Synthesis and characterisation of aroylhydrazone complexes derived from some piperidin-4-ones

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Ni(II) and Cu(II) complexes of the types [ML(H)_2(ONO)_2]·nH_2O, [M(HL)^2]^2 and [M_2(HL)_2(NO)_3]·nH_2O [L^1 = cis-2,6-diphenylpiperidin-4-one benzoylhydrazone (DPBH), HL^2 = cis-2,6-diphenylpiperidin-4-one salicyloylhylazone (DPSH)] and HL^3 = trans-3-methyl-cis-2,6-diphenylpiperidin-4-one salicyloylhylazone (MDPSH)] have been synthesized and characterized on the basis of elemental, electronic, IR and ESR spectral analyses and also by conductivity measurements, magnetic moment measurements and thermogravimetric analyses (TGA/DTA). The results reflect coordination of the ligands through >C=O and >C=N groups. In bimetallic MDPSH complexes coordination occurs through phenolic oxygen and amide nitrogen atoms. The powder X-ray diffraction analysis reveals that DPBH and DPSH complexes of Ni(II) crystallize in simple cubic unit lattice.

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Ligands with N-N bonds have been much studied in recent years because of their relationship to the problem of conversion of dinitrogen to ammonia or hydrazine. The interest in the study of hydrazones has been growing due to their use in biological systems and analytical chemistry. Transition metal complexes of aroylhydrazones have attracted considerable interest not only because of their potential application in antitubercular agents but also because of the various bonding and stereochemical possibilities that they offer. A survey of literature shows many reports on aroylhydrazone complexes derived from aliphatic, aromatic and heterocumulic carbonyl compounds. However, no systematic work has been done on complexes derived from saturated heterocyclic carbonyl compounds. This prompted us to undertake an investigation of the complexation tendency of aroylhydrazones derived from saturated six-membered heterocyclic ketones. We report here the synthesis and characterisation of three aroylhydrazones (Scheme 1) and their complexes with Cu(II) and Ni(II) ions.

Materials and Methods
Preparation of ligands and complexes
The ligands DPBH, DPSH and MDPSH were prepared as reported in literature by reacting benzoyl/salicyloylhylazone with appropriate heterocyclic ketones and characterised on the basis of NMR spectral measurements.

Dry finely powdered ligand (5 mmol) [1.85 g (DPBH)/1.93 g (DPSH)] was added slowly to a hot methanolic (80 cm^3) solution of metal(II) salt (5 mmol) [copper(II) nitrate trihydrate (1.21 g)/nickel(II) nitrate hexahydrate (1.45 g)] with stirring. The solution was heated under reflux for 8-10 h. The green coloured complexes 1-4 separated out were filtered, washed with hot benzene, followed by hot water and dried over calcium chloride in a desiccator. The yields were in the range 60-70%. The complexes decomposed at 240° (1), 274° (2), 245° (3) and 237° (4).

To a DMF solution (20 cm^3) of MDPSH (0.2 g, 5 mmol), a methanolic solution (60 cm^3) of metal(II) salt (5 mmol) [nickel(II) nitrate hexahydrate L^1 = cis-2,6-Diphenylpiperidin-4-one benzoylhydrazone (DPBH)]
HL^2 = cis-2,6-Diphenylpiperidin-4-one salicyloylhydrazone (DPSH)
HL^3 = trans-3-Methyl-cis-2,6-diphenylpiperidin-4-one salicyloylhydrazone (MDPSH)

Scheme 1
(1.45 g)/copper(II) nitrate trihydrate (1.21 g) was added and heated under reflux for 8 h. The pH of the solution was adjusted to 7 using 1% alcoholic KOH in the case of nickel(II) complex preparation and then refluxed. The pink coloured Ni(II) complex 5 and green coloured copper(II) complex 6 which separated out, were filtered, washed with hot benzene, followed by hot water and dried over calcium chloride in a desiccator. The yield was 50% (5) and 70% (6) and both the complexes decomposed above 300°C.

Results and Discussion

The formation of the complexes is shown in Scheme 2.

![Scheme 2](image)

The analytical data (Table 1) reveal that DPBH and DPSH complexes 1-4 have 1:2 metal to ligand stoichiometries whereas MDPSH complexes 5 and 6 have 2:1 stoichiometries. The molar conductivities of DPBH and DPSH complexes indicate 1:2 electrolytes in DMF. These complexes are soluble only in coordinating solvents like DMF and DMSO while MDPSH complexes are insoluble in these solvents.

Electronic spectra of complexes 1-4 were recorded in DMF. Diffuse reflectance spectra were recorded for...
complexes 5 and 6. The bands observed in the region 275-315 nm and 360-400 nm are attributed to the transitions within the ligand molecules and charge transfer transitions, respectively in all the complexes. The Cu(II) complexes 2 and 4 show additional bands in the visible region (672 and 603 nm) and these bands are assigned to d-d transition, i.e. $^2B_g \rightarrow ^2B_{2g}$ transition suggesting square planar geometry. The Cu(I) complexes 2 and 4 show additional bands relative to the free ligands which indicates carbonyl vibrations are observed at 1363 cm$^{-1}$ in the complexes. Coordination of amide NH to metal ions in complexes 5 and 6 is supported by the observed magnetic moment of copper(II) complex 4 is closer to spin only value and somewhat lower value is observed for copper(II) complex 2. Magnetic moments of nickel(II) complexes 1 and 3 are substantially lower than that of spin only value expected for octahedral and tetrahedral geometries. Besides, the fully paramagnetic octahedral and tetrahedral complexes and fully diamagnetic square planar complexes a number of complexes with the same stoichiometry have been reported to have magnetic values ranging from 0.6 to 2.5 BM at room temperature and show the rare phenomenon of spin state isomerism. In the solid state, probably mixed stereochemistries exist, i.e., both the diamagnetic square planar complex and the paramagnetic tetrahedral complex may be present in solid state in the present study. The magnetic moments of DPHS complexes 5 and 6 also support square planar geometries for these complexes.

Broad bands of medium intensity centered around 3450-3000 cm$^{-1}$ in the IR spectra are assigned to $\nu_{OH}$ and $\nu_{NH}$ present in the complexes. The striking feature (Table 2) is shifting of $\nu_{C=O}$ of carbonyl group and $\nu_{C=N}$ of azomethine group to lower frequencies relative to the free ligands which indicates carbonyl oxygen and azomethine nitrogen coordination. Absence of appreciable change in the frequency corresponding to the bending mode of hydroxyl group ($\delta_{OH}$) in DPHS complexes 3 and 4 compared to the free ligand DPHS reveals that the phenolic OH is not deprotonated in these complexes. The $\delta_{OH}$ band for phenolic hydroxyl group observed at 1363 cm$^{-1}$ in the free ligand MDPHS moves to higher frequencies in the MDPHS complexes 5 and 6, thus supporting the coordinating nature of phenolic oxygen during complexation. Coordination of amide NH to metal ions in complexes 5 and 6 is supported by the appearance of sharp bands due to $\delta_{NH}$ around 1560 cm$^{-1}$. The appearance of new intense peaks around 1380 and 820 cm$^{-1}$ in complexes 3 and 4 and 1380 and 1000 cm$^{-1}$ in complexes 1 and 2 are attributed to the presence of ionic nitrate in these complexes. The new peaks around 1330 cm$^{-1}$ are attributed to the monodentate coordinating nature of the nitrate group in complexes 5 and 6. Non-ligand bands due to $\nu_{MO}$ and $\nu_{MN}$ vibrations are observed in the 500-500 and 500-400 cm$^{-1}$ regions respectively.

The observed magnetic moment of copper(II) complex 4 is closer to spin only value and somewhat lower value is observed for copper(II) complex 2. Magnetic moments of nickel(II) complexes 1 and 3 are substantially lower than that of spin only value expected for octahedral and tetrahedral geometries. Besides, the fully paramagnetic octahedral and tetrahedral complexes and fully diamagnetic square planar complexes a number of complexes with the same stoichiometry have been reported to have magnetic values ranging from 0.6 to 2.5 BM at room temperature and show the rare phenomenon of spin state isomerism. In the solid state, probably mixed stereochemistries exist, i.e., both the diamagnetic square planar complex and the paramagnetic tetrahedral complex may be present in solid state in the present study. The magnetic moments of DPHS complexes 5 and 6 also support square planar geometries for these complexes.

### Table 2—IR (cm$^{-1}$) and electronic spectral data of complexes

<table>
<thead>
<tr>
<th>System</th>
<th>$\nu_{OH}$ and $\nu_{NH}$</th>
<th>$\nu_{C=O}$</th>
<th>$\nu_{C=N}$</th>
<th>$\delta_{OH}$</th>
<th>$\delta_{NH}$</th>
<th>$\nu_{NO}$</th>
<th>$\nu_{MO}$</th>
<th>$\nu_{MN}$</th>
<th>$\lambda_{max}$ (nm) (log e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L^1$ (DPBH)</td>
<td>3428, 1647</td>
<td>1600</td>
<td>1292</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>271 (4.52)</td>
</tr>
<tr>
<td>[Ni(L$^1$)$_2$][NO$_3$]$_2$H$_2$O (1)</td>
<td>3433, 1593</td>
<td>1528</td>
<td>1304</td>
<td>-</td>
<td>1382</td>
<td>540</td>
<td>435</td>
<td>-</td>
<td>281, 293, 311 (4.02) 262, 376</td>
</tr>
<tr>
<td>[Cu(L$^1$)$_2$][NO$_3$]$_2$H$_2$O (2)</td>
<td>3425, 1595</td>
<td>1532</td>
<td>1305</td>
<td>-</td>
<td>1383</td>
<td>601</td>
<td>506</td>
<td>-</td>
<td>257, 296 (4.15) 672 (1.85)</td>
</tr>
<tr>
<td>$HL^1$ (DPBH)</td>
<td>3727, 3250</td>
<td>1604</td>
<td>1233</td>
<td>1306</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>308 (4.10) 370 (2.30)</td>
</tr>
<tr>
<td>[Ni(HL$^1$)$_2$][NO$_3$]$_3$ (3)</td>
<td>3408, 1601</td>
<td>1541</td>
<td>1270</td>
<td>1305</td>
<td>1383</td>
<td>543</td>
<td>451</td>
<td>-</td>
<td>293, 311 (3.92) 362, 376</td>
</tr>
<tr>
<td>[Cu(HL$^1$)$_2$][NO$_3$]$_3$ (4)</td>
<td>3757, 3432</td>
<td>3003</td>
<td>3013</td>
<td>1308</td>
<td>1383</td>
<td>544</td>
<td>-</td>
<td>-</td>
<td>291, 315 (3.87) 481 (2.15)</td>
</tr>
<tr>
<td>$HL^1$ (MDPHS)</td>
<td>3757, 3409</td>
<td>3296</td>
<td>1608</td>
<td>1557</td>
<td>1237</td>
<td>1363</td>
<td>-</td>
<td>-</td>
<td>275 (4.52) 305, 365 (3.80)</td>
</tr>
<tr>
<td>[Ni(HL$^1$)$_3$][NO$_3$]$_4$3H$_2$O (5)</td>
<td>3375, 3292</td>
<td>3217</td>
<td>1599</td>
<td>1518</td>
<td>1266</td>
<td>1393</td>
<td>1564</td>
<td>1338</td>
<td>$= 350^a$</td>
</tr>
<tr>
<td>[Cu$_2$(HL$^1$)$_3$][NO$_3$]$_4$2H$_2$O (6)</td>
<td>3601, 3286</td>
<td>3155</td>
<td>1604</td>
<td>1506</td>
<td>1255</td>
<td>1398</td>
<td>1561</td>
<td>1326</td>
<td>$= 500$, $= 360^a$</td>
</tr>
</tbody>
</table>

*Diffuse reflectance spectral values.
The ligands DPBH and DPSH are reduced in a single step during electrochemical reduction and the observed cathodic potentials correspond to the reduction of carbonyl group. The anodic potentials observed at +1.46 V in DPBH and +0.92 V in DPSH are attributed to oxidation of amide NH23. The Ni(II) complex 1 undergoes one electron reduction to Ni(I) species in DMF solution at -1.54 V24. However, Ni(II) complex 3 exhibits ligand based reduction at -1.29 V. The high anodic potential at +1.57 V in this complex is probably due to intramolecularly hydrogen bonded phenolic OH group present in the complex. Table 3 reveals that the reduction processes are metal centered reductions in Cu(II) complexes. In Cu(II) complexes, Cu(II) is oxidized to Cu(III) ion at the anodic potentials +0.40 (2) and +0.58 V (4) and this process is found to be quasireversible (appearance of peaks at +0.18 and 0.23 V in the reverse scan)25. The peak at -0.13 V in 2 and at -0.036 V in 4 correspond to the reduction of Cu(II)-Cu(I) ions25. This process is found to be irreversible in nature. The highly cathodic potentials at -1.07 (2) and at -1.18 V (4) correspond to the reduction of bound ligand present in the complex.

The Cu(II) complex 6 exhibits isotropic ESR spectrum, i.e. having only one intense broad signal with no hyperfine structure. This may be due to dipolar exchange and unresolved hyperfine interaction20. The giso value suggests the presence of grossly misaligned tetragonal axes. For the other copper(II) complexes 2 and 4, anisotropy in g values is observed. The two major components of the g tensor in the axially symmetric field (g || and g ⊥) are computed from the spectra. The hyperfine coupling constant (A ||) was measured directly from the spectra.

Table 3 reveals that g || values are greater than g ⊥ values which suggest that dxy z orbital is strongly mixed with the ground state and the 3d unpaired electron of Cu(II) ion should occupy the dxy z orbital26. Kivelson and Nieman27 have reported that g || is moderately sensitive function for indicating covalency. Normally, g || is 2.3 or more for ionic environment and it is less than 2.3 for more covalent environment. The present EPR results show that the bond between Cu(II) and ligand is covalent in nature.

G factor is defined as \( \frac{(g_\parallel - 2.0023)}{(g_\perp - 2.0023)} \) and is in the range 4.11 to 6.31 for the present complexes. These values indicate that the local tetragonal axes are only slightly misaligned and the presence of dxy z ground state. The bonding parameter \( \alpha^2 \), measure of the covalency of the in-plane \( \sigma \) bonds is calculated according to:

\[
\alpha^2 = \langle A_0/P \rangle + (g_\parallel - 2.0023) + 3/7(g_\perp - 2.0023) + 0.04
\]

where \( P = 0.036 \text{ cm}^{-1} \). The \( \alpha^2 \) values for the complexes fall in the range of 0.75 indicating appreciable in-plane covalency26.

The combined TG/DTA diagrams depict two stage decompositions in all the complexes. In stage I, two molecules of salicylaldehyde are eliminated in DPBH complexes. The observed weight loss (34%) is in good agreement with the calculated values (31.9% 3; 31.8% 4). In MDPSH complexes, one molecule of nitrate ion and the water molecules

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Electrochemical data</th>
<th>ESR spectral data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Electrochemical reduction</td>
<td>Electrochemical oxidation</td>
</tr>
<tr>
<td>DPBH</td>
<td>Ni(II)-DPBH</td>
<td>-0.98</td>
<td>+1.46</td>
</tr>
<tr>
<td></td>
<td>Cu(II)-DPBH</td>
<td>-1.54</td>
<td>+1.45</td>
</tr>
<tr>
<td>DPSH</td>
<td>Ni(II)-DPSH</td>
<td>-1.05</td>
<td>+0.92</td>
</tr>
<tr>
<td></td>
<td>Cu(II)-DPSH</td>
<td>-0.13</td>
<td>+0.40</td>
</tr>
<tr>
<td></td>
<td>Cu(II)-MDPSH</td>
<td>-1.07</td>
<td>+1.74</td>
</tr>
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### Table 4 — Kinetic parameters of complexes

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>Decomp. range (K)</th>
<th>Peak temp. (DTA) (K)</th>
<th>Order (n) of reaction</th>
<th>$E^*$ (J mol$^{-1}$)</th>
<th>$\log A$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$S^*$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni(II)-DPBH</td>
<td>526 - 618 (Stage I)</td>
<td>548.75</td>
<td>1</td>
<td>$25.85 \times 10^5$</td>
<td>24.34</td>
<td>$2.16 \times 10^2$</td>
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<tr>
<td></td>
<td></td>
<td>619 - 780 (Stage II)</td>
<td>737.40</td>
<td>0</td>
<td>$8.45 \times 10^5$</td>
<td>5.50</td>
<td>$1.47 \times 10^2$</td>
</tr>
<tr>
<td>2</td>
<td>Cu(II)-DPBH</td>
<td>423 - 603 (Stage I)</td>
<td>503.90</td>
<td>1</td>
<td>$22.48 \times 10^5$</td>
<td>23.24</td>
<td>$1.96 \times 10^2$</td>
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<td></td>
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<td>604 - 832 (Stage II)</td>
<td>783.69</td>
<td>1/2</td>
<td>$7.45 \times 10^5$</td>
<td>4.61</td>
<td>$1.65 \times 10^2$</td>
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<tr>
<td>3</td>
<td>Ni(II)-DPSH</td>
<td>535 - 619 (Stage I)</td>
<td>548.30</td>
<td>1</td>
<td>$7.40 \times 10^5$</td>
<td>6.40</td>
<td>$1.27 \times 10^2$</td>
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<tr>
<td></td>
<td></td>
<td>620 - 789 (Stage II)</td>
<td>740.67</td>
<td>1/2</td>
<td>$9.64 \times 10^5$</td>
<td>4.41</td>
<td>$1.30 \times 10^2$</td>
</tr>
<tr>
<td>4</td>
<td>Cu(II)-DPSH</td>
<td>501 - 621 (Stage I)</td>
<td>521.36</td>
<td>1</td>
<td>$4.54 \times 10^5$</td>
<td>3.76</td>
<td>$1.78 \times 10^2$</td>
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<tr>
<td></td>
<td></td>
<td>622 - 794 (Stage II)</td>
<td>757.28</td>
<td>1/2</td>
<td>$11.68 \times 10^5$</td>
<td>7.78</td>
<td>$1.65 \times 10^2$</td>
</tr>
<tr>
<td>5</td>
<td>Ni(II)-MDPSH</td>
<td>321 - 540 (Stage I)</td>
<td>494.74</td>
<td>0</td>
<td>$2.56 \times 10^5$</td>
<td>2.92</td>
<td>$2.05 \times 10^2$</td>
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<tr>
<td></td>
<td></td>
<td>541 - 676 (Stage II)</td>
<td>656.74</td>
<td>1/2</td>
<td>$14.12 \times 10^5$</td>
<td>11.21</td>
<td>$3.7 \times 10^2$</td>
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<tr>
<td>6</td>
<td>Cu(II)-MDPSH</td>
<td>312 - 527 (Stage I)</td>
<td>524.27</td>
<td>1</td>
<td>$0.96 \times 10^4$</td>
<td>0.75</td>
<td>$2.35 \times 10^2$</td>
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<tr>
<td></td>
<td></td>
<td>528 - 634 (Stage II)</td>
<td>573.05</td>
<td>1</td>
<td>$10.77 \times 10^3$</td>
<td>9.05</td>
<td>$0.77 \times 10^2$</td>
</tr>
</tbody>
</table>

Present in the complex are eliminated in stage I decomposition. The observed mass loss of 14% in Ni(II) and Cu(II) complexes are in agreement with those of calculated values (14.2% - 5; 12% - 6). In Ni(II) complex 1, one molecule of benzoilhydrazine, two molecules of nitrate and water molecules are eliminated in the step I, with the observed mass loss of 30% (calcd 29.6%). One molecule of ligand and water molecules are eliminated with the observed mass loss of 40% as against the calculated mass loss of 42% in Cu(II) complex 2. In the second stage, remaining organic matter gets decomposed leaving metal oxide with some residual carbon in all the complexes. The decomposition of complexes was also studied using non-isothermal kinetic studies. Thermokinetic parameters (Table 4) were evaluated according to Coats and Redfern method$^{28}$. The initial decomposition temperature of the TG curves and the peak temperature of DTA curves have been used to compare the thermal stabilities of metal chelates. The stabilities of Ni(II) complexes are greater than those of Cu(II) complexes. The X-ray diffraction data of Ni(II) complexes 1 and 3 reveal that these complexes crystallise in simple cubic system with lattice constants 20.41 and 23.89 Å, respectively. These studies show that the probable structures of the metal complexes can be depicted by Scheme 3.
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