CHAPTER - IV

SECTION--A: SYNTHESIS AND SPECTRAL STUDIES OF ZINC(II), CADMIUM(II) AND MERCURY(II) COMPLEXES WITH 1,5–BENZO–DIAZEPINES

I. INTRODUCTION:

The study of diazepines have attracted the attention to a considerable extent because of their potential therapeutic properties.\(^{(1)}\) Some work on the metal complexes of 6,7–benz–1,4–diazepines and 6,7–benz–1,5–diazepines and N–oxide with various transition and inner transition metals have been reported in the literature\(^{(2–5)}\). Real and Borras\(^{(6)}\) have reported the preparation and characterization of 1:2 metal thiocyanato bromozepam complexes of divalent Co, Ni and Cu with pseudo octahedral environment around the metal ions.\(^{(7–11)}\)

Here we report the synthesis and characterization of Zinc(II), Cadmium(II) and mercury(II) complexes with 6,7–benz–1,5–diazepine derivatives (I–V).

\[
\begin{align*}
\text{I : } R & = H; \quad \text{II : } R = \text{CH}_3; \quad \text{III : } R = \text{Cl}; \quad \text{IV : } R = \text{NO}_2; \quad \text{V : } R = \text{COOH}
\end{align*}
\]

II. EXPERIMENTAL TECHNIQUES:

Ortho–phenylenediamine and 4–substituted–o–phenylenediamine used for the preparation of benzodiazepines were BDH reagents. Acetylacetone was a laboratory grade reagent and was used as such without further puririfcation. The 6,7–benz–1,5–diazepines(I–V) were prepared by standard procedures\(^{(12)}\).
Zinc(II), cadmium(II) and mercury(II) halides were AR grade BDH reagents. Absolute ethanol required for the synthesis was prepared according to the standard procedures.\(^{(12)}\)

III. GENERAL METHOD FOR THE PREPARATION OF COMPLEXES:

To a solution of the ligand (0.01 mol) in ethanol (25 ml) was added metal(II) halide (0.05 mol) in ethanol (30 ml) with constant stirring. The reaction mixture was kept under stirring for another half an hour. The complex separated was filtered, washed successively with 5 ml portions of ethanol and then with dry ether and dried over fused calcium chloride in vacuo. The dried complex was powdered and further purified by extracting in a soxhlet thimble using dry ethanol.

Zinc(II) in the complexes was estimated volumetrically with standard EDTA. Cadmium(II) was estimated gravimetrically as pyrophosphate and mercury(II) was estimated as sulphide\(^{(12)}\). Halides were estimated gravimetrically as AgCl. Nitrogen was determined by Dumas’ method. Melting points, analytical data including C and H are given in Table (4.1A).

Molar conductances of these complexes were determined with an ELICO CL–82T conductivity bridge using a cell of cell constant 1.03 cm\(^{-1}\). Electronic spectra of the ligands and the complexes were recorded on a Hitachi model 200–20 UV spectrophotometer. Infrared spectra of the ligands and the complexes were recorded on a Perkin–Elmer infrared spectrophotometer model 297 in the range 4000–200 cm\(^{-1}\). Mass spectra were recorded on a Hitachi mass spectrophotometer model RMU–6E.

IV. RESULTS AND DISCUSSION:

These complexes are bluish ash coloured substances soluble in DMF and DMSO and insoluble in chloroform, carbon tetrachloride and benzene. It is evident
FIG (4.1 A): IR SPECTRA OF COMPLEXES
(I) (C_{11}H_{12}N_{2})_2ZnCl_2 (II) (C_{12}H_{14}N_{2})CdCl_2 (III) (C_{11}H_{11}N_{2}Cl)_2HgCl_2
from Table (4.1A) that the complexes formed are of the type $L_2MX_2$ [where $L$ = ligands $I^{-}$-$V$, $X$ = Cl$^{-}$, Br$^{-}$ or I$^{-}$ and $M$ = Zn(II), Cd(II) or Hg(II)].

Molar conductance values of these complexes in DMF at the concentration $10^{-3}$ M fall in the range 71–89 ohm$^{-1}$ cm$^2$ mol$^{-1}$ indicating their 1:1 electrolytic behavior which may be due to dissociation of $M$–$X$ bond.

(i) **Infrared Spectral Studies:**

A broad IR band of high intensity located around 3350 cm$^{-1}$ in these ligands may be assigned to $\nu$(NH) vibrations$^{(13)}$. A high intensity band in the region 1660–1630 cm$^{-1}$ may be attributed to the $\nu$(C=C) of the azepine residue. In addition to this a medium intensity band observed around 1630 cm$^{-1}$ has been assigned to the $\nu$(C=\text{N}). These assignments are in accordance with the literature values$^{(14-16)}$.

In the complexes, a band due to the $\nu$(NH) of the ligand appears in the region 3300–3100 cm$^{-1}$ as a medium intensity split band, suggesting coordination of NH group to the metal moiety.$^{(17)}$

The band due to $\nu$(C=\text{N}) appears in the 1610–1600 cm$^{-1}$ region in these complexes indicating that the C=\text{N} group of the diazepine residue is involved in coordination to the metal (II) ion through nitrogen. Coordination of these groups has profound impact on $\nu$(C=C) and it appears around 1640 cm$^{-1}$ as a band of medium intensity.

In view of the literature assignments$^{(18-20)}$, we have attributed medium intensity bands in the 480–450 cm$^{-1}$ and 380–350 cm$^{-1}$ regions to the $\nu$(M–N) vibrations. The medium intensity bands appearing in the 300–200 cm$^{-1}$ region are attributed to the $\nu$(M–X) vibrations.$^{(21-22)}$
FIG (4.2 A) : IR SPECTRA OF COMPLEXES

(I) (C_{12}H_{14}N_2)_2ZnBr_2 (II) (C_{11}H_{11}N_3O_2)CdBr_2 (III) (C_{11}H_{11}N_2Cl)_2HgBr_2
(ii) **Mass Spectral Studies:**

Mass spectra of a few selected complexes have been studied. We observed distinct peaks at m/z 80 and m/z 172 due to bromide ion and ligand respectively. Further, a molecular ion peak at m/z 452 indicates the formation of the species of the type LHgBr which subsequently loses CH$_3$Br and is converted into [C$_{10}$H$_6$N$_2$Hg]. This is evident from the appearance of molecular ion peak at m/z 357. The observed ion peaks at 65, 112 and 200 m/z may be due to the metal ions, Zn(II), Cd(II) and Hg(II) respectively.$^{(23-27)}$

The above observations suggest the following hexa coordinate structure for all these complexes.

\[
\begin{align*}
M & = \text{Zn(II), Cd(II), Hg(II)}, \quad X = \text{Cl, Br, I} \\
\text{I : } & R = \text{H; II : } R = \text{CH}_3; \quad \text{III : } R = \text{Cl; IV : } R = \text{NO}_2; \quad \text{V : } R = \text{COOH}
\end{align*}
\]
FIG (4.3 A) : IR SPECTRA OF COMPLEXES
(I) (C$_{11}$H$_1$N$_2$Cl)$_2$ZnI$_2$ (II) (C$_{11}$H$_{12}$N$_2$)$_2$CdI$_2$ (III) (C$_{11}$H$_{11}$N$_3$O$_2$)$_2$CdI$_2$
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligand</th>
<th>Complex</th>
<th>m.p. (°C)</th>
<th>% Chemical analysis</th>
<th>Found (Calcd.)</th>
<th>μ_{eff} (B.M.)</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>1.</td>
<td>I</td>
<td>(C_{11}H_{12}N_{2})<em>{2}.ZnCl</em>{2}</td>
<td>243</td>
<td>(54.94)</td>
<td>(5.33)</td>
<td>(11.65)</td>
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<td></td>
<td></td>
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<td></td>
<td>54.80</td>
<td>5.20</td>
<td>11.50</td>
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<td>2.</td>
<td>II</td>
<td>(C_{12}H_{14}N_{2})<em>{2}.CdCl</em>{2}</td>
<td>238</td>
<td>(51.85)</td>
<td>(5.04)</td>
<td>(10.08)</td>
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<td></td>
<td>51.70</td>
<td>4.80</td>
<td>9.88</td>
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<td>3.</td>
<td>III</td>
<td>(C_{11}H_{11}N_{2}Cl)<em>{2}.HgCl</em>{2}</td>
<td>240</td>
<td>(38.56)</td>
<td>(3.21)</td>
<td>(8.18)</td>
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<td>38.42</td>
<td>3.10</td>
<td>8.02</td>
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<td>4.</td>
<td>II</td>
<td>(C_{12}H_{14}N_{2})<em>{2}.ZnBr</em>{2}</td>
<td>241</td>
<td>(48.21)</td>
<td>(9.37)</td>
<td>(9.37)</td>
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<td>48.10</td>
<td>9.17</td>
<td>9.20</td>
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<td>5.</td>
<td>IV</td>
<td>(C_{11}H_{11}N_{3}O_{2})<em>{2}.CdBr</em>{2}</td>
<td>220</td>
<td>(37.21)</td>
<td>(3.11)</td>
<td>(11.89)</td>
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<td>37.15</td>
<td>3.0</td>
<td>11.70</td>
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<td>6.</td>
<td>II</td>
<td>(C_{12}H_{14}N_{2})<em>{2}.HgBr</em>{2}</td>
<td>195</td>
<td>(39.31)</td>
<td>(3.82)</td>
<td>(7.64)</td>
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<td></td>
<td>39.10</td>
<td>3.70</td>
<td>7.50</td>
</tr>
<tr>
<td>7.</td>
<td>III</td>
<td>(C_{11}H_{11}N_{2}Cl)<em>{2}.ZnI</em>{2}</td>
<td>229</td>
<td>(36.04)</td>
<td>(3.00)</td>
<td>(7.65)</td>
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<td></td>
<td></td>
<td>35.86</td>
<td>2.90</td>
<td>7.53</td>
</tr>
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</table>
FIG (4.4 A): IR SPECTRA OF COMPLEXES
(I) \((C_{11}H_{11}N_3O_2)_2HgI_2\) (II) \((C_{12}H_{12}N_2O_2)ZnCl_2\) (III) \((C_{12}H_{12}N_2O_2)_2CdCl_2\)
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligand</th>
<th>Complex</th>
<th>m.p. (°C)</th>
<th>% Chemical analysis Found (Calcd.)</th>
<th>μ$_{\text{eff}}$ (B.M.)</th>
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<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>8.</td>
<td>I</td>
<td>(C$<em>{11}$H$</em>{12}$N$<em>{2}$)$</em>{2}$.CdI$_{2}$</td>
<td>223</td>
<td>(37.16)</td>
<td>(3.38)</td>
</tr>
<tr>
<td>9.</td>
<td>IV</td>
<td>(C$<em>{11}$H$</em>{11}$N$<em>{2}$O$</em>{2}$)$<em>{2}$.CdI$</em>{2}$</td>
<td>205</td>
<td>(32.98)</td>
<td>(2.75)</td>
</tr>
<tr>
<td>10.</td>
<td>IV</td>
<td>(C$<em>{11}$H$</em>{11}$N$<em>{3}$O$</em>{2}$)$<em>{2}$.HgI$</em>{2}$</td>
<td>200</td>
<td>(29.70)</td>
<td>(2.47)</td>
</tr>
<tr>
<td>11.</td>
<td>V</td>
<td>(C$<em>{12}$H$</em>{12}$N$<em>{2}$O$</em>{2}$)$<em>{2}$.ZnCl$</em>{2}$</td>
<td>215</td>
<td>(50.66)</td>
<td>(4.22)</td>
</tr>
<tr>
<td>12.</td>
<td>V</td>
<td>(C$<em>{12}$H$</em>{12}$N$<em>{2}$O$</em>{2}$)$<em>{2}$.CdCl$</em>{2}$</td>
<td>235</td>
<td>(46.79)</td>
<td>(3.69)</td>
</tr>
<tr>
<td>13.</td>
<td>V</td>
<td>(C$<em>{12}$H$</em>{12}$N$<em>{2}$O$</em>{2}$)$<em>{2}$.HgCl$</em>{2}$</td>
<td>222</td>
<td>(40.93)</td>
<td>(3.41)</td>
</tr>
<tr>
<td>14.</td>
<td>V</td>
<td>(C$<em>{12}$H$</em>{12}$N$<em>{2}$O$</em>{2}$)$<em>{2}$.CdI$</em>{2}$</td>
<td>226</td>
<td>(36.07)</td>
<td>(3.00)</td>
</tr>
</tbody>
</table>
FIG (4.5 A): IR SPECTRA OF COMPLEXES
(I) \((C_{12}H_{12}N_2O_2)_2HgCl_2\) (II) \((C_{12}H_{12}N_2O_2)_2CdCl_2\)
CHAPTER-IV SECTION-A

REFERENCES