</td>
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<td></td>
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<tr>
<td>6.6</td>
<td>[Ni(_2\text{nsh})(\text{H}_2\text{O})_4])</td>
<td>3401 m 3055 m</td>
<td>1618 s 1602 w</td>
<td>1540 vs 1508 w</td>
<td>1302 m 1282 w</td>
<td>1030 w 897 w</td>
<td>569 w 525 w</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>6.7</td>
<td>[Ni(_2\text{nsh})(\text{py})_4])</td>
<td>3419 m 3051 m</td>
<td>1617 vs 1602 s</td>
<td>1540 vs 1508 w</td>
<td>1303 m 1283 w</td>
<td>1093 w 882 w</td>
<td>595 w 528 w 1069 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.8</td>
<td>[Ni(_2\text{nsh})(2\text{-pic})_4])</td>
<td>3421 m 3055 m</td>
<td>1617 vs 1602 vs</td>
<td>1540 vs 1508 w 1302 m 1281 w</td>
<td>1093 w 883 w</td>
<td>589 w 567 w 1076 w</td>
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<tr>
<td>6.9</td>
<td>[Ni(_2\text{nsh})(3\text{-pic})_4])</td>
<td>3409 m 3051 m</td>
<td>1617 vs 1602 vs</td>
<td>1541 vs 1508 w 1302 m 1282 w</td>
<td>1049 w 862 w</td>
<td>585 w 532 w 1061 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.10</td>
<td>[Ni(_2\text{nsh})(4\text{-pic})_4])</td>
<td>3398 m 3050 z</td>
<td>1617 vs 1602 vs</td>
<td>1541 vs 1508 w 1302 m 1282 w</td>
<td>1094 w 861 w</td>
<td>570 w 528 w 1070 w</td>
<td></td>
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</tbody>
</table>
Fig. 6.11. Tentative structure of [Ni(H₂nsh)(A)₂] (where A = water (H₂O) (6.1), pyridine (py, 6.2); 2-picoline(2-pic, 6.3); 3-picoline(3-pic, 6.4); 4-picoline (4-pic, 6.5)
Fig. 6.12. Tentative structure of [Ni₂(nsh)(A)₄] (where A = water (H₂O, (6.6)); pyridine (py, 6.7); 2-picoline(2-pic, 6.8); 3-picoline(3-pic, 6.9); 4-picoline (4-pic, 6.10)
References


