Chapter 3

Square-planar nickel(II) complexes with a tridentate O,N,O-donor Schiff base and monodentate N-heterocycles

3.1. Abstract

A couple of nickel(II) complexes having the general formula [Ni(bhac)hc] with tridentate acetylacetone benzyolhydrazone (H₂bhac) and monodentate heterocycles (hc = 3,5-dimethylpyrazole (Hdmpz) and imidazole (Himdz)) are reported. The complexes were synthesized in ethanol media by reacting Ni(O₂CCH₃)₂·4H₂O, H₂bhac and hc in 1:1:1 mole ratio and characterized by analytical, magnetic and spectroscopic methods. X-ray crystal structures of both complexes have been determined. In each complex, the metal ion is in square-planar N₂O₂ coordination geometry. In the solid state, a one-dimensional assembly of the [Ni(bhac)(Himdz)] molecules is formed via intermolecular hydrogen bonds between the imidazole N−H groups and the uncoordinated N-atoms of the deprotonated amide functionalities. On the other hand, two [Ni(bhac)(Hdmpz)] molecules are involved in a pair of complementary hydrogen bonds between the pyrazole N−H groups and the coordinated O-atoms of the deprotonated amide functionalities forming a dinuclear species.

§ A part of this work has been published in Inorg. Chem. Commun., 2003, 6, 381.
3.2. Introduction

In recent years, extended assemblies of complexed metal ions are receiving immense attention primarily due to their photophysical, magnetic and conducting properties.\textsuperscript{1-4} The general strategies used for the self-assembly of transition metal ion complexes into such extended assemblies are the metal ion’s preference for different coordination geometry, use of suitable ligands and weak intermolecular interactions such as hydrogen bonding and \( \pi-\pi \) interaction.\textsuperscript{1,5-7} In this chapter, we report the self-assembly of two square-planar mixed-ligand nickel(II) complexes. The common ligand in both complexes is the deprotonated acetylacetone benzoylhydrazone (\( \text{H}_2\text{bhac} \), two \( \text{H} \) represent the dissociable enolic-\( \text{OH} \) and the amide proton) that can coordinate the metal ion through the enolate-\( \text{O} \), the imine-\( \text{N} \) and the deprotonated amide-\( \text{O} \) atoms. Neutral N-donor imidazole (\( \text{Himdz} \)) or 3,5-dimethylpyrazole (\( \text{Hdmpz} \)) has been used as the ancillary ligand to satisfy the fourth coordination number around the metal ion. The reasons behind the choice of these ligands are as follows. The tridentate planar \( \text{bhac}^{2-} \) will enforce the square-planar coordination geometry and it will also satisfy the +2 charge of the metal ion so that a neutral monodentate ligand can occupy the fourth site. The heterocycles (\( \text{Himdz} \) and \( \text{Hdmpz} \)) used as the monodentate ligands can be either coplanar with the \{\( \text{Ni(bhac)} \)\} moiety or can have a different orientation. In the first case, there is a distinct possibility for a \( \pi \)-stacked one-dimensional assembly of the molecules. In the second case, the acidic N–H protons of \( \text{Hdmpz} \) and \( \text{Himdz} \) can participate in intermolecular hydrogen bonding with the O- or N-atoms of the tridentate ligand to form extended assemblies. Herein, we describe the synthesis, characterization and solid state structures of [\( \text{Ni(bhac)(Himdz)} \)] (3) and [\( \text{Ni(bhac)(Hdmpz)} \)] (4). The self-assembly of the complex molecules via intermolecular N–H⋯O and N–H⋯N interactions has been demonstrated.
3.3. Experimental

3.3.1. Materials

The Schiff base H₂bhac was prepared as reported before. All other chemicals and solvents were of analytical grade available commercially and were used as received.

3.3.2. Physical measurements

Elemental (C, H, N) analysis data were obtained with a Perkin-Elmer Model 240C elemental analyzer. Infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. Room temperature solid state magnetic susceptibilities were measured by using a Sherwood Scientific magnetic susceptibility balance. Solution electrical conductivities were measured with a Digisun DI-909 conductivity meter. A Shimadzu 3101-PC UV/vis/NIR spectrophotometer was used to record the electronic spectra. Proton NMR spectra of the complexes in CDCl₃ solutions were recorded on a Bruker 200 MHz spectrometer using Si(CH₃)₄ as an internal standard.

3.3.3. Synthesis of nickel(II) square planar complexes

[Ni(bhac)(Himdz)] (3)

This complex was synthesized in 55% yield by using the same procedure as described above by reacting Ni(O₂CCH₃)₂·4H₂O, H₂bhac and Himdz in ethanol. Single crystal for X-ray structure determination was
selected from the crystalline product obtained directly from the reaction mixture. *Anal.* Calc. for C$_{15}$H$_{16}$N$_{4}$O$_{2}$Ni: C, 52.52; H, 4.70; N, 16.33. Found: C, 52.35; H, 4.53; N, 16.17. Electronic spectral data in CH$_3$CN solution ($\lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1}))$: 530sh (125), 482 (450), 382 (15100), 298 (4900), 235sh (19000). $^1$H NMR (200 MHz) data in CDCl$_3$: $\delta$ 1.91 (s, 3H, -(H$_3$C)C=N-); 2.34 (s, 3H, H$_3$C-C(-O-)=); 5.09 (s, 1H, =CH- of bhac$^{2+}$); 7.29 (m, 3H, phenyl ring protons); 7.89 (t, 2H, phenyl ring protons); 6.93, 7.11, 7.72 (s, s, s, imidazole C–H protons), 9.71 (s, imidazole N–H proton).

**[Ni(bhac)(Hdmpz)] (4)**

An ethanol solution (10 ml) of Ni(O$_2$CCH$_3$)$_2$·4H$_2$O (125 mg, 0.5 mmol) was added to another ethanol solution (15 ml) of H$_2$bhac (110 mg, 0.5 mmol) and Hdmpz (48 mg, 0.5 mmol). The resulting brown solution was refluxed for 3 h. Slow evaporation of this reaction mixture at room temperature in air afforded the complex as brown crystalline material. This material was collected by filtration, washed with ice-cold ethanol and dried in air. Yield obtained was 85 mg (46%). Single crystal for X-ray structure determination was selected from this material. *Anal.* Calc. for C$_{17}$H$_{20}$N$_{4}$O$_{2}$Ni: C, 55.02; H, 5.43; N, 15.10. Found: C, 55.24; H, 5.12; N, 14.91. Electronic spectral data in CH$_3$CN solution ($\lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1}))$: 540sh (120), 378 (17 400), 292sh (5 700), 222 (25 000). $^1$H NMR (200 MHz) data in CDCl$_3$: $\delta$ 1.80 (s, 3H, -(H$_3$C)C=N-); 2.17 (s, 3H, 3-methyl of dmpz); 2.26 (s, 3H, H$_3$C-C(-O-)=); 2.52 (s, 3H, 5-methyl of dmzp); 5.03 (s, 1H, =CH- of bhac$^{2+}$); 5.80 (s, 1H, =CH- of dmpz); 7.26 (m, 3H, phenyl ring protons); 7.76 (m, 3H, phenyl ring protons); 7.78 (m, 2H, phenyl ring protons); 10.67 (s, 1H, -NH- of dmpz).

**3.3.4. X-ray crystallography**

For crystals of both 3 and 4 data were collected on an Enraf-Nonius Mach-3 single crystal diffractometer using graphite monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) by $\omega$-scan method at 298 K. In each case, unit cell
parameters were determined by least-squares fit of 25 reflections having 2θ values in the range 18-22°. Intensities of 3 check reflections were measured after every 1.5 h during the data collection to monitor the crystal stability. In both cases, there is no significant change in the intensities of the check reflections. Empirical absorption corrections were applied to both datasets based on the ψ-scans. The structures were solved by direct methods and refined on F² by full-matrix least-squares procedures. In each case, the asymmetric unit contains one molecule of the complex. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealised positions by using riding model, but not refined. The programs of WinGX were used for data reduction and absorption correction. Structure solution and refinement were performed with the SHELX-97 programs. The platon package was used for molecular graphics. Selected crystal and refinement data are listed in Table 3.1.
Table 3.1. Crystallographic data for 3 and 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C(<em>{15})H(</em>{16})N(_4)O(_2)Ni</td>
<td>C(<em>{17})H(</em>{20})N(_4)O(_2)Ni</td>
</tr>
<tr>
<td>Formula weight</td>
<td>343.03</td>
<td>371.08</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_1/c)</td>
<td>(Pbcn)</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>14.384(4)</td>
<td>19.058(4)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>5.8031(13)</td>
<td>11.318(2)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>18.082(4)</td>
<td>15.931(4)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>93.56(3)</td>
<td>90</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>1506.4(6)</td>
<td>3436.4(14)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) (g cm(^{-3}))</td>
<td>1.513</td>
<td>1.435</td>
</tr>
<tr>
<td>(\mu) (mm(^{-1}))</td>
<td>1.300</td>
<td>1.146</td>
</tr>
<tr>
<td>Crystal size (mm(^3))</td>
<td>0.48 x 0.36 x 0.12</td>
<td>0.51 x 0.48 x 0.36</td>
</tr>
<tr>
<td>(\theta) range (°)</td>
<td>1.42 to 27.47</td>
<td>2.09 to 27.45</td>
</tr>
<tr>
<td>Reflections collected/unique</td>
<td>3796/3448</td>
<td>4417/3945</td>
</tr>
<tr>
<td>Reflections having (I \geq 2\sigma(I))</td>
<td>1874</td>
<td>2521</td>
</tr>
<tr>
<td>Data/restr./parameters</td>
<td>3448/0/201</td>
<td>3945/0/221</td>
</tr>
<tr>
<td>(R1^{a}), (wR2^{b}) ([I \geq 2\sigma(I)])</td>
<td>0.0625, 0.1533</td>
<td>0.0435, 0.0837</td>
</tr>
<tr>
<td>(R1^{a}), (wR2^{b}) (all data)</td>
<td>0.1348, 0.1914</td>
<td>0.0861, 0.0976</td>
</tr>
<tr>
<td>Goodness-of-fit(^{c})</td>
<td>1.020</td>
<td>1.001</td>
</tr>
<tr>
<td>Largest peak/hole (e Å(^{-3}))</td>
<td>0.679/-0.598</td>
<td>0.350/-0.263</td>
</tr>
</tbody>
</table>

\(^a\)R1 = \(\sum||F_o|| - |F_c||/\sum|F_o|/\sum|F_o|\).  
\(^b\)wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]\}^{1/2}.
\(^c\)GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2} where ‘n’ is the number of reflections and ‘p’ is the number of parameters refined.
3.4. Results and discussion

3.4.1. Synthesis and some properties

The dark brown complexes were synthesized in moderate yields by reacting Ni(O_2CCH_3)_2·4H_2O, H_2bhac and Hdmpz or Himdz in 1:1:1 mole ratio in boiling ethanol. Elemental analysis data are consistent with the molecular formula [Ni(bhac)hc] (hc = Himpz, Hdmpz). Both complexes are non-conducting in acetonitrile solutions. The complexes are diamagnetic and NMR active. Thus in each complex, the nickel ion is in +2 oxidation state and the coordination geometry around the metal centre is square-planar.

3.4.2. Spectral characteristics

The infrared spectra of the complexes do not display any amide or secondary amine N–H stretch in the range 3300-3500 cm^{-1}. Several sharp weak peaks observed in the range 2855-3180 cm^{-1} are likely to be due to the aromatic C-H stretches. The absence of any peak assignable to the heterocycle N-H group is consistent with their involvement in strong intermolecular hydrogen bonding (vide infra). The C=O stretch (1675 cm^{-1}) of the amide functionality in free H_2bhac is also absent in both spectra. Thus the Schiff base is completely deprotonated (bhac^{2-}) and acts as a dibasic enolate-O, imine-N and amide-O donor ligand in both complexes. The X-ray structures confirm such coordination. A strong peak at ~1600 cm^{-1} might involve the C=N stretches.

Electronic spectral profiles of both complexes in acetonitrile solutions are very similar (Figure 3.1). A weak absorption band observed at ~535 nm is assigned to the spin-allowed d-d transition (^{1}A_{1g} \rightarrow ^{1}A_{2g}) for a square-planar nickel(II) complex. At higher energy, several strong absorptions are observed in the range 482-222 nm. Each of the three ligands (H_2bhac, Himdz and Hdmpz) in methanol solution displays a single absorption in the range 250-
215 nm. Thus the higher energy absorptions displayed by 3 and 4 are most likely due to charge transfer and ligand band transitions.

![Electronic spectra of 3 (---) and 4 (—) in acetonitrile.](image)

**Fig. 3.1.** Electronic spectra of 3 (---) and 4 (—) in acetonitrile.

The \(^1\)H NMR spectra of the complexes in CDCl\(_3\) solutions are consistent with the [Ni(bhac)L] formulation. Protons of the two methyl groups on the bhac\(^2\)- moiety appear as singlets at \(\delta\) 1.92 and 2.34 for 3 and \(\delta\) 1.80 and 2.26 for 4. The =CH- proton of the bhac\(^2\)- appears at \(\delta\) 5.09 and 5.03 for 3 and 4, respectively. For both complexes, the five phenyl protons appear in two groups at \(\delta\) ~7.3 and ~7.8. The imidazole C–H protons in 3 are observed as three singlets at \(\delta\) 6.93, 7.11 and 7.72. On the other hand, the lone C-H proton of Hdmpz in 4 appear as a singlet at \(\delta\) 5.80. Two singlets observed at \(\delta\) 2.17 and 2.52 for 4 are assigned to the 3- and 5-methyl group protons of the Hdmpz ligand, respectively. The heterocycle N–H proton appears as a singlet at \(\delta\) 9.71 and 10.67 for 3 and 4, respectively.
3.4.3. Molecular structures

The solid state molecular structures of 3 and 4 are shown in Figures 3.2 and 3.3, respectively. Selected bond parameters associated with the metal ions are listed in Table 3.2. In each complex, the tridentate bhac$_{2}$$^{2-}$ coordinates the metal ion via the enolate-O, the imine-N and the deprotonated amide-O atoms forming one five- and one six-membered chelate ring. The fourth site is occupied by the sp$^{2}$ N-atom of the heterocycle to complete a square-planar geometry around the metal centre. In both complexes, there is no deviation of the metal centre from the N$_{2}$O$_{2}$ square-plane. For 3, the maximum and minimum deviations from the mean plane constituted by O1, O2, N1, N2 and Ni are 0.032(2) and 0.017(2) Å, respectively. For 4, the corresponding values are 0.091(1) and 0.028(1), respectively. The N-N, N-C and C-O bond distances (Table 3.2) in the =N-N=C(O-) fragment of bhac$_{2}$$^{2-}$ are consistent with the enolate form of the amide functionalities.$^{8,15}$ The Ni-N$_{\text{imine}}$ and Ni-O$_{\text{amide}}$ distances are comparable with those observed in other Ni(II) complexes with
arylhydrazones.\textsuperscript{17,18} In both structures, the Ni-O\textsubscript{enolate} bond distances are similar to those reported for Ni(II) complexes where the metal centres have the same coordinating atom.\textsuperscript{19} Structurally characterized mononuclear tetracoordinated Ni(II) complexes containing neutral pyrazole or imidazole as a ligand are extremely rare.\textsuperscript{20,21} The Ni-N\textsubscript{pyrazole} bond distance in 4 is comparable with the distances observed in the lone example of a tetracoordinated Ni(II) complex containing monodentate neutral pyrazole moiety.\textsuperscript{20} In 3, the Ni-N\textsubscript{imidazole} bond distance is normal, as observed in a similar square-planar Ni(II) complex with a tridentate ligand and a neutral imidazole.\textsuperscript{21}

![Figure 3.3](image-url)

**Fig. 3.3.** Molecular structure of 4 showing 50% probability thermal ellipsoids for the non-hydrogen atoms and the atom-labeling scheme.
Table 3.2. Selected bond lengths (Å) and bond angles (°) of 3 and 4

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-O1</td>
<td>1.824(4)</td>
<td>1.814(2)</td>
</tr>
<tr>
<td>Ni-O2</td>
<td>1.841(4)</td>
<td>1.850(2)</td>
</tr>
<tr>
<td>Ni-N1</td>
<td>1.825(4)</td>
<td>1.819(2)</td>
</tr>
<tr>
<td>Ni-N3</td>
<td>1.904(5)</td>
<td>1.915(2)</td>
</tr>
<tr>
<td>N1-N2</td>
<td>1.412(5)</td>
<td>1.404(3)</td>
</tr>
<tr>
<td>N2-C6</td>
<td>1.307(7)</td>
<td>1.292(4)</td>
</tr>
<tr>
<td>C6-O2</td>
<td>1.302(6)</td>
<td>1.319(3)</td>
</tr>
<tr>
<td>O1-Ni-O2</td>
<td>179.19(6)</td>
<td>177.05(9)</td>
</tr>
<tr>
<td>O1-Ni-N1</td>
<td>96.66(19)</td>
<td>96.59(11)</td>
</tr>
<tr>
<td>O1-Ni-N3</td>
<td>88.68(18)</td>
<td>88.92(10)</td>
</tr>
<tr>
<td>O2-Ni-N1</td>
<td>83.90(17)</td>
<td>83.89(10)</td>
</tr>
<tr>
<td>O2-Ni-N3</td>
<td>90.71(18)</td>
<td>90.97(9)</td>
</tr>
<tr>
<td>N1-Ni-N3</td>
<td>173.54(18)</td>
<td>171.06(10)</td>
</tr>
</tbody>
</table>

3.4.4. Hydrogen bonding and self-assembly

As mentioned earlier we were expecting a square-planar Ni(II) complex with the planar tridentate ligand bhac²⁻ and a neutral monodentate heterocycle. The main quest was to see the orientation of the heterocycle plane with respect to the \{Ni(bhac)\} plane. If both are coplanar there is a possibility of \(\pi\)-stacked assembly of the molecules. In case of their non-coplanarity, self-assembly of the molecules via intermolecular hydrogen bonding between the heterocycle N-H and the O- or N-atoms of bhac²⁻ is the next possibility. Indeed the coordination geometry around the metal centres are square-planar (vide supra) in 3 and 4. For a \(\pi\)-stacked arrangement planarity of the whole molecule is one of the prerequisites.⁹²,²³ However, excluding the phenyl ring atoms all other
atoms in the \{Ni(bhac)\} moiety are satisfactorily planar in both molecules. The mean deviations are 0.05 and 0.01 Å for 3 and 4, respectively. In each case, the phenyl ring plane is significantly twisted. The dihedral angles between the phenyl ring plane and the plane constituted by Ni, O1, O2, N1, N2, C1-C6 are 21.1(2)° and 34.4(1)° for 3 and 4, respectively. In addition to the twisting of the phenyl ring, the heterocycle plane also has a different orientation with respect to the plane containing Ni, O1, O2, N1, N2, C1-C6. However, these orientations are different for the two complexes (Figures 3.2 and 3.3). In case of 3, the dihedral angle between the imidazole plane (mean deviation 0.003 Å) and the above mentioned plane is 19.5(3)°. On the other hand, the dihedral angle between the pyrazole plane (mean deviation 0.017 Å) and the same plane is 69.12(7)° in 4. Most likely the two methyl groups in 4 on the Hdmpz make it sterically more un favourable and hence the dihedral angle is larger. As a result of this non-planarity of both the molecules neither of them is involved in intermolecular π-π interactions in the crystal lattice. However, as we have anticipated the acidic heterocycle N–H in both molecules are involved in strong intermolecular hydrogen bonding. In the case of 3, the uncoordinated N-atom of the deprotonated amide functionality acts as the acceptor atom in the hydrogen bonding and a one-dimensional assembly (Figure 3.4) of the molecules is formed via this N–H···N interactions. The N4···N2 distance and the N4–H···N2 angle are 2.893(6) Å and 163.26°, respectively. The Ni···Ni distance in this uniform chain-like arrangement is 9.079(2) Å. On the other hand, the metal coordinated amide-O atom acts as the acceptor atom in the hydrogen bonding in 4. However, instead of a one-dimensional assembly two 4 molecules participate in a pair of complementary N4–H···O2 hydrogen bonds and form a dimeric structure (Figure 3.5). The N4···O2 distance and the N4–H···O2 angle are 2.830(3) Å and 162.95°, respectively. In this dimeric arrangement, the Ni···Ni distance is 3.209(1) Å.
Square-planar Ni(II) complexes...

Fig. 3.4. One-dimensional ordering of 3.
The possible reasons for the difference in the hydrogen bonding pattern and hence in the self-assembly are as follows. The orientations of the heterocycle plane with respect to the plane containing Ni, O1, O2, N1, N2, C1-C6 are very different in the two complex molecules. In addition, the N–H proton in Himdz is one C-atom apart from the coordinating heterocycle N-atom compared to that in Hdmpz. Thus the direction of the Himdz N–H group as well as relatively more planar nature of the molecules of 3 lead to intermolecular N–H···N interactions and a one-diemensional assembly in the solid state. Whereas in case of 4, the orientation of Hdmpz plane and the close proximity of Hdmpz N–H group and the coordinating N-atom leads to a dimeric arrangement via two reciprocal N4–H···O2 interactions.

### 3.5. Conclusions

We have synthesized and characterized two new mixed-ligand nickel(II) complexes with a tridentate enolate-O, imine-N and amide-O donor ligand and N-donor heterocycles such as imidazole (Himdz) and 3,5-dimethylpyrazole (Hdmpz). In both complex molecules, the metal ions are in a square-planar N$_2$O$_2$ coordination geometry. However, none of the molecules is planar primarily due to different orientation of the heterocycle plane with respect to the rest of the molecule. The extent of this difference in orientation is less for the complex containing Himdz than the complex containing Hdmpz. As a result of this variance in orientation and also due to different types of heterocycles, the molecules of these two essentially similar complexes display two different types of self-assembly via two different intermolecular hydrogen bonding interactions involving the acidic heterocycle N–H group in the solid state. The Himdz containing complex molecules form a one-dimensional chain via N–H···N$_{amide}$ hydrogen bonds and two molecules of the Hdmpz containing complex form a dimer via a pair of N–H···O$_{amide}$ hydrogen bonds.
3.6. References