NEW PYRIDINE-3-SULFONATO TIN (IV), ANTIMONY (III) AND (V) HALO ADDUCTS AND COMPLEXES: SYNTHESIS AND INFRARED STUDY

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Abstract: Six new tin (IV), antimony (III) and antimony (V) adducts and complexes have been synthesized. Discrete structures were suggested on the basis of infrared data. Within the structures, the anion behaves as a bidentate, monochelating and monodentate, monodentate and tri O-chelating ligand. The environments around metallic centres are octahedral. Considering preamble of extra hydrogen bonds in compounds containing water molecules and/or OH groups, supramolecular architectures may be given rise.

Keywords: bidentate, monochelating and monodentate, monodentate and tri O-chelating ligand anion, discrete structures, octahedral tin and antimony centres, supramolecular architectures

1. INTRODUCTION

Organic and inorganic oxyanions behaving as ligand coordinated to various metallic centres are well known. Pyridine-3-sulfonate anion has not been studied as anion in the coordinating ability of oxyanions summarized by Hathaway [1]. Several worldwide groups among them our own, focused in this field through isolation and characterization of numerous compounds with oxyanions as ligands [2-6]. In the work reported herein, we have initiated the study of the interactions between PySO₃NMe₄ and SnCl₂2H₂O, SnBr₂, SbCl₃ or SbCl₅: this enabled to isolate and characterize by infrared six new pyridine-3-sulfonate adducts and complexes.

2. EXPERIMENTAL SETUP

Neutralization of a tetramethylammonium hydroxide (Me₄NOH) solution (20 wt. % in H₂O) with pyridine-3-sulfonic acid (PySO₃H) allowed to obtain tetramethyl ammonium pyridine-3-sulfonate, Me₄NPySO₃ (L) as a white powder collected after a forced water evaporation at 60°C. The analytical data [% calculated (% found): %C = 46.53 (46.45), %H = 6.94 (6.91), % N = 12.06 (11.98), % S = 13.80 (13.84)] have allowed to suggest the formula for L. In ethanol solutions of L were added SnCl₂2H₂O, SnBr₂, SbCl₃ and SbCl₅ in 1:1 (1 - 3) and 2:1 (4 - 6) ratio, respectively. A white precipitate is quickly obtained then stirred around 2 hours and filtered off.

The analytical data reported below have allowed to suggest the formulae of the complexes and adducts (Table 1). Chemicals were purchased from Aldrich Company (Germany) and used without any further purification. The elemental analyses are performed from the CNRS “Service Central d’Analyses” – Vernaison-France. IR spectra

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were recorded at the University of Padova (Italy) using a PE 580 spectrometer with CsI pellets, the sample being as Nujol mulls. IR abbreviations: vs (very strong), s (strong), m (medium).

Table 1. Results of the elemental analyses of compounds 1 – 6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Suggested formulae</th>
<th>Chemical composition [% mass]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>1</td>
<td>SbCl$_5$Me$_4$NPySO$_3$</td>
<td>20.34</td>
<td>3.04</td>
</tr>
<tr>
<td>2</td>
<td>SbCl$_3$Me$_4$NPySO$_3$</td>
<td>23.48</td>
<td>3.50</td>
</tr>
<tr>
<td>3</td>
<td>SnCl$_4$Me$_4$NPySO$_3$</td>
<td>21.93</td>
<td>3.27</td>
</tr>
<tr>
<td>4</td>
<td>SnBr$_5$Me$_4$NPySO$_3$ EtOH$_2$O</td>
<td>20.27</td>
<td>3.23</td>
</tr>
<tr>
<td>5</td>
<td>2SnCl$_5$OH Me$_4$NPySO$_3$ 2H$_2$O Me$_4$NCl</td>
<td>15.40</td>
<td>4.14</td>
</tr>
<tr>
<td>6</td>
<td>2SnCl$_2$(OH)$_2$Me$_4$NPySO$_3$ Me$_4$NCl</td>
<td>19.79</td>
<td>4.09</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

Let us consider the main IR data (in cm$^{-1}$) of the six studied adducts and complexes:

1: $\nu$Sb-Cl 330 (vs), $\nu$Sb-O or $\nu$Sb-N 245 (s);
2: $\nu$Sb-Cl 275 (s), $\nu$Sb-O or $\nu$Sb-N 240 (vs);
3: $\nu$Sn-Cl 325 (vs), $\nu$Sn-O or $\nu$Sn-N 250 (vs);
4: $\nu$Sn-Br 210 (vs), $\nu$Sn-O or $\nu$Sn-N 190 (vs);
5: $\nu$Sn-Cl 290 (vs), $\nu$Sn-O or $\nu$Sn-N 215 (m);
6: $\nu$Sn-Cl 295 (vs), $\nu$Sn-O or $\nu$Sn-N 235 (s).

While considering the complex-anion [PySO$_3$SbCl$_3$], within the suggested discrete structure of 1, Me$_4$NPySO$_3$ SbCl$_5$, reported on Figure 1, the pyridine-3-sulfonate ligand behaves as a N-donor (even we cannot exclude the O-coordination).

For 2, Me$_4$NPySO$_3$ SbCl$_5$, we have considered the complex-anion [PySO$_3$SbCl$_3$]. The suggested structure is discrete reported on Figure 2 with a tri O-chelating ligand. These monomers may interact through N-Sb dative bonds leading to an infinite chain.
While considering the tin compounds, an oxidation of tin occurs *in situ* during the synthesis process [7]. \( \nu_{\text{at}}(\text{SnCl}_4) \) appears in the IR spectrum of 3 as a very strong and sharp band (Eu type) indicating a *trans*-coordination according to Groups Theory. So, considering the anion \([\text{PySO}_3\text{SnCl}_4]^–\) an infinite chain, in which the pyridine-3-sulfonate anion behaves as a bridging bidentate O and N-donors (Figure 3), can be proposed.

![Figure 3. Proposed structure for the compound 3.](image1)

The water and ethanol molecules as well as the anion may be considered coordinated to \([\text{SnBr}_5]^–\) in compound 4. We arbitrary chosen the oxyanion coordinated to \([\text{SnBr}_5]^–\) leading to the discrete structure reported on Figure 4, the water and ethanol molecules being lattice or linked to the complex-anion through hydrogen bonds leading a supramolecular arrangement.

![Figure 4. Proposed structure for the compound 4.](image2)

For the complex-anion, \([\text{PySO}_3(\text{SnCl}_3\text{OH})_2\text{Cl}]^2–\) of 5, considering the water molecules coordinated, the suggested structure is discrete and contains two \(\text{SnCl}_3\text{OH} \cdot \text{H}_2\text{O}\) adducts [8] linked to \(O\) and \(N\) atoms rather than to two \(O\) atoms because of presumable strong steric effects (Figure 5).

![Figure 5. Proposed structure for the compound 5.](image3)

For \([\text{PySO}_3\text{SnCl}_2(\text{OH})_2\text{Cl}]^2–\) complex-anion, the suggested structures are discrete. In the first, a chloride and a pyridine-3-sulfonate anion bridge two \(\text{SnCl}_2(\text{OH})_2\) molecules (Figure 6a). The second structure is dimeric and...
centrosymmetric comprising two chlorides bridging two molecules of SnCl₂(OH)₂ and two pyridine-3-sulfonate anions which bridge the former bridged molecules (Figure 6b).

![Proposed structures for the compound 6.](image)

In all compounds, the anion can interact through N or O; it appears very difficult from the infrared data to choose between these two possible behaviours.

In all these structures, the tetramethyl ammonium ion interacts electrostatically with the complex-anion. Hydrogen bonds may be considered in OH and water containing structures leading to supramolecular arrangements.

4. CONCLUSIONS

Along this study, the suggested structures are discrete or of infinite chain. Pyridine-3-sulfonate anion behaves as a bridging bidentate, N-donor and tri O-chelating. The environments around the tin(IV) and Sb centres are both octahedral. The possible inter species hydrogen bonds may give rise to supramolecular architectures.

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REFERENCES


