

## Coordination in organotin chemistry. Evidence for penta-coordinated anions of $\text{RSnCl}_4^-$ and $\text{RSn}_2\text{Cl}_3^-$ type

It is known that organotin(IV) compounds may achieve penta- and hexacoordination<sup>1</sup>. Such coordination is present<sup>2</sup>, for example, in several adducts of  $\text{R}_{4-n}\text{SnX}_n$  compounds with monodentate ligands such as ammonia, pyridine etc.<sup>3</sup>. Recently, attention has been given to the organotin complex anions with ligands such as halogens or pseudo-halogens<sup>4-8</sup>. In these cases hexacoordination seems to be preferred for negatively charged complexes arising from  $\text{RSnX}_3$  and  $\text{R}_2\text{SnX}_2$  compounds, whereas five-coordination is encountered only for complexes from  $\text{R}_3\text{SnX}$  compounds<sup>9-10</sup>.

In a previous paper<sup>11</sup>, evidence for the formation of penta-coordinated organotin chloride anions,  $\text{RSnCl}_4^-$  and  $\text{R}_2\text{SnCl}_3^-$  (with  $\text{R} = \text{C}_4\text{H}_9$  and  $\text{C}_6\text{H}_5$ ), in acetonitrile was obtained from potentiometric titrations of  $\text{RSnCl}_3$  and  $\text{R}_2\text{SnCl}_2$  compounds with tetraethylammonium chloride: the formation of the same anions in acetone was confirmed by means of conductometric measurements.

We have now succeeded in preparing the solid compounds:  $[(\text{C}_6\text{H}_5)_4\text{As}] [\text{RSnCl}_4]$  (I) and  $[(\text{C}_6\text{H}_5)_4\text{As}] [\text{R}_2\text{SnCl}_3]$  (II), with  $\text{R} = \text{C}_2\text{H}_5$ ,  $\text{C}_4\text{H}_9$  or  $\text{C}_6\text{H}_5$ .

Addition to an aqueous solution of HCl (5–6 M) or HCl-NaCl (both 2.5–3 M) containing the  $\text{R}_{4-n}\text{SnCl}_n$  compound, of tetraphenylarsonium chloride in 1 to 1 ratio with the metallorganic salt, leads to immediate precipitation of a white solid.

Analyses are in agreement with those expected, and m.p.'s are as follows: (I),  $\text{R} = \text{C}_2\text{H}_5$ , 180–185°; (I),  $\text{R} = \text{n-C}_4\text{H}_9$ , 142–143°; (I),  $\text{R} = \text{C}_6\text{H}_5$ , 161–162°; (II),  $\text{R} = \text{C}_2\text{H}_5$ , 165–166°; (II),  $\text{R} = \text{n-C}_4\text{H}_9$ , 94–96°; (II),  $\text{R} = \text{C}_6\text{H}_5$ , 225–227°.

The same solids can be obtained by adding excess of tetraphenylarsonium chloride. Under the experimental conditions used, only 1:1 adducts are formed. The existence of these adducts indirectly supports the evidence previously reported<sup>11</sup> for the formation of pentacoordinated negatively charged complexes of the  $\text{RSnCl}_4^-$  and  $\text{R}_2\text{SnCl}_3^-$  type. Investigations in this area are continuing.

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