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Preliminary communication

THE STRUCTURE OF BIS(TRIALKYLTIN) CARBONATES: EVIDENCE FOR TWO NON-EQUIVALENT TIN SITES

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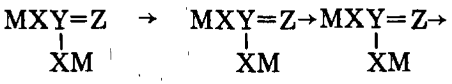
Summary

Bis(tributyltin) oxide or trimethyltin hydroxide react with carbon dioxide to afford the bis(trialkyltin) carbonates, $(R_3SnO)_2CO$; ^{119}Sn NMR (in the case of R = Bu) or ^{119m}Sn Mössbauer spectroscopy show that these compounds contain 4- and 5-coordinate tin atom sites.

Autoassociation of metallic derivatives, M_rL_s, may give rise to either coordination polymers or ring systems, the structure of which will depend on the relative number of metal acceptor (M) and ligand donor (L) sites. For example, a monomer, $(MX)_2Y{=}Z$, in which the metal has coordination n could associate to give a linear polymer containing equal amounts of the metal with coordination numbers n and $n + 1$ (eq. 1).

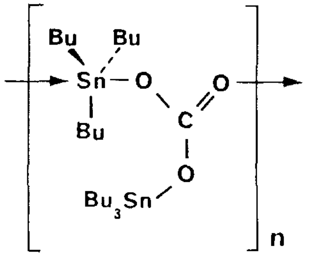


$$\mathrm{MX\underset{\underset{XM}{|}}{Y}{=}Z \rightarrow MX\underset{\underset{XM}{|}}{Y}{=}Z{\rightarrow}MX\underset{\underset{XM}{|}}{Y}{=}Z{\rightarrow}} \qquad (1)$$

Trialkyltin(IV) compounds are very susceptible to autoassociation [1], and compounds $(R_3SnX)_2Y{=}Z$ might be expected to form polymers in this way, containing both 4- and 5-coordinate tin. However, the potential for this does not appear to be recognised. The only evidence of which we are aware relates to the ^{31}P NMR spectrum of bis(tributyltin) methylphosphonate, $(Bu_3SnO)_2P(O)Me$, which shows that the phosphorus is coupled to two non-equivalent tin atoms [2].

We report here a study of the structure of the bis(trialkyltin) carbonates, which illustrates unequivocally the phenomenon illustrated in eq. 1.

Bis(tributyltin) oxide, in toluene solution shows a single ^{119}Sn NMR signal at approximately 82 ppm (with respect to Me_4Sn), characteristic of a 4-coordinate tin atom [3]. This solution reacts [4] rapidly with carbon dioxide to give bis(tributyltin) carbonate, a viscous oil, the ^{119}Sn NMR spectrum (Fig. 1) of which shows two broad signals of equal intensity, δ(^{119}Sn) 82 and −66.7 ppm, indicative of 4-coordinate and 5-coordinate tin atoms in the polymer I. In contrast, tributyltin methoxide, in toluene (δ(^{119}Sn) 94.5 ppm) reacts [4] with carbon dioxide to give methyl tributyltin carbonate (II), showing only a single NMR signal (δ(^{119}Sn) −27 ppm) (see Fig. 2).



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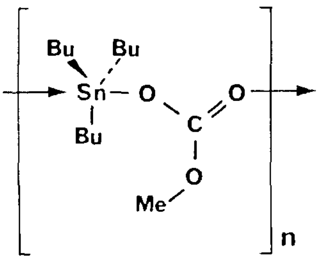

II

The broadness of the signals shown in Fig. 1, compared to those obtained from the same solution at −50°C, indicates that the tributyltin groups undergo exchange between 4- and 5-coordination at a rate commensurate with the NMR time scale. If pyridine is added to the solution of I only a single ^{119}Sn NMR resonance is now observed, with δ(^{119}Sn) −25 to −28 ppm, depending on the pyridine concentration. This indicates that the bis(pyridine) adduct, $(C_5H_5NSnBu_3O)_2CO$, is formed, in which both tin atoms are now equivalently 5-coordinate. It is of interest to note that, upon the addition of pyridine to a solution of bis(tributyltin) oxide, no change in the ^{119}Sn chemical shift occurs, indicating that the pyridine adduct is not produced.

Similar evidence for the existence of non-equivalent tin environments came from the ^{119m}Sn Mössbauer spectra. Bis(tributyltin) carbonate (I) shows the pre-

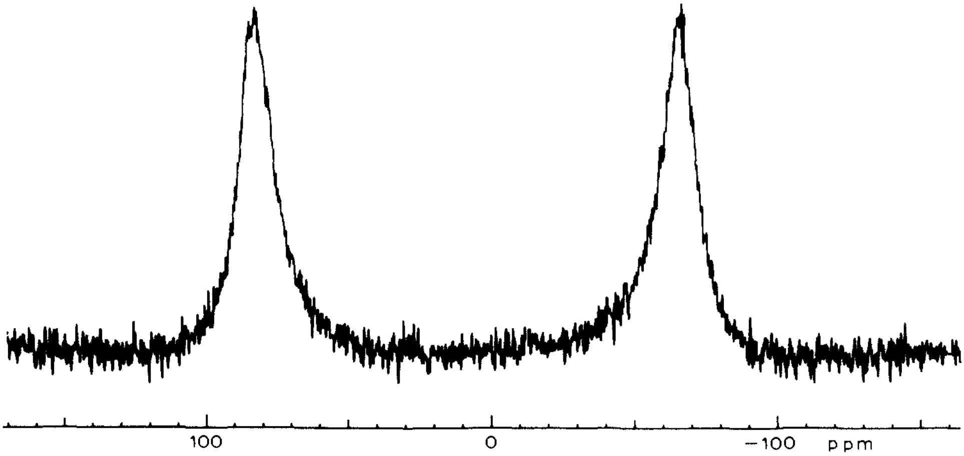

Fig. 1. A ^{119}Sn NMR spectrum of a 50% m/m solution of $(Bu_3SnO)_2CO$ in toluene, at 30°C.

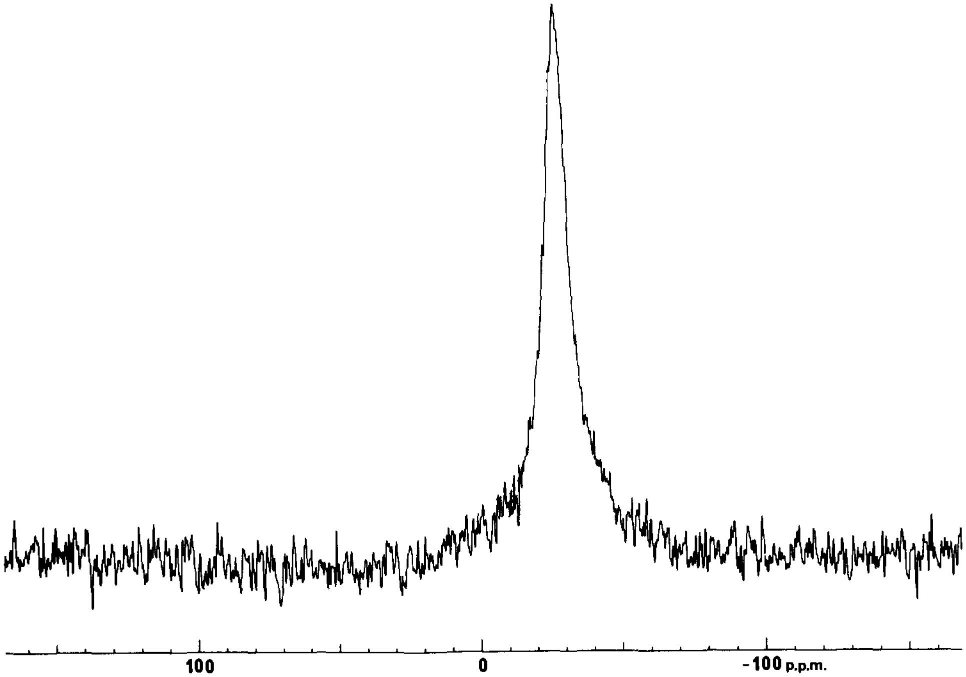

Fig. 2. A ^{119}Sn NMR spectrum of a 50% m/m solution of Bu$_3$SnOC(O)OMe in toluene, at 30°C.

sence of two overlapping doublets, with parameters, δ 1.43, ΔE_Q 3.79 and δ 1.38, ΔE_Q 2.70 mm s^{-1} (at −193°C relative to BaSnO$_3$), which are in the range expected [1] for *trans*-trigonal bipyramidal R$_3$SnX$_2$ and tetrahedral R$_3$SnX configurations respectively; whereas methyl tributyltin carbonate only shows the presence of a trigonal bipyramidal tin site, δ 1.49, ΔE_Q 3.72 mm s^{-1}.

The ^{119m}Sn Mössbauer spectrum of bis(trimethyltin) carbonate, a white solid prepared from the reaction [5] of trimethyltin hydroxide with carbon dioxide in toluene, was resolvable into two overlapping doublets, δ 1.26, ΔE_Q 2.66; δ 1.27, ΔE_Q 3.57 mm s^{-1}, indicating a structure analogous to I, at −193°C. In contrast, however, the ^{119}Sn NMR spectrum of a solution (~ 10% m/m) of bis(trimethyltin) carbonate in toluene, at 30°C, showed only one broad resonance at 44.6 ppm with respect to Me$_4$Sn, suggesting an exchange between 4- and 5-coordinate tin sites at a rate faster than that occurring for bis(tributyltin) carbonate. A confirmatory low temperature ^{119}Sn NMR study on this compound was precluded by its insolubility at such temperatures.

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