

Coordination in organotin chemistry. Evidence for penta-coordinated anions of RSnCl_4^- and $\text{RSn}_2\text{Cl}_3^-$ type

It is known that organotin(IV) compounds may achieve penta- and hexa-coordination¹. Such coordination is present², for example, in several adducts of $\text{R}_{4-n}\text{SnX}_n$ compounds with monodentate ligands such as ammonia, pyridine etc.³. Recently, attention has been given to the organotin complex anions with ligands such as halogens or pseudo-halogens⁴⁻⁸. In these cases hexacoordination seems to be preferred for negatively charged complexes arising from RSnX_3 and R_2SnX_2 compounds, whereas five-coordination is encountered only for complexes from R_3SnX compounds⁸⁻¹⁰.

In a previous paper¹¹, evidence for the formation of penta-coordinated organotin chloride anions, RSnCl_4^- and $\text{R}_2\text{SnCl}_3^-$ (with $\text{R} = \text{C}_4\text{H}_9$ and C_6H_5), in acetonitrile was obtained from potentiometric titrations of RSnCl_3 and R_2SnCl_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 $\text{R} = \text{C}_2\text{H}_5$, C_4H_9 or C_6H_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°; (II), $\text{R} = n\text{-C}_4\text{H}_9$, 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), $\text{R} = n\text{-C}_4\text{H}_9$, 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 reported¹¹ for the formation of pentacoordinated negatively charged complexes of the RSnCl_4^- and $\text{R}_2\text{SnCl}_3^-$ type. Investigations in this area are continuing.

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