SECTION 7

MERCURY (II) COMPLEXES
(a) Previous Work :

The mercury(II) ion possess a strong tendency to complex formation and the characteristic coordination numbers and stereochemical arrangements are two coordinate linear and four coordinate tetrahedral. Octahedral coordination is less common, other complexes which are three and five-coordinated are also known. There appears to be considerable covalent character in the mercury ligand bonds, especially in the two coordinate complexes. The most stable complexes are those with halogen, carbon, nitrogen, phosphorus and sulphur ligands. For the halogens, there are the species HgX, HgX₂, HgX₃⁻ and HgX₄²⁻. Mercury cyanide is soluble in excess cyanide to give the tetrahedral [Hg(CN)₄]²⁻ ion, the thiocyanate [Hg(SCN)₄]²⁻ is similar.

There are a number¹ of oxoanions, e.g. [Hg(SO₃)₂]²⁻, [HgOX₂]²⁻ and [Hg(NO₃)₄]²⁻. The yellow crystals long considered to be 'potassium mercury nitrates' obtained by adding KNO₂ to Hg(NO₃)₂ solutions, have been shown to be K₃[Hg(NO₂)₄NO₃] with a tetrahedral [Hg(NO₂)₄]²⁻ ion. Dialkylsulfides give complexes of the type R₂S.HgX₂ (X = Cl, Br, I) which are dimeric and also monomeric (R₂S)₂HgX₂ complexes. Phosphines and arsines form complexes with the halides similarly and also give more highly bridged structures. Although there is a tendency to form ammonobasic compounds, a variety of amines form complexes² with mercury(II) ion and the affinity of Hg(II) for nitrogen ligands in aqueous solution exceeds that of transition metals. In addition to the ammonia and amine complexes
of the type \([Hg(NH_3)_2X_2]\), tetraamines such as \([Hg(NH_3)_4](NO_3)_2\) can be prepared in a saturated aqueous ammonium nitrate. The ion \([Hg(en)_3]^{2+}\) has octahedral Hg(II) as have complexes of the type \([HgL_6](ClO_4)_2\) obtained from suitable oxygen donors are added to mercury(II) perchlorate in ethanol. Although less sterically hindered donors such as pyridine-N-oxide react more bulky oxides such as Ph_3PO donor. Tetrahedral complexes are of course given by such ligands e.g. \(HgCl_2 \cdot 2Ph_3ASO^4\).

Mercury beta-diketonates have been shown not to have the usual chelate rings but to be enolates of the type \(Hg(OCR=CHCOR)_2\). It also appears that mercuric perchlorate and nitrate react with aqueous acetone to give complex species which have the acetone bound to mercury as the enolate ion. Complexes of the formula \(HgL_2\) have been reported where \(L = \text{o-tolylthioacetamide}, 2,5\)-dimethylphenylthioacetamide and \(\text{o-methoxythioacetamide}\). In all these complexes mercury(II) atom is S-bonded. Marta et al. have prepared a number of four coordinated mixed halomercurates(II) having a tetrahedral stereochemistry. Mercury(II) complexes with tritolylphosphine and tritolyl phosphine oxide have been synthesised. Ahuja et al. have reported a number of complexes of Hg(II) halides with ethylenediamine and \(\beta\)-naphthylamine and showed that 'SCN' is S-bonded.

Negoin and others have synthesised complexes of dithiols of the composition \([Hg_2(HL)_2(NO_3)_2]\) and \([Hg(HL)_2Cl_2]\) where \(HL = \text{2,3-dimercapto quinoxaline}\). A compound of the composition \(HgL_2Cl_2\) where \(L = \text{benzoic acid hydrazide}\) has been synthesised and X-ray crystal structure of this compound indicated an octahedral stereochemistry. Nyholm et al. have reported mercury(II) halide complexes of Co(II) and Ni(II) of the composition \((PET_3)_2HgZ_2MX_2\) where \(M = Co(II)\),
X = Z = Cl, Br; M = Ni(II), x = z = Cl having bridging chlorine atoms. Marta and coworkers\textsuperscript{15} have synthesised mixed halomercurates(II) of coordination number three, the quarternary ammonium salts used are N-cetyl pyridinium and N-cetyl-2,4-lutidinium halides. A number of mercury(II) complexes both monomeric and polymeric have been prepared\textsuperscript{16} with methylthiourea. Ahuja and Singh have reported\textsuperscript{17} complexes of Hg(II) with 2,2'-bipyridyl-N-N'-dioxide, the (1:1) Hg(II) chloride, bromide and thiocyanate complexes have pseudo tetrahedral structure with terminal halogen or pseudohalogen group whereas the cyanide complex is polymeric involving cyanobridges. Trimethylphosphine Hg(II) complexes have been reported\textsuperscript{18} by Schmidbaur. Pseudohalogen complexes of Hg(II) of the formula \([\text{LH}]_2[\text{HgX}_4]\) where \(L = 1,4\)-dihydrazinophthalazine, \(X = \text{I, SCN}\) have been synthesised\textsuperscript{19}.

Infrared studies have been made\textsuperscript{20} of Hg(II), Zn(II) and Sn(IV) complexes of 1,2-dithiol-3-thiones and a distorted tetrahedral configuration is proposed for Hg\(_2\)X\(_4\)L\(_2\) (X = Cl, Br, I and L = 5-phenyl-1,2-dithiol-3-thione). Mercury(II) chelates of bidentate schiff bases have been synthesised\textsuperscript{21} by Upadhyaya and Saxena. Five coordinate mercury(II) complexes with tripod like tetramines have been prepared by Ciampoline and coworkers\textsuperscript{22}. Malhotra has reported\textsuperscript{23} complexes of mercury(II) with triphenylphosphine sulfide of the composition MX\(_2\)L. Tetrahedral structure for these complexes for these adducts have been proposed. Thiourea complexes of Hg(II) have been reported\textsuperscript{24}. These have the composition Hg\(_{tu2}\)A\(_2\) and Hg\(_{tu2}\)XA where X = Cl, Br, I and A = perchlorate, tetrafluroborate and tetrafluroacetate. Mercury(II) complexes of substituted sulfonamides have been isolated\textsuperscript{25} by Sukla and his coworkers. Brown et al. have reported Hg(II) complexes of the composition HgX\(_2\)L\(_2\) where X = Cl, Br, I and L = morpholine-4-thiocarbanic acid anilide.
Mercury(II) complexes with dibenzoylsulfide have been prepared by Malhotra et al. and a monomeric octahedral configuration has been suggested to these complexes. Three coordinated complexes of Hg(II) have been reported by Ahuja et al. Kashyap and others have studied Hg(II) complexes of N-aryl-N'-2(5-halopyridyl)thioureas of the composition HgL2Cl2. Thiosemicarbazone complexes of Hg(II) of composition HgL4Cl2 have been well studied. A series of Zn, Cd and Hg(II) halide complex with ethyl thiourea have been prepared. HgL2I2 is tetrahedral whereas [HgLX2]2 (X = Cl, Br) have a dimeric halide-bridged structure. Zn, Cd and Hg(II) complexes with N-acetyl glycine and their amine adducts have been synthesised. Mercury(II) complexes with N,N'-dimethylthiourea have been reported. A number of complexes of Zn, Cd and Hg(II) with 1-substituted-3-(2-pyridyl)-2-thioureas have been reported by Banerjee et al.

Canty et al. have prepared the dimeric Hg(II) complexes of the type Me3HgO2CMe and Me3HgO2CMe.L (L = pyridine, γ-picoline) and characterised to have tetrahedral configuration with methanethiolate bridges on the basis of Raman spectra. Mercury acetate complexes with acetamide have been reported by Khodzhaev and coworkers. Mepacrine-mercuric chloride complex has been synthesised by Gupta et al. Mercury(II) complexes with formamide have been reported and characterised by i.r. spectra, X-ray diffraction and thermal decomposition studies. Gupta et al. have reported Hg(II) complexes with 1,2,4-triazole-3(5)-thiol. Mercury(II) complexes with dimethylthioacetamide have been prepared by Aarts and his coworkers and characterised to possess tetrahedral configuration on the basis of chemical analysis, conductance, i.r. and Raman spectra. Mahapatra
et al. have reported mercury(II) thiosalicylic acid (TSA) complexes with nitrogen and sulphur donor ligands. Also they have prepared Hg(II) complexes with dithioureas. HgX₂ (X = Cl, Br) react with di-2-pyridylketone (L) to give complexes of composition HgLX₂. The tetrahedral complexes are formed through N,N-coordination. Tetrahedral mercury(II) acetate, tetrafluoroborate, sulphate and nitrate complexes have been reported with benzoxazole-2-thione. Some three coordinated Hg(II) complexes of the composition HgL(CN)₂, HgL'(SCN)₂ have been prepared where L and L' are 2- and 4- benzylpyridines respectively. They have also reported some coordinated complexes of composition HgLX₂ (X = Cl, Br, CN, SCN; L = 2, and 4-benzoylpyridine. Coordination takes place through pyridine nitrogen atom.

HgX (X = Cl, Br, I) reacted with the imidazolinethiones [CR = H, R' = Me, Et(L); R = R' = Me = Et(L')] to give HgL₂X₂ and HgL'L₂X₂ respectively. The structures have been determined by X-ray crystallography studies. In HgL₂X₂, mercury adopts distorted-tetrahedral coordination but in HgL'L₂X₂, it has trigonal pyramidal geometry. Tetrahedral Hg(II) complexes of 1,4-diphenylthiosemicarbazide have been reported. Mercury(II) complexes of 2-methyl-5-mercapto-1,3,4-thiazole have been isolated. The ligand is bonded through thio-carbonyl sulphur atom and the complexes are tetrahedral. Burman et al. have reported tetrahedral Hg(II) complexes with 2-thioacetamido-thiazole. The complexes are characterised by i.r., u.v. and proton and 13C NMR spectra. The ligand is bonded to the Hg(II) ions through sulphur atom. Mercury(II) complexes of 1-amino-4,4,6-trimethyl-1H, 4H-pyrimidine-2-thiol have been reported by Singh et al. The crystal structure and vibrational spectra of the discrete dimer β-HgCl₂(PBu₃) and a comparison with the tetrameric α-form have been
reported by Bell and his coworkers\textsuperscript{51}. Mixed ligand complexes of mercury(II) including nonlinear pseudohalide group have been isolated\textsuperscript{52}.

(b) EXPERIMENTAL

In this section several tetra-, penta- and hexa-coordinated mercury(II) complexes with nitrogen and sulphur donor ligands are reported. For the sake of convenience, they have been classified into four maingroups.

(A) Mercury(II) complexes with tetradentate ligands

(B) Polymetallic complexes of mercury(II) with bi-bidentate and tridentate Schiff bases.

(C) Mercury(II) complexes with tri- and bidentate ligands

(D) Anionic mixed ligand complexes of Mercury(II).

(A) Mercury(II) complexes with tetradentate ligands

1. Mercury(II) complexes with methylene-bis-(1,1'-diphenyl-2-phenyl-2'-methyl ethylacrylate) :-

(a) Preparation of the ligand is mentioned in Section 4(b).

(b) Preparation of the complexes :- To an ethanolic solution of Hg(II) salts, the ligand in ethanol was added and refluxed over a waterbath for 2 hrs. On cooling, Hg(II) complexes separated out. These were then filtered, washed with ethanol, ether and dried in vacuo.

2. Mercury(II) complexes with N,N'-bis-(acetoacetanilide)ethylenediamine

(a) Preparation of the ligand is given in Section 4(b).

(b) Preparation of the complexes :- An ethanolic solution of Hg(II).
salts were added separately to the ligand solution in dioxane and the resulting solution refluxed over a waterbath for 2 hrs. On cooling, the Hg(II) complexes separated out. These were then filtered, washed with ethanol followed by ether and dried in vacuo.

3. Mercury(II) complexes with N,N'-bis(benzoin)1,2-diaminopropane
(a) Preparation of the ligand is given in Section 4(b).
(b) Preparation of the complex : - The ethanolic solution of HgCl₂ was added to the ligand solution in ethanol and the resulting mixture refluxed for about 1 hr. On cooling, conc. ammonia was added dropwise to the above solution when a metal complex separated out. It was then filtered, washed with ethanol followed by ether and dried in vacuo.

Elemental analysis, conductance and i.r. spectral data are recorded in Table 19.

Table 19. Analysis, conductance and i.r. spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. °C</th>
<th>% Mercury Found (Reqd.)</th>
<th>% Nitrogen Found (Reqd.)</th>
<th>ΔM</th>
<th>$\gamma(C=N)$</th>
<th>$\gamma(C=O)$</th>
<th>$\gamma(NH)$</th>
<th>$\gamma(Hg-O)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HgL]Cl₂</td>
<td>150</td>
<td>32.27 (32.38)</td>
<td>4.45 (4.51)</td>
<td>225.0</td>
<td>2215</td>
<td>1700</td>
<td>-</td>
<td>360</td>
</tr>
<tr>
<td>[HgL]Br₂</td>
<td>143</td>
<td>28.21 (28.30)</td>
<td>3.91 (3.95)</td>
<td>220.0</td>
<td>2210</td>
<td>1710</td>
<td>-</td>
<td>360</td>
</tr>
<tr>
<td>[HgL']Cl₂</td>
<td>&gt;250</td>
<td>30.7 (30.9)</td>
<td>8.6 (8.6)</td>
<td>108.0</td>
<td>1625</td>
<td>3310,3250</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td>[HgL']Br₂</td>
<td>&gt;250</td>
<td>25.0 (25.2)</td>
<td>7.4 (7.6)</td>
<td>110.0</td>
<td>1620</td>
<td>3330,3240</td>
<td>520</td>
<td></td>
</tr>
<tr>
<td>[HgL']I₂</td>
<td>&gt;250</td>
<td>23.9 (24.1)</td>
<td>6.7 (6.7)</td>
<td>115.0</td>
<td>1625</td>
<td>3320,3260</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td><a href="SCN">HgL''</a>₂</td>
<td>&gt;250</td>
<td>28.6 (28.9)</td>
<td>13.4 (13.5)</td>
<td>105.0</td>
<td>1630</td>
<td>3330,3250</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td>[HgL'']I₂</td>
<td>&gt;250</td>
<td>30.21 (30.36)</td>
<td>4.18 (4.23)</td>
<td>7.5</td>
<td>1645</td>
<td>1190</td>
<td>-</td>
<td>510</td>
</tr>
</tbody>
</table>
L = Methylene-bis-(1,1'-dicyano-2-phenyl-2'-methylethylacrylate
L' = N,N'-bis-(acetoacetanilide)ethylenediamine
L''H₂ = N,N'-bis-(benzoin)1,2-diaminopropane.

(B) Polymetallic complexes with bi-bidentate and tridentate schiff bases:

1. Mercury(II) complexes with N,N'-bis(benzoin)1,2-phenylenediamine
   (a) Preparation of the ligand is given in Section 4(b).
   (b) Preparation of the complex: Ethanolic solution of HgCl₂ was reacted with an ethanolic solution of the schiff base in 1:1 ratio followed by the dropwise addition of ammonia, when the metal chelate separated out. It was then filtered, washed with ethanol, ether and dried in vacuo.

2.(i) Mercury(II) complex with tridentate schiff base
   (a) Preparation of the ligand is given in Section 4(b).
   2.(ii) Mercury(II) complex with tridentate schiff base
      (a) Preparation of the ligand is given in Section 4(b).
      (b) Preparation of the complexes: Ethanolic solution of the mercury(II) chloride was reacted separately with an ethanolic solution of the schiff bases and the mixture refluxed for 1-1½ hrs. over a waterbath. Then it was allowed to cool and pH of the solution was raised to around 7 by adding conc. NH₄OH drop by drop when the metal chelates separated out. These were then filtered, washed with ethanol, ether and dried in vacuo.

3. Mercury(II) complex with [BnOAPH₂]
   (a) Preparation of the ligand is given in Section 4(b).
(b) **Preparation of the complex** :- Ethanoic solution of Hg(II) chloride was reacted with an ethanoic solution of the schiff base in 1:1 ratio followed by the dropwise addition of ammonia when the metal chelate separated out. It was then filtered, washed with ethanol, ether and dried in *vacuo*.

Elemental analysis, melting point, conductance and i.r. spectral data are given in Table 20.

Table 20. Analysis, m.p., conductance and i.r. spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. °C</th>
<th>Colour</th>
<th>% Mercury Found</th>
<th>% Nitrogen Found (Reqd.)</th>
<th>ΔM</th>
<th>ν(C=N) (C-O)</th>
<th>ν(Hg-O)</th>
<th>ν(Hg-N)</th>
<th>ν(C-O)</th>
<th>ν(C=O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg₂L₂</td>
<td>&gt;250</td>
<td></td>
<td>28.76 (28.83)</td>
<td>3.97 (4.02)</td>
<td>9.0</td>
<td>1590</td>
<td>1260</td>
<td>445</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td>Hg₂L'₂</td>
<td>205</td>
<td></td>
<td>41.54 (41.65)</td>
<td>2.85 (2.90)</td>
<td>4.7</td>
<td>1620</td>
<td>1210</td>
<td>440</td>
<td>505</td>
<td></td>
</tr>
<tr>
<td>Hg₂L&quot;₂</td>
<td>260</td>
<td></td>
<td>42.71 (42.89)</td>
<td>2.90 (2.99)</td>
<td>3.8</td>
<td>1605</td>
<td>1230</td>
<td>445</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td>Hg₂L&quot;&quot;₂</td>
<td>244</td>
<td></td>
<td>39.74 (39.91)</td>
<td>-</td>
<td>8.5</td>
<td>1600</td>
<td>1205</td>
<td>1525</td>
<td>440</td>
<td></td>
</tr>
</tbody>
</table>

LH₂ = N,N'-bis-(benzoin)m-phenylenediamine, L'H₂ = Schiff base derived from benzoin with 2-amino-2-methyl-1-propanol [BnAMPH₂], L"H₂ = Schiff base derived from benzoin with l-amino-2-propanol [BnAPH₂], L""H₂ = Schiff base derived from benzoin with o-aminophenol[BnOAPH₂]

(C) **Mercury(II) complexes with tri- and bi-dentate ligands**

1.(i) **Mercury(II) complex with benzoinsemicarbazone**

(a) **Preparation of the ligand** is given in Section 4(b).

(ii) **Mercury(II) complex with benzointhiosemicarbazone**
(a) Preparation of the ligand is given in Section 4(b).
(b) Preparation of the complexes: Ethanol solution of mercury(II) chloride was reacted separately with the ligands in ethanol in 1:2 ratio and the conc. NH₃ was added drop by drop until the metal chelates separated out. These were then filtered, washed with ethanol, ether and dried in vacuo.

2.(i) Mercury(II) complex with benzoinphenylhydrazone
(a) Preparation of the ligand is given in Section 4(b).
2.(ii) Mercury(II) complex with benzoin-2,4-dinitrophenylhydrazone
(a) Preparation of the ligand is given in Section 4(b).
(b) Preparation of the complexes: An ethanolic solution of mercury(II) chloride was reacted separately with the hydrazones in ethanol in stoichiometric ratio, the resulting solution refluxed for 1 hr. over a waterbath. On cooling, crystalline compounds separated out. These were then filtered, washed with ethanol, ether and dried in vacuo.

3. Mercury(II) complex with the schiff base
(a) Preparation of the ligand is given in Section 4(b).
(b) Preparation of the complex: The ethanolic solution of the schiff base was added to HgCl₂ solution in ethanol in 2:1 ratio followed by the dropwise addition of ammonia when the metal chelate separated out. It was then filtered, washed with ethanol, ether and dried in vacuo.

4. Mercury(II) complexes with dithioxamide
(a) Preparation of the complexes: An ethanolic solution of Hg(II) chloride and thiocyanate were reacted separately with dithioxamide
in ethanol in 1:2 ratio and refluxed over a waterbath for about 1 hr. The metal complexes thus separated were then filtered under suction, washed with ethanol, ether and dried in vacuo.

5. **Mercury(II) complexes with ethyl-l-phenyl-2-cyanoacrylate**
   (a) Preparation of the ligand is given in Section 4(b).
   (b) Preparation of the complexes: The ethanolic solution of mercury(II) salts were added separately to the ethanolic solution of the ligand and the resulting mixture refluxed over a waterbath for 2 hrs. On cooling, mercury complexes separated out. These were then filtered, washed with ethanol followed by ether and dried in vacuo.

6. **Mercury(II) complexes with ethylmethylketonethiosemicarbazone**
   (a) Preparation of the ligand is given in Section 6(b).
   (b) Preparation of the complexes: An ethanolic solution of mercury(II) salts were reacted separately with the ligand in ethanol and refluxed for 2 hrs. over a waterbath. The compounds thus appeared on cooling were then filtered, washed with ethanol, ether and dried in vacuo.

7. **Mercury(II) complexes with N,N'-diphenylthiocarbazide**
   (a) Preparation of the ligand is given in Section 6(b).
   (b) Preparation of the complexes: Ethanol solution mercury salts were reacted separately with ethanolic solution of the ligand in 1:1 ratio and refluxed for 1 hr. On cooling white crystalline complexes separated out. These were then filtered, washed with ethanol followed by ether and dried in vacuo.

   Elemental analysis, conductance and i.r. spectral data are recorded in Table 21.
### Table 21. Analysis, conductance and i.r. spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Mercury Found (Reqd.)</th>
<th>% Nitrogen Found (Reqd.)</th>
<th>$\Delta_M$ mhos cm$^2$</th>
<th>$\gamma(C=O)$</th>
<th>$\gamma(C=O')$</th>
<th>$\gamma(C=O)$</th>
<th>$\gamma(C=O)$</th>
<th>$\gamma(NH)$</th>
<th>$\gamma(Hg-O)$</th>
<th>$\gamma(Hg-Cl)$</th>
<th>$\gamma(Hg-N)$</th>
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<td>8.19 (8.31)</td>
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<td>-</td>
<td>-</td>
<td>1595</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'C1</td>
<td>38.24 (38.47)</td>
<td>7.85 (8.07)</td>
<td>12.0</td>
<td>-</td>
<td>-</td>
<td>1075</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'</td>
<td>25.0 (25.05)</td>
<td>6.88 (6.99)</td>
<td>10.4</td>
<td>-</td>
<td>-</td>
<td>1590</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'2</td>
<td>20.37 (20.45)</td>
<td>11.38 (11.42)</td>
<td>12.5</td>
<td>-</td>
<td>-</td>
<td>1605</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'4</td>
<td>25.76 (26.03)</td>
<td>3.52 (3.63)</td>
<td>10.0</td>
<td>-</td>
<td>-</td>
<td>1595</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'Cl2</td>
<td>39.05 (39.21)</td>
<td>5.38 (5.47)</td>
<td>10.5</td>
<td>-</td>
<td>-</td>
<td>1200</td>
<td>3250</td>
<td>350</td>
<td>260</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'(SCN)$_2$</td>
<td>35.87 (36.03)</td>
<td>11.25 (11.45)</td>
<td>11.49</td>
<td>-</td>
<td>-</td>
<td>1190</td>
<td>3300</td>
<td>355</td>
<td>265</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'Cl2</td>
<td>42.38 (42.53)</td>
<td>9.84 (10.08)</td>
<td>12.0</td>
<td>-</td>
<td>-</td>
<td>1600</td>
<td>2210</td>
<td>450</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>HgCl'2'I2</td>
<td>35.50 (35.73)</td>
<td>8.16 (8.30)</td>
<td>10.5</td>
<td>-</td>
<td>-</td>
<td>1600</td>
<td>2210</td>
<td>440</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'I2</td>
<td>37.61 (37.95)</td>
<td>6.73 (7.00)</td>
<td>11.4</td>
<td>-</td>
<td>-</td>
<td>1600</td>
<td>2215</td>
<td>445</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>HgCl'2'(SCN)$_2$</td>
<td>47.87 (48.26)</td>
<td>9.83 (10.10)</td>
<td>7.5</td>
<td>-</td>
<td>-</td>
<td>1100</td>
<td>3180</td>
<td>360</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'I2</td>
<td>33.25 (33.45)</td>
<td>7.20 (7.17)</td>
<td>9.2</td>
<td>-</td>
<td>-</td>
<td>1105</td>
<td>3150</td>
<td>370</td>
<td>245</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'(SCN)$_2$</td>
<td>45.08 (45.62)</td>
<td>8.92 (9.01)</td>
<td>10.4</td>
<td>-</td>
<td>-</td>
<td>1100</td>
<td>3230</td>
<td>360</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'I2</td>
<td>37.88 (37.42)</td>
<td>10.57 (10.32)</td>
<td>8.0</td>
<td>-</td>
<td>-</td>
<td>1190</td>
<td>3100, 350</td>
<td>3280</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'Br2</td>
<td>32.43 (32.07)</td>
<td>9.05 (8.69)</td>
<td>11.5</td>
<td>-</td>
<td>-</td>
<td>1185</td>
<td>3120, 365</td>
<td>3250</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'I2</td>
<td>28.18 (28.10)</td>
<td>7.86 (7.54)</td>
<td>12.0</td>
<td>-</td>
<td>-</td>
<td>1190</td>
<td>3100</td>
<td>360</td>
<td>270</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'(NO$_3$)$_2$</td>
<td>34.43 (34.19)</td>
<td>14.46 (14.17)</td>
<td>9.5</td>
<td>-</td>
<td>-</td>
<td>1180</td>
<td>3250</td>
<td>380</td>
<td>265</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl'2'(SCN)$_2$</td>
<td>34.91 (34.58)</td>
<td>14.74 (14.43)</td>
<td>10.6</td>
<td>-</td>
<td>-</td>
<td>1190</td>
<td>3110</td>
<td>375</td>
<td>260</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(D) Anionic mixed ligand complexes of mercury(II)

(a) Preparation of the simple complex: The simple complex [Hg(Qd)2Cl2] was prepared by reacting quinaldine and mercury(II) chloride in 2:1 ratio in ethanolic medium. The complex compound thus precipitated out was suction filtered, washed with ethanol followed by ether and dried in vacuo.

(b) Preparation of tetrachloro complex: Pure and dry chlorine gas was passed slowly to the ethanolic suspension of the simple complex [Hg(Qd)2Cl2] till a clear solution was obtained with an exothermic reaction. The solution was then kept overnight when crystalline compound of composition [QdH]2[HgCl4] separated out. It was then filtered, washed with ethanol, ether and dried in vacuo.

(c) Preparation of mixed ligand complexes: The mixed ligand complexes were prepared by adding stoichiometric proportion (1:2 ratio) of the nitrogen donor ligands to the ethanolic suspension of bis-(quinaldinium)tetrachloromercurate(II) and refluxing for 2 hrs. over a waterbath. On cooling, crystalline compounds separated out. These were then filtered, washed with ethanol followed by ether and dried in vacuo.

Elemental analysis, melting points, conductance and i.r. spectral data are recorded in Table 22.
Table 22. Analysis, melting point and conductance data

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. °C</th>
<th>Colour</th>
<th>% Mercury Found (Reqd.)</th>
<th>% Chlorine Found (Reqd.)</th>
<th>% Nitrogen Found (Reqd.)</th>
<th>Ω M cm² mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[QdH][HgCl₄]</td>
<td>180</td>
<td>Yellow</td>
<td>31.57 (31.82)</td>
<td>22.28 (22.49)</td>
<td>4.29 (4.44)</td>
<td>235.0</td>
</tr>
<tr>
<td>[QdH][HgCl₄Py₂]</td>
<td>212</td>
<td>-do-</td>
<td>25.31 (25.44)</td>
<td>17.82 (17.98)</td>
<td>7.01 (7.10)</td>
<td>224.0</td>
</tr>
<tr>
<td>[QdH][HgCl₄(γ-pic)₂]</td>
<td>209</td>
<td>White</td>
<td>24.42 (24.57)</td>
<td>17.18 (17.36)</td>
<td>6.27 (6.85)</td>
<td>232.0</td>
</tr>
<tr>
<td>[QdH][HgCl₄en]</td>
<td>260</td>
<td>-do-</td>
<td>28.92 (29.05)</td>
<td>20.35 (20.42)</td>
<td>8.08 (8.11)</td>
<td>220.0</td>
</tr>
<tr>
<td>[QdH][HgCl₄BP]</td>
<td>243</td>
<td>-do-</td>
<td>24.37 (25.50)</td>
<td>17.90 (18.03)</td>
<td>7.04 (7.12)</td>
<td>225.0</td>
</tr>
<tr>
<td>[QdH][HgCl₄Phe]</td>
<td>170</td>
<td>Yellow</td>
<td>24.58 (24.72)</td>
<td>17.32 (17.49)</td>
<td>6.83 (6.91)</td>
<td>234.0</td>
</tr>
<tr>
<td>[QdH][HgCl₄OPD]</td>
<td>185</td>
<td>White</td>
<td>27.05 (27.11)</td>
<td>19.12 (19.20)</td>
<td>7.43 (7.58)</td>
<td>230.0</td>
</tr>
<tr>
<td>[QdH][HgCl₄PD]</td>
<td>210</td>
<td>White</td>
<td>28.35 (28.47)</td>
<td>20.06 (20.13)</td>
<td>7.72 (7.95)</td>
<td>228.0</td>
</tr>
<tr>
<td>[QdH][HgCl₃Q]</td>
<td>175</td>
<td>Brown</td>
<td>34.38 (34.59)</td>
<td>18.24 (18.33)</td>
<td>4.75 (4.82)</td>
<td>125.0</td>
</tr>
<tr>
<td>[QdH][HgCl₃P-dtc]</td>
<td>216</td>
<td>Yellow</td>
<td>34.43 (34.65)</td>
<td>18.18 (18.37)</td>
<td>4.72 (4.83)</td>
<td>120.0</td>
</tr>
<tr>
<td>[QdH][HgCl₃M-dtc]</td>
<td>180</td>
<td>-do-</td>
<td>34.42 (34.53)</td>
<td>18.19 (18.30)</td>
<td>4.75 (4.82)</td>
<td>115.0</td>
</tr>
</tbody>
</table>

QdH = quinaldinium cation; Py = Pyridine, γ-pic = γ-picoline, en = ethylenediamine, BP = 2,2'-bipyridine, Phe = 1,10-phenanthroline, OPD = o-phenylenediamine, PD = 1,2-diaminopropane, Q = quinoline, P-dtc = piperidyldithiocarbamate, M-dtc = morpholyldithiocarbamate.
Divalent mercury(II) ion possesses a spherical symmetrical completely filled 5d\(^{10}\) nonbonding shell. So from theoretical standpoint no particular stereochemistry is energetically favoured relative to another due to absence of crystal field effect. However, actually Hg(II) ion has a strong tendency of complex formation and show two alternative stereochemical shapes, viz: two coordinate linear and four coordinate tetrahedral. Tetrahedral anionic complexes are more common and though many of the natural complexes are three-coordinated, actually these are four-coordinated involving the anion bridges.

In the present investigation mercury(II) complexes have been classified in to four categories (A), (B), (C) and (D) for ease of discussion.

(A) Mercury(II) complexes with tetradentate ligands

1. Mercury(II) complexes with methylene-bis-(1,1'-dicyano-2-phenyl-2'-methyl ethyl acrylate) :

The two complexes under report have the composition \([HgL]X_2\) where \(X = \text{Cl, Br and 'L' is the title ligand. Complexes are yellow in colour and have high molar conductance values in acetone indicating 1:2 electrolytic nature of the complexes. In the ligand, i.r. active bands are noticed at 1720, 1640 and 2230 cm\(^{-1}\) assignable to \(\nu(C=O)\), \(\nu(C=C)\) and \(\nu(C=N)\) vibrations respectively. In the chloro and bromo complexes the bands appeared at around 2210 and around 1700 cm\(^{-1}\) can be ascribed to \(\nu(C=N)\) and \(\nu(C=O)\) vibrations respectively. This lowering of frequencies indicate the coordination of cyano nitrogen and esteric carbonyl oxygen atoms to the metal ion. The conclusive evidence of bonding is provided by the occurrence of \(\nu(Hg-O)\) and
\(\gamma(\text{Hg-N})\) around 440 and around 360 cm\(^{-1}\) respectively. On the basis of analysis, conductance and i.r. spectral data the two Hg(II) complexes presumably have a tetrahedral configuration.

2. **Mercury(II) complexes with N,N'-bis-(acetoacetanilide)ethylenediamine**

The complexes under report are of the type \([\text{HgL}]X_2\) where \(X = \text{Cl}, \text{Br}, \text{I}, \text{SCN}\) and \(L = \) title ligand. The complexes are light yellow, cement and grey in colour, have high melting points and are 1:2 electrolytes as evident from \(\Delta M^+\) values in dimethyl formamide medium which falls in the range 105-115 mhos cm\(^2\) mole\(^{-1}\). In the ligand the appearance of bands at 1645, 3300 and 1600 cm\(^{-1}\) may be assigned to \(\gamma(\text{C=O}), \gamma(\text{NH})\) and \(\gamma(\text{C=C})\) vibrations. In the complexes splitting of \(\gamma(\text{NH})\) band occurs, polarisation of C=C bond and decrease of \(\gamma(\text{C=O})\) frequency indicate the bonding of the ligand molecule to the metal ions through both the amine nitrogen and amidic carbonyl oxygen atoms. The conclusive evidence of bonding is provided by the observation of \(\gamma(\text{Hg-O})\) and \(\gamma(\text{Hg-N})\) around 440 and 510 cm\(^{-1}\) respectively. In the thiocyanate complex, \(\gamma(\text{C=S})\) appears at 2075 cm\(^{-1}\) indicating the ionic nature of the thiocyanate group, supported by the conductance data. Hence the four complexes presumably possess tetrahedral stereochemistries around the Hg(II) ions.

3. **Mercury(II) complex with N,N'-bis-(benzoin) 1,2-diaminopropane**

The complex prepared is of the composition \([\text{HgL}]\) where \(L = \) title ligand. The complex is yellow in colour and has low conductance value in dimethylformamide indicating the non-electrolytic nature of the complex. The Schiff base can function as tetradeutate ligand using two hydroxylic oxygens and two imine nitrogen atoms as
potential bonding sites. Assignments have been made for $\nu$(C-O) and $\nu$(C=N) and shifting of these bands to lower frequency regions indicates\textsuperscript{56,57} the bonding at these sites. Further $\nu$(OH) which appears as a medium strong band at 3390 cm$^{-1}$ (lowered due to intramolecular hydrogen bonding) in the ligand has disappeared in case of complexes providing further evidence at the oxygen sites. This has been further substantiated by the observation\textsuperscript{54} of $\gamma$(Hg-N) and $\gamma$(Hg-O) at 510 and 450 cm$^{-1}$ respectively in the far i.r. spectrum of the complex. So this complex is supposed to possess a tetrahedral environment around the metal ion.

(B) Polymetallic complexes of mercury(II)

1. Mercury(II) complex with N,N'-bis-(benzoin)m-phenylenediamine

The complex under report has the composition \([\text{Hg}_2\text{L}_2]\) where 
L is the title ligand. The complex has high melting point, amorphous and insoluble in common organic solvents but sparingly soluble in dimethylformamide. Non-electrolytic nature of the complex is indicated by the low conductance value in DMF.

Assignments have been made for the principal bands like $\nu$(C=N), $\nu$(C-O), $\nu$(OH), $\sigma$(OH), $\gamma$(Hg-O) and $\gamma$(Hg-N). The bands at 1210 and 1600 cm$^{-1}$ in the ligand may be ascribed to $\gamma$(C-O) and $\gamma$(C=N) vibrations respectively. On complexation, a decrease of these frequencies is observed indicating\textsuperscript{56,57} the bonding of oxygen and imine nitrogen atoms to the Hg(II) ion. Further, the $\sigma$(OH) appears at 1445 cm$^{-1}$ and $\gamma$(OH) at 3350 cm$^{-1}$ as a relatively sharp band, lowered due to intramolecular hydrogen bonding in the ligand and its conspicuous absence in the complex supports the bonding of oxygen atoms to the Hg(II) ions. However, conclusive evidence of bonding
of oxygen and nitrogen atoms have been provided by the occurrence of $^{\gamma}(\text{Hg-O})$ and $^{\gamma}(\text{Hg-N})$ at 445 and 510 cm$^{-1}$ respectively. The complex is presumably polymetallic having a tetrahedral arrangement around each Hg(II) ions on the basis of analysis, conductance, sparing solubility, high melting point and i.r. spectral data as represented by the diagram 36.

![Diagram 36]

2. Mercury(II) complexes with [BnAMPF$_2$] and [BnAPH$_2$]

Complexes prepared in the present investigation have the compositions [Hg$_2$L$_2$] and [Hg$_2$L'$_2$] where LH$_2$ and L'H$_2$ are the tridentate schiff bases derived from benzoin with 2-amino-2-methyl-1-propanol [BnAMPF$_2$] and 1-amino-2-propanol [BnAPH$_2$] respectively. The complexes are white in colour, amorphous, high melting points and do not dissolve in common organic solvents but slightly soluble in dimethylformamide. Low conductance values in dimethylformamide indicate the non-electrolytic nature of the complexes. The analytical data indicate a 1:1 (metal:ligand) stoichiometry and hence the schiff bases act as dibasic tridentate ligands. A band of medium intensity around 2750 cm$^{-1}$ may be assigned to intramolecularly hydrogen bonded $^{\gamma}$(O-H). In the spectra of the complexes, absence of this band indicate the deprotonation of the alcoholic group and the bonding through the oxygen atoms. The
\( \gamma(C=O) \) vibration of both the ligands undergoes a positive shift indicating the formation\(^{58} \) of \( \text{Hg} \cdots \text{Hg} \) bridge. The bands at \( 1670 \text{ cm}^{-1} \) [BNAMPH\(_2\)] and at \( 1620 \text{ cm}^{-1} \) [BNAPH\(_2\)] can be assigned to \( \gamma(C=N) \) vibration. The lowering of these frequencies in the complexes indicates the bonding\(^{59,60} \) of azomethine group to the Hg(II) ions through the imine nitrogen atoms. However, the conclusive evidence of bonding of the potential donor atoms of the ligands is provided by the bands around 450 and \( 510 \text{ cm}^{-1} \) attributable to \( \gamma(Hg-O) \) and \( \gamma(Hg-N) \) vibrations respectively.

So on the basis of above formulations, a dimetallic structure\(^{[37]} \) with alcoholic oxygen bridge has been proposed for these two complexes.

3. Mercury(II) complex with [BNOAPH\(_2\)]

The complex reported in the present investigation has the composition [Hg\(_2\)L\(_2\)] where LH\(_2\) = tridentate Schiff base derived from benzoin with \( o \)-aminophenol [BNOAPH\(_2\)]. The complex is amorphous, possesses high melting point and insoluble in common organic solvents but sparingly soluble in dimethylformamide. Non-electrolytic nature of the complex is indicated by the low \( \Lambda_M \) value of the complex.

In the i.r. spectra, the three principal bands \( \gamma(C=N) \), \( \gamma(C-O) \) (alcoholic) and \( \gamma(C-O) \) (phenolic) have been assigned. The first two bands shift to lower frequency regions in the chelate indicating the bonding of imine nitrogen and alcoholic oxygen atoms to the metal atom. The \( \gamma(C-O) \) (phenolic) vibration shifts to higher frequency region on complexation which indicates\(^{61,62} \) the formation of phenolic oxygen bridge \( \text{Hg} \cdots \text{Hg} \). However, evidence of bonding of oxygen and nitrogen atoms have been provided by the occurrence\(^{54} \) of \( \gamma(Hg-O) \) and
\(\gamma(\text{Hg-N})\) at 440 and 505 cm\(^{-1}\) in the far i.r. spectra of the complex. So a dinuclear tetrahedral configuration with phenolic oxygen bridge has been assigned to the complex.

(C) Mercury(II) complexes with tri- and bidentate ligands

1. Mercury(II) complexes with benzoin semicarbazone and benzoin thiosemicarbazone

Two complexes under report have the composition \([\text{HgLCl}]\) and \([\text{HgL'C}l]\) where \(LH\) and \(L'H\) are benzoin semicarbazone and benzoin thiosemicarbazone respectively. The complexes are white in colour, have low melting points and non-electrolytes, evident from low \(\Delta M\) values. The bands at 1085, 1670, 1590 and 1200 cm\(^{-1}\) in the free ligands may be assigned to \(\gamma(\text{C=S})\), \(\gamma(\text{C=O})\), \(\gamma(\text{C=N})\) and \(\gamma(\text{C-O})\) vibrations. The shifting of these bands to lower frequency regions in the complexes indicates the bonding of thiocarbonyl sulphur, carbonyl-oxygen, imine nitrogen and hydroxylic oxygen atoms to the Hg(II) ions. However, the evidence of the mode of bonding is obtained by the occurrence of bands around 220, 260, 350 and around 450 cm\(^{-1}\) which correspond to \(\gamma(\text{Hg-Cl})\), \(\gamma(\text{Hg-S})\), \(\gamma(\text{Hg-N})\) and \(\gamma(\text{Hg-O})\) respectively. Hence the complexes are presumed to possess a tetrahedral stereochemistry around the metal ions.

2. Mercury(II) complexes with benzoin phenylhydrazone and benzoin-2,4-dinitrophenylhydrazone

The two complexes isolated are of the types \([\text{HgL}_2]\) and \([\text{HgL'}_2]\) where \(LH\) and \(L'H\) are benzoin phenylhydrazone \([\text{BnPH}]\) and benzoin-2,4-dinitrophenylhydrazone \([\text{BnNPH}]\) respectively. The complexes are yellow and greyish-white in colour, have low molar
conductances in acetone medium indicating non-electrolytic nature of the complexes.

In the ligands \( \gamma(C=\text{N}) \) appears at 1600 cm\(^{-1} \) in [BnPH\(^+\)] and at 1615 cm\(^{-1} \) in [BnNPH\(^+\)]. A decrease of 10-15 cm\(^{-1} \) in the complexes indicates the bonding of hydrazinic nitrogen atoms to the Hg(II) ions. The band at 1210 cm\(^{-1} \) in the ligands can be ascribed to \( \gamma(C-O) \) vibration which has been shifted down to lower frequency regions in the complexes showing the bonding of hydroxylic oxygen atoms to the metal ions. However, the conclusive evidence of bonding of oxygen and nitrogen atoms have been provided by the occurrence of \( \gamma(Hg-O) \) and \( \gamma(Hg-N) \) around 450 and around 360 cm\(^{-1} \) respectively. On the basis of above evidences a tetrahedral structure is proposed for these complexes.

3. Mercury(II) complex with the schiff base [BnAH]

The complex compound has the composition \([\text{HgL}_2]\) where LH = bidentate schiff base derived from benzoin with aniline. The complex is yellowish white in colour, has low melting point and low conductance value indicating the non-electrolytic nature of the complex. The two principal bands \( \gamma(C-O) \) and \( \gamma(C=\text{N}) \) have been assigned. The shifting of these bands to lower frequency regions indicates the coordination of azomethine nitrogen and heterocyclic oxygen atoms to the Hg(II) ion. The complex is found to be four-coordinated having a tetrahedral environment around the metal ion.

4. Mercury(II) complexes with dithioxamide

The complexes have the composition \([\text{HgL}_2X_2]\) where L = dithioxamide and \( X = \text{Cl, SCN} \). Two complexes are brown in colour, have
fairly low melting points and non-electrolytic in nature, indicated by the low \( \Lambda_M \) values in acetone medium. In the complexes several bands are noticed in the 3300 - 3100 cm\(^{-1}\) region due to splitting of \( \gamma(N-H) \) indicating the coordination of nitrogen atom of the amino group. Also the band at 1205 cm\(^{-1}\) attributable to \( \gamma(C=S) \) appear at lower frequency region suggesting the bonding of sulphur atom of the thiocarbonyl group. Bonding of nitrogen and sulphur atoms to the Hg(II) ions is further provided by observation of \( \gamma(Hg-N) \) and \( \gamma(Hg-S) \) at around 350 and 260 cm\(^{-1}\) regions respectively in the low frequency i.r. spectra of the complexes. The two Hg(II) complexes have presumably an octahedral environment around the metal ions.

5. Mercury(II) complexes with ethyl-1-phenyl-2-cyanoacrylate

The complexes reported here have the composition \( [\text{HgLX}_2] \) where \( L \) is the title ligand, \( X = \text{Cl, Br, I} \). The complexes are white to greyish white in colour, have low melting points and low \( \Lambda_M \) values indicating non-electrolytic nature of the complexes. The appearance of bands at 2200 and 1605 cm\(^{-1}\) in the ligand can be assigned to \( \gamma(\text{C=N}) \) and \( \gamma(\text{C=O}) \) vibrations respectively. On complexation, a decrease of these bands to lower frequency regions is observed indicating the bonding of cyano nitrogen and carboxy oxygen atoms to the metal ions. This has been further substantiated by the observation of \( \gamma(Hg-N) \) and \( \gamma(Hg-O) \) around 350 and 450 cm\(^{-1}\) region. Hence all the complexes presumably possess a tetrahedral configuration around the Hg(II) ion.

6. Mercury(II) complexes with ethylmethylketonethiosemicarbazone

The three complexes reported here have the composition
[HgLX₂] where L = ethylmethylketonethiosemicarbazone, X = Cl, I, SCN. The complexes are white in colour, have low melting points and non-electrolytic in nature, evident from low Δ_M values.

Thiocyanate complex has two sharp bands at 2065 cm⁻¹ and at 700 cm⁻¹ assignable to ν(C≡N) and ν(C=S) vibrations respectively. In the Hg(II) complex, an increase of 35 cm⁻¹ is observed which indicates the N-bonded thiocyanate group. ν(C≡S) in the ligand occurs at 1120 cm⁻¹ which shifts to lower frequency region in the complexes, supporting the thiocarbonyl sulphur coordination to the Hg(II) ions. Broadening and splitting of ν(N-H) occuring around 3000 cm⁻¹ in the complexes indicates the bonding of through the amino group. Direct evidence of bonding is obtained by the occurrence of ν(Hg-O) and ν(Hg-N) around 440 and around 360 cm⁻¹ respectively.

Hence the complexes possess tetrahedral stereochemistry around the metal ion.

7. Mercury(II) complexes with N,N'-diphenylthiocarbazide

Five complexes reported in the present investigation have the composition [HgLX₂] where L = N,N'-diphenylthiocarbazide, X = Cl, Br, I, NO₃, SCN. The complexes are white in colour, have low melting points and have low Δ_M values indicating non-electrolytic nature of the complexes. In the complexes, splitting of ν(N-H) band and decrease of ν(C-N) and ν(C≡S) to lower frequency regions provide evidence of bonding through thiocarbonyl sulphur and nitrogen of one of the -NH groups. This has been further substantiated by observation of ν(Hg-S) and ν(Hg-N) around 260-285 cm⁻¹ and around 360 cm⁻¹ region.
In the thiocyanato complex $\nu(C=N)$ is observed at 2125 cm$^{-1}$. An increase of 55 cm$^{-1}$ indicates the thiocyanate group to be terminally S-bonded on the basis of earlier observation. In the nitrato complex the $\nu_4(NO_2$ assymmetric stretch) and $\nu_1(NO_2$ symmetric stretch) bands are observed at 1400 and 1275 cm$^{-1}$ and the difference ($\Delta \nu$) is 125 cm$^{-1}$ indicating the presence of monodentate nitrato group in conformity with earlier observations.

Hence all the complexes presumably have a tetrahedral environment around the Hg(II) ions.

(D) Anionic mixed ligand mercury(II) complexes

On the basis of analysis and conductance data, all the ten mixed ligand complexes have the compositions $[QdH]_2[HgCl_4L_2]$, $[QdH]_2[HgCl_4L']$ and $[QdH][HgCl_3L'']$ where QdH = quinaldinium cation; L = pyridine, $\gamma$-picoline; L' = ethylenediamine, 2,2'-bipyridine, 1,10-phenanthroline, o-phenylenediamine, 1,2-diaminopropane, L'' = quinoline, piperidyldithiocarbamate and morpholyldithiocarbamate.

All the complexes are white, yellow and brown in colour and have high melting points. The complexes of the third category are found to be 1:1 electrolytes and rest are 2:1 electrolytes, evident from the $\Delta M$ values in acetone medium.

When pure and dry chlorine gas is passed in to the ethanolic suspension of the simple complex $[HgQd_2Cl_2]$, two possible reactions may take place: (i) substitution in the quinaldine ring and (ii) solvolysis of the halogen and consequent addition of the hydrogen halide to the ligand moiety forming quaternary halide. In the present case, definitely halogenation has resulted in the formation of quinaldinium chloride which subsequently react with Hg(II) chloride forming
bis-quinaldinium tetrachloromercurate(II). This complex further accept N and S-donors giving rise to complexes of higher coordination numbers, five and six.

IR spectra indicate the \( \nu(N-H) \) and \( \sigma(N-H) \) frequencies around 3300 and around 1580 cm\(^{-1}\) respectively in agreement with the above formulations. Hence it is clear that the anionic complexes are formed involving \([QdH]^+\) cation formed due to solvolytic reaction mechanism. Most of the absorption bands due to free nitrogen donors have been modified in the mixed ligand complexes indicating their coordination to the Hg(II) ions. The bands, observed around 1260 and around 890 cm\(^{-1}\), can be assigned to thiocarbonyl (C=S) and thiol (C-S) absorption bands respectively in piperidyl/morpholyldithiocarbamates and shifting of these bands to lower frequency regions indicates the bonding of both the sulphur atoms to the Hg(II) ions. Evidence for the co-ordination of the bases N-and S-donor ligands is further substantiated by the occurrence\(^5\) of bands at around 320 cm\(^{-1}\), 440 cm\(^{-1}\), 260 cm\(^{-1}\) and 220 cm\(^{-1}\) assignable to \( \nu(Hg-N) \), \( \nu(Hg-O) \), \( \nu(Hg-S) \) and \( \nu(Hg-Cl) \) vibrations respectively.

Hence it is presumed that the complexes of the first and second categories are octahedral and the third type are four-coordinated tetrahedral and five-coordinated squarepyramidal or trigonal bipyramidal. However, the X-ray crystallograph study will reveal the exact stereochemistry of these complexes.
REFERENCES