COORDINATION COMPLEXES OF PHENYLMERCURY(II) WITH PYRIDINE- AND QUINOLINE CARBOXYLIC ACIDS

Coordination complexes of quinaldinic acid, picolinic acid, nicotinic acid and dipicolinic acid have been studied by many workers with different metal ions\textsuperscript{1-6}. We report in this chapter a series of hitherto unknown phenylmercury(II) complexes where monoprotic monodentate and monoprotic bridging bidentate behaviour of nicotinic acid, monoprotic chelating bidentate and neutral chelating bidentate behaviours of picolinic acid, monoprotic chelating bidentate behaviour of quinaldinic acid, and biprotic bridging tridentate character of dipicolinic acid have been brought to light.

The abbreviations used in this chapter are:

\begin{tabular}{ll}
DipicH\textsubscript{2} & Dipicolinic acid = Pyridine-2,6-dicarboxylic acid. \\
LH & Monoprotic ligand \\
NicH & Nicotinic acid = Pyridine-3-carboxylic acid. \\
PicH & Picolinic acid = Pyridine-2-carboxylic acid. \\
QuinH & Quinaldinic acid = Quinoline-2-carboxylic acid. \\
\end{tabular}

**EXPERIMENTAL :**

**Materials :**

Basic phenylmercuric nitrate \([C\textsubscript{6}H\textsubscript{5}.Hg.OH.Hg.C\textsubscript{6}H\textsubscript{5}]\textsubscript{NO\textsubscript{3}}\) was a product of Ward Blenkinsop and Co.Ltd. (m.p. 134°C, dec.).
Phenylmercuric acetate was prepared according to the procedure given in the literature\textsuperscript{7} (m.p. 150°C, lit. 149°C).

Picolinic acid and nicotinic acid were reagent grade (BDH). Quinaldine acid and dipicolinic acid were synthesised according to standard procedures\textsuperscript{8,9}.

A. General method of synthesis of \([C_6H_5\cdot Hg(L)]\) :

0.002 mole of phenylmercuric acetate were dissolved in hot ethanol (~ 25 ml) and filtered into an ethanolic solution (~ 10 ml) of 0.002 mole of the ligand (QuinH, PicH or NicH) concerned. The mixture was refluxed for half an hour and the complex was obtained on concentrating the solution to about 15-20 ml. The product was recrystallised from ethanol.

The compounds \([C_6H_5\cdot Hg(Pic)]\) and \([C_6H_5\cdot Hg(Quin)]\) were also obtained from basic phenylmercuric nitrate by reacting with the ligands concerned in appropriate molar ratio.

B. Synthesis of \([C_6H_5\cdot Hg(Pic)(PicH)]\) :

A solution of phenylmercuric acetate (0.002 mole in ~ 25 ml ethanol) was refluxed with an ethanolic solution of picolinic acid (0.004 mole in 10 ml ethanol) on a steam-bath for about one hour. Colourless needle shaped crystals separated out on concentrating the solution to about 15 ml. The product was recrystallised from ethanol.
This compound was also obtained from basic phenylmercuric nitrate by reacting with picolinic acid in 1:4 molar ratio.

C. Synthesis of $\left[ \text{C}_6\text{H}_5\text{Hg(Nic)Hg.C}_6\text{H}_5 \right] \text{NO}_3$:

0.001 mole of basic phenylmercuric nitrate was dissolved in hot ethanol (~ 150 ml) and filtered into an ethanolic solution (~ 10 ml) of 0.001 mole of nicotinic acid. The mixture was refluxed for half an hour and concentrated on a steam-bath to about 15-20 ml and then cooled to room temperature. Colourless glistening crystals separated out. These were recrystallised from ethanol.

D. Synthesis of $\left[ \text{C}_6\text{H}_5\text{Hg(Dipic)Hg.C}_6\text{H}_5 \right]$:

0.001 mole of basic phenylmercuric nitrate was dissolved in 1:1 ethanol-water mixture (~ 120 ml) and to this solution 0.001 mole of dipicolinic acid dissolved in water (~10 ml) was added. The mixed solution was refluxed for one hour, concentrated on a steam-bath to about 60 ml and filtered. The filtrate (pH ~2-3) was then cooled to room temperature. Colourless glistening crystals so obtained were then digested for half an hour on a steam-bath to remove any unreacted DipicH$_2$. These were collected on a filter and washed several times with hot ethanol and dried in air.

This compound was also synthesised by the reaction of phenylmercuric acetate with dipicolinic acid in 2:1 molar ratio.
Elemental analyses:

Carbon and hydrogen analyses were performed by M/s. Alfred Bernhardt Mikro-analytische Laboratorium, West Germany. Nitrogen was estimated by Duma's method and mercury was estimated as described earlier.  

Physical measurements:

Electrical conductance was measured with a Phillips PR 9500 Conductivity Bridge. Infrared spectra in the range 4000-200 cm\(^{-1}\) were recorded at Central Drug Research Institute, Lucknow (India). Elemental analyses along with conductance data and infrared data of the phenylmercury(II) complexes appear in table 4.1 and table 4.2 respectively.  

RESULTS AND DISCUSSION

Mercury(II) being a d\(^{10}\) ion, the structure and stereochemistry of the complexes had to be derived from elemental analyses, infrared spectral studies and conductivity data. Low solubility of the samples in suitable solvents did not permit to have \(^1\)H pmr spectra and molecular weight determination.  

Several groups of workers have tried to utilise some slight variations in the vibrational spectra of pyridine containing ligands to ascertain the coordination or otherwise of the
Table 4.1: Characterisation Data of Phenylmercury(II) Complexes of Pyridine- and Quinoline Carboxylic Acids.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar conductance in methanol (0.001 M)</th>
<th>M.P. (°C)</th>
<th>Hg(%) Found (Calc.)</th>
<th>N(%) Found (Calc.)</th>
<th>C(%) Found (Calc.)</th>
<th>H(%) Found (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([C_6H_5,Hg(Pic)])</td>
<td>3.5</td>
<td>216</td>
<td>50.57 (50.20)</td>
<td>3.58 (3.50)</td>
<td>35.89 (36.04)</td>
<td>2.20 (2.25)</td>
</tr>
<tr>
<td>([C_6H_5,Hg(Quin)])</td>
<td>4.6</td>
<td>211</td>
<td>44.36 (44.86)</td>
<td>2.94 (3.12)</td>
<td>42.56 (42.76)</td>
<td>2.44 (2.45)</td>
</tr>
<tr>
<td>([C_6H_5,Hg(Nic)])</td>
<td>4.5</td>
<td>206</td>
<td>50.50 (50.12)</td>
<td>3.55 (3.51)</td>
<td>35.94 (36.04)</td>
<td>2.22 (2.25)</td>
</tr>
<tr>
<td>([C_6H_5,Hg(Pic)(PicH)])</td>
<td>0</td>
<td>186</td>
<td>38.61 (38.33)</td>
<td>5.31 (5.36)</td>
<td>41.22 (41.38)</td>
<td>2.61 (2.73)</td>
</tr>
<tr>
<td>([C_6H_5,Hg(Nic)Hg.C_6H_5]NO_3)</td>
<td>81.6</td>
<td>203</td>
<td>54.58 (54.20)</td>
<td>3.73 (3.79)</td>
<td>29.21 (29.27)</td>
<td>1.35 (1.90)</td>
</tr>
<tr>
<td>([C_6H_5,Hg(Dipic)Hg.C_6H_5])</td>
<td>Insoluble</td>
<td>-</td>
<td>55.94 (55.63)</td>
<td>2.10 (1.95)</td>
<td>31.56 (31.71)</td>
<td>1.72 (1.81)</td>
</tr>
</tbody>
</table>
Table 4.2: Important Infrared Spectral Bands (cm\(^{-1}\)) of the Ligands and their Phenylmercury(II) Complexes.

<table>
<thead>
<tr>
<th>Phenylmercury(II) complexes and ligands</th>
<th>(\nu) (COO) asym.</th>
<th>Pyridine C=(\equiv)C, C=N stretching vibration</th>
<th>(\nu) (Hg-C)</th>
<th>(\nu) (Hg-O)</th>
<th>(\nu) (Hg-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PicH</td>
<td>1720s, br</td>
<td>1570m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([C_6H_5.Hg(Pic)])</td>
<td>1600s</td>
<td>1580s</td>
<td>730s</td>
<td>452s</td>
<td>400m</td>
</tr>
<tr>
<td>([C_6H_5.Hg(Pic)(PicH)])</td>
<td>1740s, br; 1610m</td>
<td>1583s</td>
<td>730s</td>
<td>452s</td>
<td>400m</td>
</tr>
<tr>
<td>QuinH</td>
<td>1690s, br</td>
<td>1585s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([C_6H_5.Hg(Quin)])</td>
<td>1630vs</td>
<td>1610s</td>
<td>730s</td>
<td>450s</td>
<td>390m</td>
</tr>
<tr>
<td>DipicH(_2)</td>
<td>1715s, br</td>
<td>1575s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([C_6H_5.Hg(Dipic)Hg.C_6H_5])</td>
<td>1610s</td>
<td>1585s</td>
<td>730s</td>
<td>450s</td>
<td>400m</td>
</tr>
<tr>
<td>NicH</td>
<td>1700s, br</td>
<td>1590s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([C_6H_5.Hg(Nic)])</td>
<td>1590vs</td>
<td>1590vs</td>
<td>725s</td>
<td>450m</td>
<td></td>
</tr>
<tr>
<td>([C_6H_5.Hg(Nic)Hg.C_6H_5]NO_3)</td>
<td>1640m</td>
<td>1605s</td>
<td>730s</td>
<td>450s</td>
<td>660m</td>
</tr>
</tbody>
</table>

\(m = \text{medium, } s = \text{strong, } \text{br} = \text{broad, } vs = \text{very strong.}\)
pyridine nitrogen to a metal ion. Chemical literature is not entirely free from ambiguity in this respect. Some workers\textsuperscript{11-14} have preferred an increase in the stretching frequencies (e.g. $\nu C=C$ and $\nu C=N$ around 1550-1600 cm$^{-1}$ of the free ligand) in the complexes as a test of coordination of the heterocyclic nitrogen to a metal ion. There are also some groups\textsuperscript{15,16} who have observed some slight lowering of these vibrations on coordination of the heterocyclic nitrogen. In view of such a situation we felt that increase or decrease of such stretching frequencies can not be taken as an unambiguous test of coordination of picolinate/quinaldinate nitrogen to the phenylmercury(II). Instead identification of the Hg-N stretching frequency in the complexes under discussion will be a straightforward and unambiguous criterion to decide whether or not the heterocyclic nitrogen takes part in the coordination process. However we wish to put on record that in all the complexes reported in this chapter we have consistently observed an increase in the (coupled) C=C and C=N frequencies in the phenylmercury(II) compounds compared to those in the ligands\textsuperscript{11-14}.

Brodersen and Becher\textsuperscript{17} have studied the infrared spectra of a number of compounds containing Hg-N bonds and have opined that the Hg-N stretching band may be observed over a wide range 700 to 400 cm$^{-1}$. Hg-O stretching band also appears in a wide range 550-400 cm$^{-1}$\textsuperscript{18}. The Hg-C stretching band appears at ca. 784 cm$^{-1}$ in the complexes of penta-fluorophenylmercury(II).\textsuperscript{11}
A. Structure of \([\text{C}_6\text{H}_5\text{Hg}(\text{L})]\) :

Picolinato phenylmercury(II), quinaldinato phenylmercury(II) and nicotinato phenylmercury(II) have very low molar conductance values (3.5, 4.6 and 4.5 ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\) respectively) in methanol, which indicates that the complexes are non-electrolytes.

The asymmetric stretching mode of COO group at 1720 cm\(^{-1}\) in picolinic acid is shifted to 1600 cm\(^{-1}\) in the complex. This is strong evidence that the carboxylate anion is bonded to mercury(II). A small shift to higher frequency of the pyridine (coupled) C=C and C=N stretch\(^{11-14}\) in the complex (Table 4.2) is attributable to pyridine coordination. The strong new band at ca. 450 cm\(^{-1}\) in the spectrum of picolinato phenylmercury(II) is assigned to Hg-O stretching vibration\(^{18}\). This band is also present in the same position in the spectrum of phenylmercuric acetate and basic phenylmercuric nitrate but absent in the pure ligand. The other new band observed at ca. 400 cm\(^{-1}\) is assigned to Hg-N stretching vibration\(^{17}\). This band is absent in the spectrum of phenylmercuric acetate, basic phenylmercuric nitrate and in the pure ligand. The Hg-C stretching frequency is observed as a strong band at ca. 730 cm\(^{-1}\); this band is also present at the same position in the spectrum of phenylmercuric acetate and basic phenylmercuric nitrate. In view of these observations we wish to suggest either structure (I) (where the mercury is three-coordinate) or structure (II) (where the coordination number of mercury is four). Poor
solubility in benzene did not permit any cryoscopic molecular weight determination to distinguish between the two alternative structures.

![Diagram of structures](image)

Infrared spectral bands of the quinaldinato phenylmercury(II) show features which are quite comparable to those of the picolinato complex. The structure of this complex is likely to be parallel to that of the picolinato complex.

The asymmetric stretching mode of COO group at 1700 cm\(^{-1}\) in nicotinic acid is shifted to 1590 cm\(^{-1}\) in the complex, suggesting the carboxylate anion is bonded to mercury(II). Pyridine nitrogen is not involved in coordination since there is no upward shift of the pyridine (coupled) C=C and C=N stretch in the complex (Table 4.2). This argument is strongly supported by the absence of \(\nu(Hg-N)\) band\(^{17}\), \(\nu(Hg-O)\) and \(\nu(Hg-C)\) bands appear at 450 cm\(^{-1}\)\(^{18}\) and 725 cm\(^{-1}\)\(^{11}\) respectively. In view of these observations we suggest structure (III) for nicotinato phenylmercury(II) where mercury(II) is involved in linear twocoordination (sp hybridisation).
B. Structure of \([C_6H_5, Hg(Pic)(PicH)]\):

Molar conductance value in methanol of this complex is 
\(-0 \ \text{ohm}^{-1} \ \text{cm}^{2} \ \text{mole}^{-1}\) which indicates that the complex is a non-
electrolyte.

In the infrared spectrum of this complex we find a strong, 
broad band at ca. \(1740 \ \text{cm}^{-1}\) and a medium intensity band at 
ca. \(1610 \ \text{cm}^{-1}\). The band at \(1610 \ \text{cm}^{-1}\) indicates that one carbo-
xylate anion is bonded to mercury(II) as in the case of pico-
linato phenylmercury(II). The well resolved band at \(1740 \ \text{cm}^{-1}\) 
is assignable to \(\nu(C=C)\) of a complexed carboxylic acid (-COOH) 
group\(^6\). A small shift (\(-13 \ \text{cm}^{-1}\)) to higher frequency of the 
pyridine (coupled) \(C=N\) and \(C=C\) stretch in the complex (Table-
4.2) is attributable to pyridine coordination\(^{11-14}\). \(\nu(Hg-O)\), 
\(\nu(Hg-N)\) and \(\nu(Hg-C)\) bands appear at \(452 \ \text{cm}^{-1}\), \(400 \ \text{cm}^{-1}\) 
and \(730 \ \text{cm}^{-1}\) respectively. In view of these observations we 
wish to suggest the structure (IV) with five coordinate 
mercury\(^{19,20}\).

A tetrahedral structure with the second molecule of pico-
linic acid functioning only as a monodentate ligand seems un-
likely. A study of an actual model shows that the five coordinate
structure is quite strain free. Extremely poor conductivity of the complex may be explained on the assumption that the carboxylic hydrogen is strongly hydrogen bonded to the oxygen of the COO\(^{-}\) group of the other picolinate ligand.

C. Structure of \([C_6H_5\text{Hg(Nic)Hg}_2C_6H_5]\)NO\(_3\) :

The infrared spectrum of this complex shows a strong, broad N-O stretching mode at ca. 1370 cm\(^{-1}\) (\(\nu_3\)) and at 835 cm\(^{-1}\) (\(\nu_2\)) and 720 cm\(^{-1}\) (\(\nu_4\)), indicating non-coordinating NO\(_3\) \(^{-}\) ion\(^{21}\) possessing D\(_{3h}\) symmetry. Molar conductance value of this complex (on bimetallic basis) in methanol (\(\Lambda_M = 81.64 \text{ ohm}^{-1}\text{cm}^{2}\text{mole}^{-1}\)) shows its 1:1 electrolytic nature.

The asymmetric stretching mode of COO group at 1700 cm\(^{-1}\) in the pure ligand is shifted to 1640 cm\(^{-1}\) in the complex, indicating carboxylate anion is bonded to mercury(II). Shift of pyridine (coupled) C=N and C=C stretching frequencies at 1590 cm\(^{-1}\) in the pure ligand to 1605 cm\(^{-1}\) in the complex is
attributable to pyridine coordination\^{11-14}. $\nu$(Hg-O) bands appear at 450 cm$^{-1}$ and 730 cm$^{-1}$ respectively. A new band observed at 660 cm$^{-1}$ in this complex is assigned to $\nu$(Hg-N) modes\^{17}, which is absent in the spectrum of nicotinato phenylmercury(II) (structure III). In view of these observations we suggest structure (V) for this bimetallic nitrate salt where both the two mercury(II) ions are involved in linear two-coordination (sp hybridisation).

![Structure V](image)

A study of the actual model of the compound shows that the mercury attached to the nicotinic acid nitrogen is situated far off from the carboxylic oxygen attached to the second mercury to make any significant bonding interaction.

D. Structure of $[C_6H_5Hg(Dipic)HgC_6H_5]$ :

Infrared spectrum of dipicolinic acid shows a broad band centred at 1715 cm$^{-1}$ which is taken as asymmetric stretching
mode of COOH group. This band is shifted to 1610 cm\(^{-1}\) in the bimetallic complex, indicating both the carboxylate anions are bonded to mercury(II). Pyridine (coupled) C=N and C=C stretching frequencies appear at 1575 cm\(^{-1}\) in the pure ligand, which are shifted to 1585 cm\(^{-1}\) in the complex\(^{11-14}\). \(\nu\)(Hg-N), \(\nu\)(Hg-O) and \(\nu\)(Hg-C) bands appear at 400 cm\(^{-1}\), 450 cm\(^{-1}\) and 730 cm\(^{-1}\) respectively. In view of the above observations we wish to suggest structure (VI) where one mercury(II) is involved in linear two-coordination and the second mercury(II) in triangular three-coordinate or tetrahedral four-coordinate (VII) through bridging oxygen, giving a tetrametallic complex. Its poor solubility in all solvents did not permit any conductance and molecular weight determination.

\[
\text{(VI)}
\]
**Concluding Remarks:**

In addition to the straightforward bidentate behaviours of picolinic acid and quinaldinic acid, monodentate and bridging bidentate behaviours of nicotinic acid, bridging tridentate behaviours of dipicolinic acid, and some unusual bridging behaviour of these ligands have been unfolded through the use of phenylmercury(II) as the probing organometallic ion.
References: