Adducts of Arsenic(III), Antimony(III) & Bismuth(III) Trichlorides with Benzothiazolines

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Adducts of arsenic(III), antimony(III) and bismuth(III) trichlorides with benzothiazolines with the general formula, MCI3·R(R')CNHC6H4S (M = As, Sb, Bi; R = Me, R' = Me, Et, Ph, C6H4F; R = H, R' = Ph) have been synthesized by the reactions of the corresponding metal trichlorides with benzothiazolines in 1:1 molar ratio in suitable organic solvents at 0 to 5°C. These adducts are highly susceptible to hydrolysis even by atmospheric moisture and are insoluble in common organic solvents. IR spectral data indicate that coordination in these adducts occurs through nitrogen of benzothiazoline.

Benzothiazoline ring generally opens up in the presence of metal ions to give the corresponding metal complexes of N-(2-mercaptophenyl)aldimines or ketimines. In these complexes the Schiff bases which do not have independent existence generally behave as bidentate ligands. In contrast to this benzothiazolines also act as simple Lewis bases, forming stable adducts (without ring-opening) with strong Lewis acids, e.g., stannic chloride. With comparatively weaker Lewis acids such as AsCl3, SbCl3 and BiCl3, benzothiazolines have now been shown to form simple adducts, which are described herein.

Solvents (benzene, carbon tetrachloride, diethyl ether and light petroleum) were dried by standard methods. Acetone (b.p. 56°), methyl ethyl ketone (b.p. 80°), benzaldehyde (b.p. 179°), acetophenone (b.p. 202°), arsenic trichloride (b.p. 130°), antimony trichloride (b.p. 80/10 mm) and o-aminothiophenol (b.p. 125-7/6 mm) were distilled before use. Benzothiazolines were synthesized by well known procedures.

The adducts were prepared under rigorous anhydrous conditions as follows: To the light petroleum (b.p. 60-80), carbon tetrachloride or benzene, and methyl ethyl ketone (b.p. 80°), benzaldehyde (b.p. 179°), acetophenone (b.p. 202°), arsenic trichloride (b.p. 130°), antimony trichloride (b.p. 80/10 mm) and o-aminothiophenol (b.p. 125-7/6 mm) were distilled before use. Benzothiazolines were synthesized by well known procedures.

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<table>
<thead>
<tr>
<th>Solvent for preparation</th>
<th>Product (Yield %)</th>
<th>Physical state</th>
<th>m.p. °C</th>
<th>Found (Calc.) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light petroleum and benzene</td>
<td>AsCl3·Me2CNHC6H4S</td>
<td>White solid powder</td>
<td>128(d)</td>
<td>22.65 (21.62)</td>
</tr>
<tr>
<td>-do-</td>
<td>AsCl3·Me(Ph)CNHC6H4S</td>
<td>-do-</td>
<td>75(d)</td>
<td>28.22 (27.58)</td>
</tr>
<tr>
<td>Carbon tetrachloride and benzene</td>
<td>SbCl3·Me2CNHC6H4S</td>
<td>White solid powder</td>
<td>200(d)</td>
<td>31.05 (30.94)</td>
</tr>
<tr>
<td>-do-</td>
<td>SbCl3·Me(PH)CNHC6H4S</td>
<td>Yellow solid powder</td>
<td>50(d)</td>
<td>25.52 (25.71)</td>
</tr>
<tr>
<td>-do-</td>
<td>SbCl3·Me(Ph)CNHC6H4S</td>
<td>Yellow sticky solid</td>
<td>—</td>
<td>39.43 (38.52)</td>
</tr>
<tr>
<td>Diethyl ether and benzene</td>
<td>BiCl3·Me2CNHC6H4S</td>
<td>White solid powder</td>
<td>65(d)</td>
<td>43.87 (43.49)</td>
</tr>
<tr>
<td>-do-</td>
<td>BiCl3·Me(Ph)CNHC6H4S</td>
<td>-do-</td>
<td>230(d)</td>
<td>40.61 (42.18)</td>
</tr>
</tbody>
</table>

Table 1—Synthesis and Properties of Adducts of Arsenic, Antimony and Bismuth Trichlorides with Benzothiazolines

In contrast to this benzothiazolines also act as simple Lewis bases, forming stable adducts (without ring-opening) with strong Lewis acids, e.g., stannic chloride. With comparatively weaker Lewis acids such as AsCl3, SbCl3 and BiCl3, benzothiazolines have now been shown to form simple adducts, which are described herein.

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diethyl ether solution of arsenic, antimony or bismuth trichloride respectively was added dropwise a benzene solution of benzothiazoline in equimolar ratio at 0-5°C with constant stirring. A white or yellow precipitate was immediately obtained. The stirring was continued for further 30 min to ensure completion of the reaction. The precipitate was filtered off and washed with the parent solvent twice or thrice and finally dried under reduced pressure to yield the desired product (Table I). The reaction can be represented by Eq. (1)

\[
MCl_3 + \text{C}_6\text{H}_5\text{N} = \text{C}_6\text{H}_4\text{C} = \text{N} + \text{C}_6\text{H}_{12} \rightarrow \text{MCl}_3 + \text{C}_6\text{H}_5\text{N} = \text{C}_6\text{H}_4\text{C} = \text{N} + \text{C}_6\text{H}_{12} \quad \text{(1)}
\]

When the reactions of metal (As, Sb, Bi) chlorides were carried out with a few typical benzothiazolines in 1:2 molar ratio, only 1:1 adducts were precipitated leaving the excess benzothiazolines as unreacted free ligands in the solutions.

The reactions of benzothiazolines with AsCl₃, SbCl₃ and BiCl₃ in suitable organic solvents at low temperature (~0°C) or even at room temperature resulted in the immediate precipitation of simple addition compounds. Liberation of hydrogen chloride gas was not observed even under reflux. The reaction of AsCl₃, SbCl₃ or BiCl₃ with benzothiazolines in the presence of Et₃N afforded the adduct of MCl₃ (M = As, Sb, Bi) with Et₃N leaving unreacted free benzothiazoline ligand in the solution. These observations show that benzothiazoline ring does not open up during reaction.

These addition compounds are white or yellow solid powders, but a few of these are sticky solids (Table I). These are insoluble in common organic solvents like benzene, carbon tetrachloride, chloroform, light petroleum, hexane, diethyl ether and nitrobenzene but dissolve in acetonitrile and alcohols. On heating, these adducts tend to decompose with charring.

The IR spectra of the ligands as well as their adducts with AsCl₃, SbCl₃ and BiCl₃ in nujol, recorded on a Perkin-Elmer 337 instrument do not exhibit any band due to  νS–H ¹² and  νC=N in the region 2600-2300 cm⁻¹ and 1630-1600 cm⁻¹ respectively indicating that the benzothiazoline ring remains intact in the adducts also.

The band due to  νN–H present in the region 3370-3330 cm⁻¹ in benzothiazolines is shifted in the adducts and appears as a weak broad band at ~3150 cm⁻¹. A band at ~1650 cm⁻¹ is also observed in the adducts; this may probably be due to the shifting of  δ(N–H) bands present in the free benzothiazoline around 1700 cm⁻¹. The shifting of N–H absorptions towards lower wave number indicates that the coordination in these adducts takes place through nitrogen.

Due to the insoluble nature of these addition compounds in common organic solvents (CDCl₃, CCl₄) the ¹H NMR spectra could not be recorded.

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References

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