them to be essentially non-electrolytic \((\Delta M \approx 30 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1})\). IR spectra (band positions in cm\(^{-1}\)) of these complexes are similar to those of 2-methylbenzothiazole complexes with other metal salts, confirming coordination through the nitrogen atom only. In addition to the absorption bands due to coordinated 2-methylbenzothiazole the far IR spectra (Beckman IR-12) of the 1:1 Hg(II) chloride and bromide complexes with this ligand show bands at 267 in the chloro and at 207 in the bromo derivative. The frequencies of these bands are halogen-dependent and are identified as vHg-Cl and Hg-Br modes, respectively, consistent with terminal Hg-X stretching modes in HgLX\(_2\) complexes, where L=PhaP; pyridine, pyridine-N-oxide or their ring substituted methyl or dimethyl derivatives, which are considered to have halogen-bridged dimeric tetrahedral structures in the solid state. Moreover, the Hg(II) chloride complex shows an additional band at 202 (but not the bromo complex) due to vHg-Cl involving bridging halogens. The bridging Hg-Br stretching mode expected at \(\approx 150\) could not be recorded with the present range of the spectrophotometer. The observed frequencies of the terminal and bridging Hg-halogen stretching modes in the 1:1 Hg(II) chloride and bromide complexes with 2-methylbenzothiazole lend support to the halogen-bridged dimeric tetrahedral structure (I) for the complexes in the solid state.

\[
\begin{array}{c}
\text{Hg} \\
\text{L} \\
\text{X} \\
\text{X}
\end{array}
\]

\(X = \text{Cl, Br or SCN}\)

IR spectrum of the 1:1 Hg(II) cyanide-2-methylbenzothiazole complex shows additional absorption bands at 2200, 455 and 360 which are identified as vCN, vHg-C and \(\delta\) Hg-C-N modes, respectively, due to coordinated cyano groups. Hg(II) cyanide has a linear cyanide-bridged polymeric chain structure in the solid state and absorbs at 2193, 442 and 341 due to vCN, vHg-C and \(\delta\) Hg-C-N modes, respectively. The frequency of vCN suffers a significant negative shift when the cyano bridges break down and Hg(II) cyanide complexes with terminal cyano groups absorb at lower energies than pure mercury cyanide while bridging cyano groups absorb at higher energies. Complexes having both terminal and bridging cyano groups display split bands in each of the vCN, vHg-C and \(\delta\) Hg-CN regions; the one appearing at higher wave number being assigned to the bridging cyano groups while the other at lower wave number to the terminal cyano groups. The observed frequencies of vCN (2200), vHg-C (455) and \(\delta\) Hg-CN (360) are consistent with the presence of only bridging cyano groups. The 1:1 Hg(II) cyanide-2-methylbenzothiazole complex may thus be assigned a cyanobridged dimeric structure in the solid state.

In addition to the ligand bands IR spectrum of the 1:1 Hg(II) thiocyanate-2-methylbenzothiazole complex shows absorption bands at 2133, 2125 and 2090 due to vCN and two bands (770, 690) in the vCS region supporting the presence of both bridging and terminal thiocyanato groups in the complex. On the basis of the stoichiometry and the IR spectral data the 1:1 Hg(II) thiocyanate complex with 2-methylbenzothiazole is tentatively assigned a thiocyanato-bridged dimeric structure in the solid state with two –SCN – bridges and a terminal SCN group bonded through sulphur to each mercury atom.

We thank Prof. O. P. Malhotra for facilities and Dr G. C. Percy, University of Cape Town, for the far IR spectra.

**References**


**Complexes of Organotinn(IV) Halides with Neutral Schiff Bases of Salicylaldehyde & 2-Hydroxy-1-naphthaldehyde with 2-Aminopyridine**

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Schiff base complexes of the type \(\text{R}_4\text{SnX}_4\text{-n(SB)}_2\) (where \(X = \text{Cl, Br, I, SB = Schiff bases derived from 2-aminopyridine and salicylaldehyde or 2-hydroxy-1-naphthaldehyde} \)) have been synthesized and characterized by elemental analysis, infrared and electronic spectroscopy and conductivity measurements. The ligands behave as monodentate coordinating through azomethine nitrogen atom. An octahedral structure is suggested for the complexes in solid state.

RECENTLY transition metal complexes of N-2-(2'-pyridyl)-ethyalsalicylidimines (Ia) have been reported, in which the bases behave as monofunc-
tional terdentate ligands. Oehmke and Bailar studied coordination compounds of N-2-(2'-pyridyl) methyldi-salicyldimine (1b, Y = H) with Fe(III), Co(II), Ni(II) and Zn(II) and concluded that the ring nitrogen may or may not take part in coordination depending upon the nature of the central metal atom. In Schiff bases 1c, the steric condition does not seem to be favourable for them to act as terdentate ligands and their anions behave as bidentate in M(II) complexes (M = Cu, Co, Ni, Zn and Pd). The coordination of such bases with organotin(IV) halides has not been investigated and the present note reports the synthesis and structure of the coordination compounds of diphenyltin dihalides, dimethyltin dichloride and phenyltin trichloride with the Schiff bases 1c (Y = H) and 1c (Y = 5, 6-benzo).

The complexes are intense yellow to red in colour, soluble in common organic solvents except ether and have sharp melting points. The analytical data show that the bases form adducts of 1:2 stoichiometry, in which they behave as neutral monodentate ligands coordinated to tin irrespective of the halogen atom attached to the metal and the nature and the number of the organic moieties σ-bonded to tin(IV).

Electronic spectrum (400-200 nm, Perkin-Elmer 202) of 1c shows four absorption bands at 226, 270, 301 and 344 nm and that of 1c consists of three bands at 234, 257 and 316 nm. The intense band of shortest wavelength is associated with the imino substituted pyridine ring. The band at ~265 nm can be assigned to the N→π* and π→π* transitions of the pyridine and 0-hydroxyaldehyde moieties. The spectra of the adducts in methanol are similar to corresponding ligands indicating considerable dissociation of the complexes in solution. Molar conductance values 10^3 M solution of complexes in methanol measured at 20° on a Philips conductivity bridge are of the same order as those reported for the corresponding Lewis acids in the same concentration range, indicating the presence of same conducting species in solution and thus supporting the conclusion derived from UV spectral studies that the complexes in solution are largely dissociated into parent components. This is in agreement with previous reports on some analogous derivatives of other Schiff bases.

The IR spectra of the free and coordinated ligands do not substantially differ in the 3000 cm⁻¹ region. The bands in the spectra of the adducts located in the region 3200-3030 cm⁻¹ correspond to the weak broad band of Schiff bases at 3055 ± 5 cm⁻¹ due to H-bonded (OH)⁻⁻⁻. The strong band appearing in the spectra of the ligands around 1275 cm⁻¹ due to phenolic C-O stretching shows negligible shift, indicating that 0-hydroxy group of the bases has not taken part in complex formation. The analytical data support the above statement.

### Table 1 — Characterization Data for the Adducts

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. °C</th>
<th>Found (%) (Calc.)</th>
<th>(\Lambda M) ohm⁻¹ cm² mol⁻¹</th>
<th>sc= N (exocyclic) cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₂SnCl₂ 2IC₁</td>
<td>148-49</td>
<td>15:92 (90:57)</td>
<td>2-94 (7:65)</td>
<td>47.9</td>
</tr>
<tr>
<td>Ph₂SnBr₂ 2IC₁</td>
<td>121-23</td>
<td>14:19 (51:98)</td>
<td>3-62 (6:64)</td>
<td>54.7</td>
</tr>
<tr>
<td>Ph₂Sn₂Cl₄</td>
<td>12:64 (46:59)</td>
<td>6-23 (6:64)</td>
<td>7-95 (9:66)</td>
<td>56.6</td>
</tr>
<tr>
<td>Me₂SnCl₂ 2IC₁</td>
<td>138</td>
<td>19:37 (50:65)</td>
<td>6-23 (6:64)</td>
<td>52.5</td>
</tr>
<tr>
<td>Ph₂Sn₂Cl₄</td>
<td>160</td>
<td>Hygroscopic compound</td>
<td>4-23 (9:66)</td>
<td>49.8</td>
</tr>
<tr>
<td>Ph₂SnIC₂Cl₂</td>
<td>180-82</td>
<td>14:26 (62:60)</td>
<td>4-13 (6:71)</td>
<td>49.8</td>
</tr>
<tr>
<td>Ph₂Sn₂Cl₄</td>
<td>120</td>
<td>12:65 (56:52)</td>
<td>6-23 (6:64)</td>
<td>74.4</td>
</tr>
<tr>
<td>Me₂SnCl₂ 2IC₁</td>
<td>176-77</td>
<td>16:56 (57:35)</td>
<td>4-45 (7:94)</td>
<td>62.2</td>
</tr>
<tr>
<td>Ph₂Sn₂Cl₄</td>
<td>179-80</td>
<td>14:45 (57:25)</td>
<td>8-40 (9:69)</td>
<td>40.3</td>
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<tr>
<td>Ph₂SnIC₂Cl₂</td>
<td>14:86 (57:14)</td>
<td>8-40 (9:69)</td>
<td>40.3</td>
<td>1612 s</td>
</tr>
</tbody>
</table>
The νC=Ν absorption of the pyridine ring\(^{8,17}\) appears at 1590 ± 5 cm\(^{-1}\) in the ligands and remains unaffected on complexation. In-plane and out-of-plane ring deformation modes of pyridine are observed at 900 and 410 cm\(^{-1}\) respectively in the spectrum of the ligands and their adducts, suggesting non-participation of the pyridine N atom in coordination\(^{18}\).

The bands appearing at 1605 and 1610 cm\(^{-1}\) in the spectra of the ligands Ic\(_1\) and Ic\(_2\) respectively may be attributed to the νC=Ν (azomethine). In the spectra of these complexes these bands appear to be split into two strong peaks at 1645 ± 20 cm\(^{-1}\) and 1618 ± 6 cm\(^{-1}\), the former may be assigned mainly to νC=Ν whilst the lower band may be due to νC=Ν coupled with aromatic νC–C stretch\(^{19}\). The shift of 20 to 60 cm\(^{-1}\), towards higher frequency suggests coordination through the exocyclic N atom\(^{19,22}\).

It is concluded that the Schiff bases behave as monodentate ligand coordinating through azomethine N atom. An octahedral structure is suggested for these complexes in the solid state.

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References