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Solid State ^{119}Sn NMR Study of Organotin Carboxylates and Thiophosphates

KIERAN C. MOLLOY

School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.

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In the absence of suitable quality crystals for X-ray diffraction, Mössbauer spectroscopy is now commonly the technique of choice for studying the solid state structures of organotin compounds. However, in cases where lattice association occurs, a common phenomenon in this area of chemistry, Mössbauer spectroscopy is largely unable to monitor the changes which accrue upon dissolution of the solid, since frozen solution studies are notoriously ambiguous. The advent of cross-polarisation magic angle spinning (CP-MAS) solid state NMR now enables the widely available, tin-specific ^{119}Sn magnetic resonance technique to be extended and so yield directly comparable data on both solution and solid phase structures. Triorganotin carboxylates [1] and thiophosphates [2] have been extensively studied in recent years, and provide a series of model systems for assessing the utility of CP-MAS as a solid state structural probe. We now report our preliminary findings in this area.

Triorganotin esters of potentially bidentate acid ligands can adopt tetrahedral or trigonal bipyramidal geometries depending on the denticity of the ligand (Fig. 1). In the latter case, both monomeric or polymeric structures are commonly encountered. For monomeric systems, structural integrity should be maintained upon dissolution, and characterised in both solid and solution state ^{119}Sn NMR experiments by a largely invariant upfield chemical shift. This is exemplified by $Ph_3SnCl_2^-$, where δ ^{119}Sn for the two phases is −236 and −251 ppm (Table I).

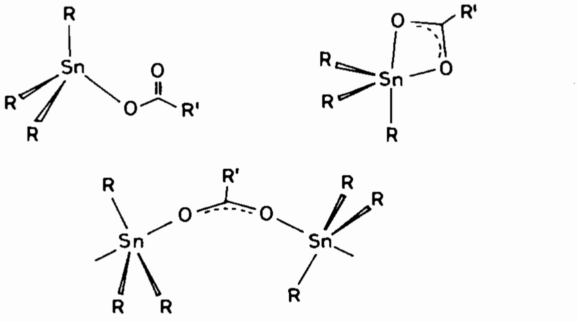

Fig. 1. Structural variations for four- and five-coordinate triorganotin compounds.

TABLE I. ^{119}Sn NMR Chemical Shifts (ppm)[a]

	Solid	Solution
$[Me_4N^+][Ph_3SnCl_2^-]$	−236	−251[b]
$Ph_3SnS_2P(OEt)_2$	−53	−82[c,d]
$Ph_3SnO_2CC_6H_3Cl_2$-2,6[e]	−73	−93[f]
Ph_3SnO_2CMe	−242	−121[f]
$Ph_3SnO_2CC_6H_4NO_2$-2[g]	−238	−92[f]

[a]Relative to Me_4Sn. [b]CD_3CN solution. [c]CD_2Cl_2 solution. [d] $^2J(^{119}Sn–S–^{31}P)$ = 43 Hz. Not observed in the solid state due to line broadening. [e]Lattice contains 0.5 Me_2CO. [f]CCl_4 solution. [g]Lattice contains 0.25 C_6H_{12}.

Data of this nature should also be typical of the *cis*-R_3SnL_2 geometry which arises with chelating bidentate ligands. The origin of the 15 ppm difference in measured shift values is currently unknown, but similar effects have been noted by others [3] and are insufficient to imply a gross structural change.

Tetrahedral systems should also exhibit a phase independent chemical shift, but now at a lower field. $Ph_3SnS_2P(OEt)_2$ characterises this grouping [4] and we assign a similar structure to $Ph_3SnO_2CC_6H_3Cl_2$-2,6 [5], which is yet to be examined crystallographically (Table I).

Compounds which undergo auto-association in the solid to yield coordination polymers should be identifiable by an upfield chemical shift in the solid, and a lower field, concentration dependent resonance in solution consistent with disruption of the polymer chain and a change of coordination number at tin from five to four. Both Ph_3SnO_2CMe [6] and $Ph_3SnO_2CC_6H_4NO_2$-2 [5, 7]* fulfill these structural criteria, and the data given in Table I can be taken as typical of this phenomena.

These results, along with others now being published [3, 8] provide a series of reference data which can be used in the development of this important structural tool.

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*A four coordination isomer of this compound is also known [5].

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