

## ORGANOSTANNATE(IV) COMPLEXES

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### A. INTRODUCTION

Organotin compounds containing at least one electronegative substituent are well known as Lewis acids [1,2], and are classified as hard in Pearson's HSAB scheme [3]. As such, they readily form coordination compounds, often with ligands containing atoms of the first row of the Periodic Table, such as nitrogen or oxygen [1,2]. One class of coordination compound formed by organotins are the organostannate(IV) complexes. Knowledge of these complexes has been growing steadily, particularly in recent years, and a review of their chemistry is therefore timely.

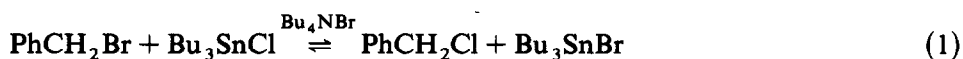
### B. ORGANOSTANNATE(IV) COMPLEXES

Organostannate(IV) complexes are ionic compounds comprising complex organotin anions which contain tin in the 4+ oxidation state, together with cations such as  $\text{Cs}^+$ ,  $\text{R}_4\text{N}^+$  and  $\text{R}_4\text{P}^+$ , i.e. ones which are generally fairly large. The anions are usually formed by reaction of organotin(IV) halides or pseudohalides with further halide or pseudohalide ions, and they may contain tin in either five- or six-coordination. Formation of these complex

anions may be regarded as involving the utilisation of vacant *d*-orbitals on the tin atom to give hybrid orbitals which are  $sp^3d$  or  $sp^3d^2$  for five- or six-coordination respectively [2,4–6].

Purely inorganic stannates are generally hexacoordinate [7]. They have been recognised for a long time in chemistry. For example, Mellor, in his classic treatise [7], described the complexes  $(\text{NH}_4^+)_2\text{SnCl}_6^{2-}$  and  $(\text{NH}_4^+)_2\text{SnBr}_6^{2-}$ . The introduction of organic groups at the tin atom reduces the Lewis acidity of the tin [1,8], and it is for this reason that it is possible to isolate pentacoordinate organostannate(IV) complexes. So far, there have been no reports of heptacoordinate organostannates though for neutral organotin complexes, coordination number seven is well established in certain cases [9].

The earliest authentic reference to organostannate(IV) complexes appears to be that of Pfeiffer in 1910 [10], in which fourteen complexes were reported, and identified by elemental analysis. Subsequently, in addition to descriptions of the synthesis of new organostannate(IV) complexes, there have been reports of the occurrence of these complexes as intermediates in certain reactions. For example, in the halogen-exchange reaction illustrated, the tetrabutylammonium bromide catalyst was held to act by formation of the complex  $\text{Bu}_4\text{N}^+[\text{Bu}_3\text{SnClBr}]^-$  [11]



This proposed complex has recently been isolated, and its structure established using Mössbauer spectroscopy [12]. Similarly, other organostannate(IV) complexes have been proposed as intermediates, notably in the direct synthesis of organotin compounds from elemental tin in the presence of certain nitrogen-containing catalysts [13].

In general for halogen-containing organostannate(IV) complexes the size of the halogens clustered around the tin atom needs to be matched by the size of the cation, an observation originally made by Devaud [14], and subsequently confirmed by Hobbs and Smith [15]. Thus, organofluorostannates can be precipitated by potassium or ammonium cations, e.g.  $\text{K}_2^+[\text{Me}_2\text{SnF}_4]^{2-}$  [16–18] and  $(\text{NH}_4^+)_2[\text{Me}_2\text{SnF}_4]^{2-}$  [19], while organochloro- and organobromostannates require larger cations, such as caesium or quaternary cations of Group VB elements. There appears to be only one report of potassium acting as a cation for an organohalogenostannate which does not contain fluorine, the salt  $\text{K}_2^+[\text{EtSnCl}_5]^{2-}$ , which Druce [20] prepared by reaction of the acid  $\text{H}_2\text{EtSnCl}_5$  with potassium chloride in dilute hydrochloric acid. Hobbs and Smith [15] prepared a mixed fluoro/chloro organostannate, potassium monobutyltetrafluorochlorostannate, by reacting  $(\text{Et}_4\text{N}^+)_2[\text{BuSnCl}_5]^{2-}$  with potassium fluoride in acetone.

Smaller cations have generally been found to favour organostannates with hexacoordinate tin. For example, there have been no reports of potassium or caesium acting as cation for pentacoordinate organostannates. The salt  $K_2^+[Me_2SnF_4]^{2-}$ , mentioned previously, has been produced a number of times [16–18], yet there has been no report of the pentacoordinate complex  $K^+[Me_2SnF_3]^-$ . The dimethyltrifluorostannate ion itself is known, having been produced in conjunction with the slightly larger ammonium ion [19]. Only two caesium salts of this kind have been reported, both hexacoordinate, the dimethyltetrachlorostannate [16–18] and the dimethyltetrabromostannate [16,18,21], and again neither of the related pentacoordinate ions has been reported.

There have been few reports of iodine-containing organostannates and they all involve the use of relatively large cations. Seyferth [22] prepared the complex  $(Me_3NH^+)_2[MeSnI_5]^{2-}$ , while Das et al. [23] prepared a further five complexes, as follows:  $(Et_4N^+)_2[MeSnI_5]^{2-}$ ,  $Bu_4N^+[Me_3SnI_2]^-$ ,  $(Bu_4N^+)_2[Me_2SnI_4]^{2-}$ ,  $(Bu_4N^+)_2[MeSnCl_3I_2]^{2-}$  and  $(Bu_4N^+)_2[MeSnBr_3I_2]^{2-}$ . Hobbs and Smith [15] attempted to prepare a large number of mono-organoiodostannates of the kind  $M_2[RSnI_5]$  and  $M[RSnI_4]$  ( $R = Bu$  and  $Ph$ ), using very large cations such as benzyltriphenylphosphonium and methyltriphenylarsonium, but were consistently unable to do so [15].

Organostannate(IV) complexes have been prepared containing mono-, di- and tri-organotin moieties, with examples of 5- and 6-coordination for all three. The hexacoordinate triphenyltrichlorostannate ion was among the first such complexes to be reported [10], though recently Nicholson et al. [12] have cast doubt on the accuracy of this observation. Also in recent years, Barbieri and Stocco [24] have reported the complex bis(tetramethylammonium)trimethyltrichlorostannate, and assigned its hexacoordinate anion the structure illustrated in Fig. 1 on the basis of the quadrupole splitting of its Mössbauer spectrum.

In general, it is more usual to find organostannates derived from tri-organotin compounds having pentacoordination, as is the case for their neutral counterparts [1]. Conversely, complexes derived from mono-organotins generally form hexacoordinate anions, though there are a few reports of pentacoordinate mono-organostannates, such as  $Et_4N^+[BuSnCl_4]^-$  [25],

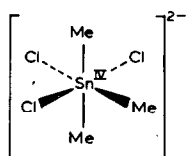
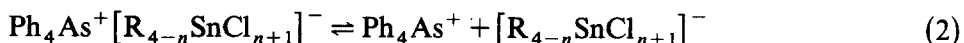


Fig. 1. The structure of  $[Me_3SnCl_3]^{2-}$  from Mössbauer spectroscopy [24].

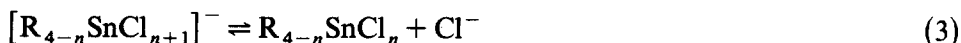
$\text{Ph}_4\text{As}^+[\text{EtSnCl}_4]^-$  [16,26] and  $\text{Ph}_4\text{As}^+[\text{MeSnCl}_4]^-$  [27].

A series of singly-charged mono- and di-organostannates has been made by Tagliavini and Zanella [26,28], who studied their stability. Molecular weight and conductance measurements were used to demonstrate that these complexes were almost completely dissociated in acetone



$\text{R} = \text{Et}, \text{Bu}, \text{Ph}; n = 2 \text{ or } 3$

At low concentrations, ( $< 4 \times 10^{-4} \text{ M}$ ), it became possible to detect a second equilibrium, that between the chloride ion and the organotin halide



There was no evidence of chloride bridging, even at higher concentrations, to give 6-coordinate tin atoms. The order of stability was found to be:  $\text{PhSnCl}_4^-$  (5400)  $>$   $\text{EtSnCl}_4^-$  (246)  $>$   $\text{BuSnCl}_4^-$  (140)  $>$   $\text{Ph}_2\text{SnCl}_3^-$  (68)  $>$   $\text{Me}_2\text{SnCl}_3^-$  (3.3)  $>$   $\text{Et}_2\text{SnCl}_3^-$  (1.2)  $>$   $\text{Pr}_2\text{SnCl}_3^-$  (1.0). The stability thus increases as the number of organic groups decreases and this is in line with the changes in Lewis acid strength of the parent organotin compounds. The decrease in stability in the order  $\text{Ph} > \text{Me} > \text{Et}$  etc. is associated with decreasing electronegativities of the organic groups, rather than with steric requirements [28].

Organostannate(IV) complexes have been synthesised containing a variety of pseudohalogen species, as well as true halogens. For example, there are reports of organostannates containing azide [29], cyanide [16,30], isothiocyanate [18,29,31], thiocyanate [32] and acetate [16]. There is also a series of reports of organostannates containing bidentate ligands with sulphur-donor

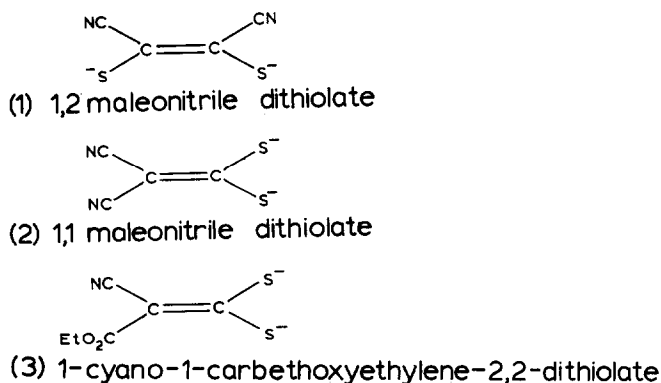


Fig. 2. Bidentate S-donor ligands.

atoms [33–35]. The ligands used were 1,2-maleonitrile dithiolate (mnt), 1,1-maleonitrile dithiolate (1,1 mnt) and 1-cyano-1-carbethoxyethylene-2,2-dithiolate (CED), all of which are illustrated in Fig. 2.

These complexes were prepared in ethanol from the sodium salts of the thiolato species, and the relevant organotin chlorides, in the presence of a quaternary salt of a Group VB element, such as  $\text{Me}_4\text{N}^+$  [34],  $\text{Et}_4\text{N}^+$  [34,35] or  $\text{Ph}_4\text{As}^+$  [33] chlorides. Mössbauer spectra have been recorded, and structures assigned [33,34] on the basis of them. The diorganotin complexes, such as  $\text{Ph}_4\text{As}^+[\text{Me}_2\text{SnCl} \cdot \text{mnt}]^-$  were assigned pentacoordinate structures; that is, the dithiolato unit was found to be bidentate [33]. The organic groups were probably *cis* to each other, as they have been found to be in hexacoordinate complexes containing two dithiolato ligands, e.g. in  $(\text{Et}_4\text{N}^+)_2[\text{Me}_2\text{Sn}(\text{mnt})_2]^{2-}$  [33].

So far, the only cations mentioned have been the heavier alkali metals and quaternary cations of Group VB. Some more interesting cations are described in the organostannate literature. For example, Ferguson et al. [36] discovered that mono- and di-organotin halides undergo disproportionation on treatment with 2,2',2''-terpyridine in light petroleum. The products, which precipitated immediately, consisted of  $(\text{R}_n\text{SnX}_{5-n} \cdot \text{terpy})^+$  cations, with  $[\text{R}_n\text{SnX}_{5-n}]^-$  anions, where  $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{R} = \text{Me}, \text{Bu}, \text{Ph}$  and  $n = 1$  or  $2$ . One exception was the reaction of monobutyltin trichloride, which gave  $(\text{BuSnCl}_2 \cdot \text{terpy})^+[\text{BuSnCl}_5]^{2-}$  as the product. Organotin compounds containing iodine did not give rise to organostannate(IV) complexes in this reaction, but to iodides of the equivalent complex cation, e.g.  $(\text{MeSnI}_2 \cdot \text{terpy})^+ \cdot \text{I}^-$  instead [36].

Einstein and Penfold [37] carried out an X-ray study on the dimethylchlorotin terpyridyl dimethyltrichlorostannate salt, and were able to assign structures to both the anion and the cation on the basis of the results obtained. The anion will be discussed later, in detail. The cation was found to contain hexacoordinate tin, the 2,2',2''-terpyridyl ligand being tridentate and occupying the equatorial plane together with the chlorine atom, while the two methyl groups occupied the axial sites. Debye et al. [38] investigated the structure of the doubly charged anion  $[\text{BuSnCl}_5]^{2-}$  produced by the action of 2,2',2''-terpyridine on monobutyltin trichloride, and assigned it an octahedral structure on the basis of its Mössbauer spectrum.

There have been other reports of organostannates having complex organotin cations. For example, hexamethylphosphoramide (HMPT) was found to react with trimethyltin bromide in a reaction analogous to that of organotin halide with 2,2',2''-terpyridine. The product was the salt  $[\text{Me}_3\text{Sn}(\text{HMPT})_2]^+[\text{Me}_3\text{SnBr}_2]^-$  [39], and similar complexes have been found to arise as the products of direct synthesis of organotins from elemental tin in which HMPT was used as catalyst [41–43]. Seyferth and Grim [44]

prepared salts in which the cations were complexes of triphenylphosphine methylene with di- or tri-methyltin moieties, i.e.  $[\text{Ph}_3\text{PCH}_2\text{Sn}(\text{Me})_2\text{-CH}_2\text{PPh}_3]^{2+}$  and  $[\text{Ph}_3\text{PCH}_2\text{SnMe}_3]^+$  respectively [44].

Vergamini et al. [45] found that an organostannate(IV) complex was one of the products of the action of tris-trimethyltin sulphide on cyclopentadienylmolybdenum tricarbonyl chloride in 1,2-dimethoxyethane. The anion proved to be  $[\text{Me}_3\text{SnCl}_2]^-$ , reported many times elsewhere [16,17,46,47] while the cation was  $[\text{Mo}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+$ , a rare example of a molybdenum cluster compound. The structure of both the anion and the cation were determined by X-ray diffraction [45], and the results for the anion are discussed later.

### C. STRUCTURAL STUDIES OF ORGANOSTANNATE(IV) COMPLEXES

Four physical techniques have been used in the determination of the structures of organostannate(IV) complexes; namely, far IR spectroscopy, proton magnetic resonance spectroscopy (PMR),  $^{119\text{m}}\text{Sn}$  Mössbauer spectroscopy and X-ray crystallography.

Interest in the technique of  $^{119\text{m}}\text{Sn}$  Mössbauer spectroscopy has led to developments in organostannate chemistry, since a large number of organostannate(IV) complexes have been prepared as part of programmes aimed at increasing understanding of the effects of coordination and ligand type on the resulting Mössbauer spectrum. As a result of this interest in correlating Mössbauer data with the chemical environment of the tin atom, the published catalogues of Mössbauer parameters [46–48] include information for such complexes, and it is possible to monitor the growth of interest in these complexes by comparing these three lists.

The technique of Mössbauer spectroscopy applied to tin compounds was reviewed by Zuckerman in 1970 [48] and by Parish in 1972 [49] and the reader who is unfamiliar with this technique is advised to consult these reviews.

The two parameters which characterise the Mössbauer spectrum are the isomer shift,  $\delta$ , and the quadrupole splitting,  $\Delta E_q$ , both of which are measured in  $\text{mm sec}^{-1}$ . It is the latter parameter which is of particular interest in assigning the structure of organostannate(IV) anions, being affected as it is by the electric field gradient at the tin nucleus [48,49]. The effect of ligands on  $\Delta E_q$  has been discussed in terms of a point-charge model, and although the underlying assumptions have been described as "naive" by Harrison et al. [50], the model has proved to be extremely effective in determining structures, particularly in the absence of unequivocal X-ray data.

The point-charge model [51,52] predicts that, for a series of octahedral

complexes  $\text{RSnX}_5$ , *cis*- $\text{R}_2\text{SnX}_4$  and *trans*- $\text{R}_2\text{SnX}_4$ , the electric field gradients will be controlled by the geometrical arrangement of the bonds only, and will be relatively insensitive to the nature of the group X. Moreover this model predicts  $\Delta E_q(\text{trans}) = 2\Delta E_q(\text{cis})$ , where  $\Delta E_q(\text{trans}) = 4 \text{ mm sec}^{-1}$ . Thus, the anion  $[\text{Ph}_2\text{SnCl}_4]^{2-}$  has been assigned a *trans* octahedral structure in a number of complexes on the basis of experimental values of  $\Delta E_q$  close to  $4 \text{ mm sec}^{-1}$  [12,16,51].

Some of the earliest structural assignments were made using far IR spectroscopy. For example, Wilkins and Haendler were able to assign the salt  $\text{NH}_4^+ [\text{Me}_2\text{SnF}_3]^-$  a trigonal bipyramidal structure having axial methyl groups and equatorial fluorines on the basis of the far IR spectrum [19]. This was a surprising result, contrasting as it did with the well-established generalisation of Muetterties et al. [53,54] that the most electronegative groups tend to occupy the axial positions in trigonal bipyramidal structures. Similarly, a far IR study was made of the dimethylchlorostannate(IV) ions [21], but the authors were not able to assign a structure to the  $[\text{Me}_2\text{SnCl}_3]^-$  ion on the basis of the results obtained. By contrast they were able to establish that the related ion,  $[\text{Me}_2\text{SnCl}_4]^{2-}$ , had octahedral geometry, with *trans* axial methyl groups and equatorial chlorine atoms. Subsequently, the  $[\text{Me}_2\text{SnCl}_3]^-$  ion has been studied by X-ray diffraction, both as the  $(\text{Me}_2\text{SnCl}\text{-terpy})^+$  salt [37] and as the quinolinium salt [55]. In both complexes, the dimethyltrichlorostannate ion was found to have trigonal bipyramidal geometry with equatorial methyl groups, as illustrated in Fig. 3. The axial tin–chlorine bonds were found to be longer than the equatorial one. In addition for  $\text{QH}^+[\text{Me}_2\text{SnCl}_3]^-$ , there was some evidence of hexacoordination at the tin atoms via chloride bridges, the anions being associated as dimers with a fourth tin–chlorine distance of 348.6 pm [55]. The widening of the bond angle between the two methyl groups was assumed to arise from this interaction [55]. Muetterties' generalisation [53,54] about the position of the most electronegative substituents was thus found to hold for this anion.

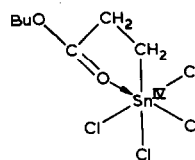
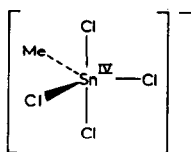
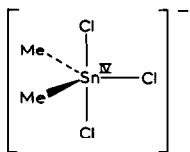


Fig. 3. The structure of dimethyltrichlorostannate(IV) as determined by X-ray diffraction.

Fig. 4. The monomethyltetrachlorostannate(IV) ion [27].

Fig. 5. Proposed structure of the anion in  $(\text{Me}_4\text{N}^+)(\text{BuO}\cdot\text{CO}\cdot\text{CH}_2\text{CH}_2\text{SnCl}_4)^-$  [15].

Das et al. [23] carried out a far IR study on a large number of organostannate(IV) complexes with tetraethyl- and tetrabutylammonium cations, and they concluded that, in general, ions of the type  $[\text{Me}_2\text{SnX}_3]^-$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{Cl}/\text{Br}$  mixtures) had trigonal bipyramidal geometry with equatorial organic groups.

Only one pentacoordinate mono-organostannate(IV) anion appears to have had its structure unambiguously assigned; the  $[\text{MeSnCl}_4]^-$  ion in tetraphenylarsonium monomethyltetrachlorostannate(IV) [27,40]. As expected the solitary organic group occupied an equatorial site, as illustrated in Fig. 4.

Hobbs and Smith [15] have reported a singly charged hexacoordinate monoorganostannate(IV) complex, the sixth coordination site being occupied by a carbonyl oxygen atom of the organic group. They assigned it the structure illustrated in Fig. 5 on the basis of its Mössbauer spectrum [15].

Triorganodihalogenostannate(IV) complexes have generally been assigned trigonal bipyramidal structures with equatorial organic groups and axial halogens. For example, the ion  $[\text{Ph}_3\text{SnCl}_2]^-$  has been shown to have this structure by PMR [56], by far IR spectroscopy [57,58] and by X-ray diffraction of the salt  $\text{Me}_4\text{N}^+[\text{Ph}_3\text{SnCl}_2]^-$  [59]. Das et al. [23] assigned analogous structures to all their  $[\text{Me}_3\text{SnX}_2]^-$  ions ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) on the basis of their far IR spectra, while Harrison et al. [60] showed by X-ray diffraction that the anions of  $[\text{Ph}_3\text{As} \cdot \text{CH}_2\text{CO} \cdot \text{Ph}]^+[\text{Ph}_3\text{SnCl}_2]^-$  and  $[\text{Ph}_3\text{P} \cdot \text{CH}_2\text{Ph}]^+[\text{Bu}_2\text{SnCl}_2]^-$  have this basic structure. The detailed results for these anions are shown in Fig. 6 [60].

A dissimilarity in the axial tin–chlorine bond lengths, as observed for the tributylchlorostannate ion [60], was found by Vergamini et al. for the trimethyldichlorostannate ion in  $[\text{Mo}_3(\text{h}^5\text{-C}_5\text{H}_5)_3 \cdot \text{S}_4]^+[\text{Me}_3\text{SnCl}_2]^-$  [45]. In this case, the tin–chlorine bonds were 257.2 and 269.6 pm respectively, the

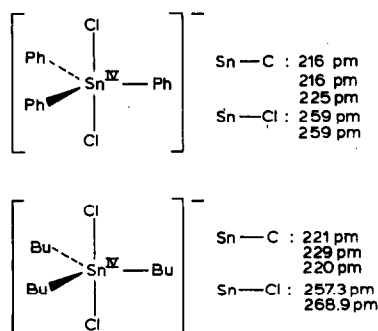


Fig. 6. Structures of triorganostannate(IV) complexes [60].



latter being unusually long for such a bond [45]. Using far IR spectroscopy [23], the ion  $[\text{MeSnCl}_4\text{I}]^-$  was assigned an octahedral structure in which the iodine atom occupied a site *trans* to the methyl group. Studies of diorgano-

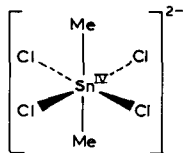


Fig. 7. The dimethyltetrachlorostannate(IV) ion [61].

tetrahalogenostannate(IV) complexes by far IR spectroscopy [21,23], Mössbauer spectroscopy [51] and X-ray diffraction [61] have all shown them to have octahedral geometry about the tin atom, with *trans* organic groups, and where all the halogens are the same, approximately  $D_{4h}$  symmetry [61]. The detailed structure of the anion in bis(pyridinium)dimethyltetrachlorostannate originally reported by Beattie and McQuillan [62], was found by X-ray diffraction to be as illustrated in Fig. 7 [61].

Finally there has been only one structural assignment of a triorganotrihalogenostannate ion, the  $[\text{Me}_3\text{SnCl}_3]^{2-}$  species, which was assigned the structure illustrated in Fig. 1 on the basis of the Mössbauer spectrum of  $(\text{Me}_4\text{N}^+)_2[\text{Me}_3\text{SnCl}_3]^{2-}$ . So far, there has been no X-ray diffraction study carried out to confirm such a structure unequivocally.

#### D. ORGANOSTANNATE(IV) COMPLEXES AS LEWIS ACIDS

It is apparent that the formation of hexacoordinate organostannates from organotin compounds involves a two-step process, and that the reaction with the second halide or pseudohalide species depends on the Lewis acidity of the pentacoordinate intermediate as in



Cunningham et al. [25] have reported a series of complexes in which the Lewis acidity of pentacoordinate organostannates was utilised to synthesise hexacoordinate species containing neutral Lewis bases. Thus, they prepared complexes of the type  $\text{Et}_4\text{N}^+[\text{RSnCl}_4 \cdot \text{L}]^-$  ( $\text{R} = \text{Bu}, \text{Ph}$ ;  $\text{L} =$  monodentate ligand containing O, N or P donor atoms).

The hexacoordinate complexes were prepared in slightly different ways, according to the nature of the organic group [25]. For the butylstannates, the pentacoordinate complex  $\text{Et}_4\text{N}^+[\text{BuSnCl}_4]^-$  was dissolved in dichloromethane, and added to the particular Lewis base in dichloromethane. The adduct was then precipitated by adding petroleum spirit. For the phenylstannates, it was not possible to prepare the complex  $\text{Et}_4\text{N}^+[\text{PhSnCl}_4]^-$  in

non-donor solvents, because the ion undergoes a redistribution reaction



Thus, to prepare the monophenylstannate(IV) adducts, tetraethylammonium chloride was dissolved in dichloromethane, and added to a solution of phenyltin trichloride in dichloromethane, and the Lewis base was added promptly to the resulting mixture. These adducts were also precipitated by adding petroleum spirit [25].

The above redistribution proceeded rapidly in dichloromethane, but did not occur at all in methanol, acetonitrile or acetone, all of which are donor solvents [25]. Previously, molecular weight and conductivity measurements were made on solutions of  $\text{Ph}_4\text{As}^+[\text{PhSnCl}_4]^-$  in acetonitrile and acetone [26], and though unable to isolate adducts of the type  $\text{Et}_4\text{N}^+[\text{PhSnCl}_4 \cdot \text{L}]^-$  (L = methanol, acetonitrile or acetone), Cunningham et al. suggested that it was likely that weak coordination of these donor solvents to the sixth coordination site of the monophenyltetrachlorostannate ion was responsible for the stability of this ion in these solvents [25].

#### E. APPLICATIONS OF ORGANOSTANNATE(IV) COMPLEXES

So far, few applications have been found for organostannate(IV) complexes. Krzeminska [63] reported that the complex decyltriphenylphosphonium triphenylbromochlorostannate(IV) inhibited housefly and cockroach reproduction. There have been other claims in the patent literature [22,64] that organostannates show some biological effect, though often as bacterio- and fungistatics, i.e. arresters of growth, rather than as bacterio- and fungicides. There do not appear to be any commercially important biological uses for organostannates.

Two non-biological uses have been suggested, however; namely the use of organostannates as flame-retardant agents for wool [65], and as transesterification catalysts [66]. This latter use was suggested following the observation [67] that various organotin compounds catalyse the transesterification reaction between propyl acetate and methanol. Hobbs and Smith [66] tested a number of mono-organostannates in the similar transesterification between butyl propionate and methanol, and found them to possess some catalytic activity.

#### ACKNOWLEDGEMENTS

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## APPENDIX

## Physical properties of organostannate(IV) complexes

Complex	Melting point (°C)	Mössbauer parameters	
		$\delta$ (mm sec <sup>-1</sup> )	$\Delta E_Q$ (mm sec <sup>-1</sup> )
$\text{Na}^+ [\text{Ph}_3\text{Sn}(\text{CN})_2]^-$ [68]			
$\text{K}_2^+ [\text{Me}_2\text{SnF}_4]^{2-}$		1.38 [16,17]	4.12 [16,17]
$\text{K}_2^+ [\text{EtSnCl}_3]^{2-}$	>200 [20]		
$\text{K}_2^+ [\text{Et}_2\text{SnF}_4]^{2-}$		1.45 [16]	4.44 [16]
$\text{K}_2^+ [\text{Me}_2\text{SnF}_4]^{2-} \cdot 2 \text{H}_2\text{O}$ [19]			
$\text{K}_2^+ [\text{BuSnF}_5]^{2-}$	>300 [15]	0.27 [15]	1.75 [15]
$\text{K}_2^+ [\text{BuSnF}_4\text{Cl}]^{2-}$	>300 [15]	0.47 [15]	2.00 [15]
$\text{K}_2^+ [\text{BuO} \cdot \text{CO} \cdot \text{CH}_2\text{CH}_2\text{SnF}_5]^{2-}$	>300 [15]	0.17 [15]	1.65 [15]
$\text{K}_2^+ [\text{EtSnF}_5]^{2-}$	>250 [14]		
$\text{K}_2^+ [\text{PhSnF}_5]^{2-}$	>250 [14]		
$\text{Cs}_2^+ [\text{Me}_2\text{SnCl}_4]^{2-}$		1.63 [16]	4.32 [16]
		1.47 [17]	4.28 [17]
		1.76 [16]	4.22 [16]
$\text{Cs}_2^+ [\text{Me}_2\text{SnBr}_4]^{2-}$			
$\text{NH}_4^+ [\text{Me}_2\text{SnF}_3]^-$ [19]			
$(\text{NH}_4^+)_2 [\text{Me}_2\text{SnF}_4]^{2-}$ [19]			
$(\text{NH}_4^+)_2 [\text{Et}_2\text{SnSO}_4(\text{O}_2\text{C} \cdot \text{C}_3\text{H}_7)]^{2-}$ [22]			
$\text{Me}_3\text{NH}^+ [\text{MeSnI}_3]^-$ [22]			
$\text{Me}_4\text{N}^+ [\text{Me}_3\text{SnCl}_2]^-$		1.27 [17]	-3.31 [17]
$\text{Me}_4\text{N}^+ [\text{Ph}_3\text{SnCl}_2]^-$	300 [69]	1.32 [16]	3.00 [16]
		1.23 [17]	-3.02 [17]
		1.44 [69]	3.76 [69]
		1.48 [16]	3.75 [16]
$\text{Me}_4\text{N}^+ [\text{Me}_2\text{SnCl}_3]^-$		1.62 [70]	3.27 [70]
$\text{Me}_4\text{N}^+ [(\text{Cyh})_2\text{SnCl}_3]^-$	184-5 [29]		
$\text{Me}_4\text{N}^+ [\text{Ph}_3\text{Sn}(\text{N}_3)_2]^-$	148-9 [29]		
$\text{Me}_4\text{N}^+ [\text{Ph}_3\text{SnN}_3 \cdot \text{NCS}]^-$			
$\text{Me}_4\text{N}^+ [\text{Me}_3\text{Sn}(1,1\text{mnt})]^-$			
$\text{Me}_4\text{N}^+ [\text{Ph}_3\text{Sn}(1,1\text{mnt})]^-$			
		1.33 [34]	2.07 [34]
		1.26 [34]	-1.53 [34]

## APPENDIX (continued)

Complex	Melting point (°C)	Mössbauer parameters	
		$\delta$ (mm sec <sup>-1</sup> )	$\Delta E_Q$ (mm sec <sup>-1</sup> )
$\text{Me}_4\text{N}^+[\text{Ph}_2\text{Sn}(\text{mnt})]^-$		1.25 [34]	1.48 [34]
$\text{Me}_4\text{N}^+[\text{Ph}_2\text{SnCl}_3]^-$	205 [68]		
$\text{Me}_4\text{N}^+[\text{EtO} \cdot \text{CO} \cdot \text{CH}_2\text{CH}_2\text{SnCl}_4]^-$	240(d) [15]	0.90 [15]	1.95 [15]
$\text{Me}_4\text{N}^+[\text{PrO} \cdot \text{CO} \cdot \text{CH}_2\text{CH}_2\text{SnCl}_4]^-$	> 300 [15]	1.00 [15]	2.00 [15]
$\text{Me}_4\text{N}^+[\text{i-PrO} \cdot \text{CO} \cdot \text{CH}_2\text{CH}_2\text{SnCl}_4]^-$	> 300 [15]	0.95 [15]	2.00 [15]
$\text{Me}_4\text{N}^+[\text{BuO} \cdot \text{CO} \cdot \text{CH}_2\text{CH}_2\text{SnCl}_4]^-$	> 300 [15]	1.03 [15]	2.00 [15]
$(\text{Me}_4\text{N}^+)_2[\text{Me}_2\text{SnCl}_4]^{2-}$ [21,22]			
$(\text{Me}_4\text{N}^+)_2[\text{Et}_2\text{SnCl}_4]^{2-}$	212–218 [10]	1.64 [16]	3.99 [16]
$(\text{Me}_4\text{N}^+)_2[\text{BuSnCl}_3]^{2-}$	> 305 [10]	1.10 [15]	2.10 [15]
$(\text{Me}_4\text{N}^+)_2[\text{Me}_2\text{SnCl}_2\text{Br}_2]^{2-}$	176–177 [10]		
$(\text{Me}_4\text{N}^+)_2[\text{Me}_3\text{SnCl}_3]^{2-}$		1.49 [24]	3.47 [24]
$(\text{Me}_4\text{N}^+)_2[\text{EtSnCl}_3]^{2-}$		1.10 [16]	1.93 [16]
		0.96 [17]	1.94 [17]
$(\text{Me}_4\text{N}^+)_2[\text{Me}_2\text{Sn}(1,1\text{mnt})_2]^{2-}$		1.44 [34]	2.75 [34]
$(\text{Me}_4\text{N}^+)_2[\text{Bu}_2\text{Sn}(1,1\text{mnt})_2]^{2-}$		1.55 [34]	2.87 [34]
$(\text{Me}_4\text{N}^+)_2[\text{Bu}_2\text{Sn}(\text{mnt})_2]^{2-}$		1.60 [34]	3.13 [34]
$(\text{Me}_4\text{N}^+)_2[\text{Ph}_2\text{Sn}(1,1\text{mnt})_2]^{2-}$		1.36 [34]	2.32 [34]
$(\text{Me}_4\text{N}^+)_2[\text{Ph}_2\text{Sn}(\text{mnt})_2]^{2-}$		1.15 [34]	1.54 [34]
$(\text{Me}_4\text{N}^+)_2[\text{Ph}_2\text{SnCl}_4]^{2-}$	> 300 [68]		
$(\text{Me}_4\text{N}^+)_2[\text{PhSnCl}_3]^{2-}$	> 300 [22]	0.84 [15]	1.72 [15]
$(\text{Me}_4\text{N}^+)_2[\text{PhSnBr}_3]^{2-}$ [22]			
$(\text{Me}_4\text{N}^+)_2[(\text{C}_2\text{H}_5)_2\text{SnCl}_4]^{2-}$ [22]			
$(\text{Me}_4\text{N}^+)_2[\text{EtSnPO}_4 \cdot \text{Cl}_2]^{2-}$ [22]			
$(\text{Me}_4\text{N}^+)_2[\text{Bu}_2\text{SnCl}_4]^{2-}$	134–136 [18]		
$(\text{Me}_4\text{N}^+)_2[\text{BuO} \cdot \text{CO} \cdot \text{CH}_2\text{CH}_2\text{SnCl}_3\text{F}_2]^{2-} \cdot \text{H}_2\text{O}$	> 300 [15]	0.74 [15]	2.08 [15]
$(\text{Me}_4\text{N}^+)_2[\text{MeO} \cdot \text{CO} \cdot \text{CH}_2\text{CH}_2\text{SnCl}_3]^{2-}$	> 300 [15]	0.96 [15]	1.88 [15]
$(\text{Me}_4\text{N}^+)_2[\text{EtO} \cdot \text{CO} \cdot \text{CH}_2\text{CH}_2\text{SnCl}_3]^{2-}$	300 [15]	0.84 [15]	1.93 [15]
$(\text{Me}_3\text{N} \cdot \text{CH}_2\text{CHO}^+)_2[\text{Me}_2\text{SnCl}_4]^{2-}$	86–90 [22]		
$(\text{Et}_3\text{NH}^+)[\text{Ph}_3\text{SnClF}]^-$	206–208 [71]	1.23 [71]	3.39 [71]

$(\text{Et}_3\text{NH}^+)(\text{Ph}_3\text{SnClBr})^-$	115–117 [71]	1.37 [71]	3.17 [71]
$(\text{Et}_3\text{NH}^+)(\text{Ph}_3\text{SnClI})^-$	91–93 [71]	1.39 [71]	2.73 [71]
$(\text{Et}_3\text{NH}^+)(\text{MePh}_2\text{SnClF})^-$	162–164 [71]	1.31 [71]	3.65 [71]
$(\text{Et}_3\text{NH}^+)(\text{MePh}_2\text{SnCl}_2)^-$	96–98 [71]	1.44 [71]	3.32 [71]
$(\text{Et}_3\text{NH}^+)(\text{MePh}_2\text{SnClBr})^-$	74–76 [71]	1.41 [71]	3.18 [71]
$(\text{Et}_3\text{NH}^+)(\text{MePh}_2\text{SnClI})^-$	62–64 [71]	1.45 [71]	3.08 [71]
$\text{Et}_3\text{NH}^+[\text{CH}_3\text{CO}\cdot\text{CN}\cdot\text{N}\cdot\text{Ph}_3\text{SnCl}]^-$	86–88 [72]		
$\text{Et}_3\text{NH}^+[\text{CH}_3\text{CH}_2\text{CO}\cdot\text{CN}\cdot\text{N}\cdot\text{Ph}_3\text{SnCl}]^-$	81–83 [72]		
$\text{Et}_3\text{NH}^+[\text{PhCO}\cdot\text{CN}\cdot\text{N}\cdot\text{Ph}_3\text{SnCl}]^-$	97–99 [72]		
$\text{Et}_3\text{NH}^+[\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{CN}\cdot\text{N}\cdot\text{Ph}_3\text{SnCl}]^-$	97–100 [72]		
$\text{Et}_3\text{NH}^+[\text{CH}_3\text{CH}_2\text{O}\cdot\text{CO}\cdot\text{CN}\cdot\text{N}\cdot\text{Ph}_3\text{SnCl}]^-$	95–98 [72]		
$\text{Et}_3\text{NH}^+[\text{PhCH}_2\text{O}\cdot\text{CO}\cdot\text{CN}\cdot\text{N}\cdot\text{Ph}_3\text{SnCl}]^-$	89–92 [72]		
$\text{Et}_3\text{NH}^+[\text{PhO}\cdot\text{CO}\cdot\text{CN}\cdot\text{N}\cdot\text{Ph}_3\text{SnCl}]^-$	95–98 [72]		
$\text{Et}_3\text{NH}^+[\text{PhSO}_2\cdot\text{CO}\cdot\text{CN}\cdot\text{N}\cdot\text{Ph}_3\text{SnCl}]^-$	80–83 [72]		
$\text{Et}_4\text{N}^+[\text{Me}_2\text{SnBr}_3]^-$ [21]		1.46 [16]	3.39 [16]
		1.52 [17]	3.41 [17]
$\text{Et}_4\text{N}^+[\text{Me}_3\text{Sn}(\text{mnt})]^-$	116–117 [35]	1.46 [33]	2.38 [33]
$\text{Et}_4\text{N}^+[\text{Ph}_3\text{Sn}(\text{mnt})]^-$	136 [35]	1.46 [33]	2.38 [33]
$\text{Et}_4\text{N}^+[\text{Me}_3\text{SnBr}_2]^-$	150–165(d) [44]	1.43 [16]	3.45 [16]
$\text{Et}_4\text{N}^+[\text{Ph}_2\text{SnCl}_3]^-$	136 [68]	1.25 [16]	2.62 [16]
$\text{Et}_4\text{N}^+[\text{Ph}_3\text{SnCl}_2]^-$	139 [68]		
$\text{Et}_4\text{N}^+[\text{Me}_3\text{Sn}(\text{SCN})_2]^-$	120–121(d) [32]		
$\text{Et}_4\text{N}^+[\text{Me}_2\text{SnCl}_3]^-$		1.40 [38]	3.30 [38]
$\text{Et}_4\text{N}^+[\text{Me}_2\text{SnCl}]^-$	157–158 [56]	1.42 [16]	3.32 [16]
		1.24 [38]	3.23 [38]
$\text{Et}_4\text{N}^+[\text{Me}_3\text{Sn}(\text{NCS})_2]^-$ [73]		1.16 [25]	1.73 [25]
$\text{Et}_4\text{N}^+[\text{BuSnCl}_4]^-$			
$\text{Et}_4\text{N}^+[\text{Ph}_3\text{Sn}(\text{mnt})]^-$ [35]		1.97 [15]	2.03 [15]
$\text{Et}_4\text{N}^+[\text{BuO}\cdot\text{CO}\cdot\text{CH}_2\text{CH}_2\text{SnCl}_3\text{Br}]^-$	104–106 [15]	1.43 [12]	3.52 [12]
$\text{Et}_4\text{N}^+[\text{Me}_2\text{SnCl}_2\text{Br}]^-$	134 [12]	1.51 [12]	3.37 [12]
$\text{Et}_4\text{N}^+[\text{Bu}_2\text{SnCl}_2\text{Br}]^-$	59–61 [12]	1.36 [12]	3.27 [12]
$\text{Et}_4\text{N}^+[\text{Ph}_2\text{SnCl}_2\text{Br}]^-$	124–125 [12]	1.48 [12]	3.63 [12]
$\text{Et}_4\text{N}^+[\text{Bu}_3\text{SnClBr}]^-$	59–60 [12]	1.34 [12]	3.14 [12]
$\text{Et}_4\text{N}^+[\text{Ph}_3\text{SnClBr}]^-$	128–129 [12]	1.39 [12]	3.60 [12]
$(\text{Et}_4\text{N}^+)_2[\text{Ph}_2\text{SnCl}_2\text{Br}_2]^{2-}$	162–165 [12]		

## APPENDIX (continued)

Complex	Melting point (°C)	Mössbauer parameters	
		$\delta$ (mm sec <sup>-1</sup> )	$\Delta E_Q$ (mm sec <sup>-1</sup> )
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [Me <sub>2</sub> Sn(mnt)] <sup>2-</sup>		1.36 [33]	2.46 [33]
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [BuSnCl <sub>3</sub> Br] <sup>2-</sup>		1.20 [74]	1.85 [74]
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [Bu <sub>2</sub> Sn(CED) <sub>2</sub> ] <sup>2-</sup>		1.50 [34]	2.50 [34]
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [Ph <sub>2</sub> Sn(mnt)] <sup>2-</sup>		1.10 [33]	1.35 [33]
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [BuSnCl <sub>3</sub> ] <sup>2-</sup>	187 [75]	1.07 [16]	1.86 [16]
		1.12 [74]	1.86 [74]
		1.09 [25]	1.86 [25]
		1.07 [38]	1.86 [38]
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [Bu <sub>2</sub> Sn(NCS) <sub>4</sub> ] <sup>2-</sup>	183–185 [76]		
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn(NCS) <sub>4</sub> ] <sup>2-</sup>	127–129 [76]		
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [Me <sub>2</sub> SnBr <sub>4</sub> ] <sup>2-</sup> [22,23]			
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [Me <sub>2</sub> Sn(SCN) <sub>4</sub> ] <sup>2-</sup>	113–115 [32]		
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [Ph <sub>2</sub> Sn(NCS) <sub>4</sub> ] <sup>2-</sup>	239–241 [76]		
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [MeSn(SCN) <sub>5</sub> ] <sup>2-</sup>	163–169 [32]		
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [Me <sub>2</sub> Sn(NCS) <sub>4</sub> ] <sup>2-</sup> [18,73]			
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [MeSn(NCS) <sub>5</sub> ] <sup>2-</sup> [73]			
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [MeSnBr <sub>5</sub> ] <sup>2-</sup> [23]			
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [MeSnBr <sub>3</sub> Cl <sub>2</sub> ] <sup>2-</sup> [23]			
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [BuSnCl <sub>4</sub> Br] <sup>2-</sup>	169–171 [15]	1.08 [15]	1.95 [15]
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [BuSnBr <sub>5</sub> ] <sup>2-</sup>	>280(d) [15]	1.38 [15]	1.80 [15]
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [BuSnBr <sub>3</sub> Cl <sub>2</sub> ] <sup>2-</sup>	148–149 [15]	1.20 [15]	1.85 [15]
(Et <sub>4</sub> N <sup>+</sup> ) <sub>2</sub> [PhSnCl <sub>5</sub> ] <sup>2-</sup>		0.90 [25]	1.65 [25]
Bu <sub>4</sub> N <sup>+</sup> [Ph <sub>2</sub> SnCl <sub>3</sub> ] <sup>-</sup>	101 [68]	1.20 [12]	2.56 [12]
Bu <sub>4</sub> N <sup>+</sup> [Me <sub>3</sub> SnI] <sup>-</sup> [23]			
Bu <sub>4</sub> N <sup>+</sup> [Ph <sub>3</sub> SnCl <sub>2</sub> ] <sup>-</sup>	115–118(d) [56]	1.31 [12]	2.86 [12]
Bu <sub>4</sub> N <sup>+</sup> [Ph <sub>3</sub> SnClBr] <sup>-</sup>	123–124(d) [56]	1.28 [12]	2.86 [12]
Bu <sub>4</sub> N <sup>+</sup> [Me <sub>2</sub> SnCl <sub>2</sub> Br] <sup>-</sup>	122 [12]	1.36 [12]	3.27 [12]
Bu <sub>4</sub> N <sup>+</sup> [Me <sub>2</sub> SnCl <sub>3</sub> ] <sup>-</sup>	117–119 [12]	1.39 [12]	3.40 [12]
Bu <sub>4</sub> N <sup>+</sup> [Me <sub>2</sub> SnCl <sub>2</sub> I] <sup>-</sup>	90–91 [12]	1.41 [12]	3.27 [12]

$\text{Bu}_4\text{N}^+ [\text{Bu}_2\text{SnCl}_3]^-$	81 [12]	1.56 [12]	3.52 [12]
$\text{Bu}_4\text{N}^+ [\text{Bu}_2\text{SnCl}_2\text{Br}]^-$	104–105 [12]	1.55 [12]	3.30 [12]
$\text{Bu}_4\text{N}^+ [\text{Bu}_2\text{SnCl}_2\text{I}]^-$	53–54 [12]	1.58 [12]	3.37 [12]
$\text{Bu}_4\text{N}^+ [\text{Ph}_2\text{SnCl}_2\text{Br}]^-$	99–101 [12]	1.28 [12]	2.66 [12]
$\text{Bu}_4\text{N}^+ [\text{Ph}_2\text{SnCl}_2\text{I}]^-$	92–93 [12]	1.32 [12]	2.69 [12]
$\text{Bu}_4\text{N}^+ [\text{Bu}_3\text{SnCl}_2]^-$	93–95 [12]	1.52 [12]	3.55 [12]
$\text{Bu}_4\text{N}^+ [\text{Bu}_3\text{SnClBr}]^-$	59–60 [12]	1.46 [12]	3.47 [12]
$\text{Bu}_4\text{N}^+ [\text{Ph}_3\text{SnClI}]^-$	92–94 [12]	1.37 [12]	3.04 [12]
$(\text{Bu}_4\text{N}^+)_2 [\text{Ph}_2\text{SnCl}_4]^{2-}$	119–122 [12]	1.33 [12]	3.42 [12]
$(\text{Bu}_4\text{N}^+)_2 [\text{Ph}_2\text{SnCl}_2\text{Br}_2]^{2-}$	121 [12]	1.39 [12]	3.65 [12]
$(\text{Bu}_4\text{N}^+)_2 [\text{PhSnCl}_5]^{2-}$	161–162 [56]		
$(\text{Bu}_4\text{N}^+)_2 [\text{Me}_2\text{SnI}_4]^{2-}$ [23]	195–200 [75]		
$(\text{Bu}_4\text{N}^+)_2 [\text{Bu}_2\text{SnBr}_2\text{Cl}_2]^{2-}$			
$(\text{Bu}_4\text{N}^+)_2 [\text{MeSnCl}_2\text{I}_2]^{2-}$ [23]			
$(\text{Bu}_4\text{N}^+)_2 [\text{MeSnCl}_3\text{Br}_2]^{2-}$ [23]			
$(\text{Bu}_4\text{N}^+)_2 [\text{MeSnBr}_2\text{I}_3]^{2-}$ [23]			
$\text{Ph}_4\text{N}^+ [\text{Ph}_2\text{Sn}(\text{OAc})_3]^-$ [22]			
$(\text{cyclo-C}_6\text{H}_{11})_4\text{N}_5^+ [\text{Et}_3\text{Sn}(\text{OAc})_4]^{2-}$ [22]			
$\text{Ph}_3\text{MeP}^+ [\text{Ph}_3\text{SnCl}_2]^-$	146–147 [64]		
$(\text{Ph}_3\text{MeP}^+)_2 [\text{BuSnBr}_5]^-$	116–119 [15]	1.38 [15]	1.90 [15]
$\text{Bu}_4\text{P}^+ [\text{Bu}_3\text{SnCl}_2]^-$	69–70 [60]		
$(\text{ClCH}_2)_4\text{P}^+ [\text{Ph}_3\text{SnCl}_2]^-$	124–126 [64]		
$\text{Bu}_3\text{CH}_3(\text{CH}_2)_{11}\text{P}^+ [\text{Ph}_3\text{SnClBr}]^-$	156–157 [64]		
$\text{Et}_3\text{P} \cdot \text{PhCH}_2\text{P}^+ [\text{Ph}_3\text{SnClBr}]^-$	129 [64]		
$\text{Et}_2\text{Ph} \cdot \text{PhCH}_2\text{P}^+ [\text{Ph}_3\text{SnClBr}]^-$	114–115 [64]		
$\text{EtPh}_2 \cdot \text{PhCH}_2\text{P}^+ [\text{Ph}_3\text{SnClBr}]^-$	178 [64]		
$\text{Ph}_3\text{ClCH}_2\text{P}^+ [\text{Ph}_3\text{SnCl}_2]^-$	171–172 [64]		
$\text{Ph}_3\text{CH}_2\text{OH} \cdot \text{P}^+ [\text{Ph}_3\text{SnCl}_2]^-$	141–142 [64]		
$\text{Ph}_3\text{CH}_2\text{CH}_2\text{OH} \cdot \text{P}^+ [\text{Ph}_3\text{Sn}(\text{SCN})_2]^-$	124–125 [64]		
$\text{Ph}_3\text{EtP}^+ [\text{Ph}_3\text{SnClBr}]^-$	139–140 [64]		
$\text{Ph}_3\text{PrP}^+ [\text{Ph}_3\text{SnClBr}]^-$	114–115 [64]		
$\text{Ph}_3\text{CH}_2=\text{CHCH}_2\text{P}^+ [\text{Ph}_3\text{SnClBr}]^-$	117–118 [64]		
$\text{Ph}_3\text{BuP}^+ [\text{Ph}_3\text{SnClBr}]^-$	127–129 [64]		
$\text{Ph}_3\text{C}_6\text{H}_{13}\text{P}^+ [\text{Ph}_3\text{SnClBr}]^-$	93–94 [64]		
$\text{Ph}_3\text{EtSCH}_2\text{P}^+ [\text{Ph}_3\text{SnCl}_2]^-$	201–203 [64]		

## APPENDIX (continued)

Complex	Melting point (°C)	Mössbauer parameters	
		$\delta$ (mm sec <sup>-1</sup> )	$\Delta E_Q$ (mm sec <sup>-1</sup> )
$\text{Ph}_3\cdot\text{CH}_2\text{CH}_2\text{CHMe}_2\cdot\text{P}^+[\text{Ph}_3\text{SnClBr}]^-$	150–153 [64]		
$\text{Ph}_3(\text{CH}_2)_6\text{MeP}^+[\text{Ph}_3\text{SnClBr}]^-$	119 [64]		
$\text{Ph}_3\cdot\text{CHPh}_2\cdot\text{P}^+[\text{Ph}_3\text{SnCl}_2]^-$	205–206 [64]		
$\text{Ph}_3(\text{CH}_2)_3\text{Ph}\cdot\text{P}^+[\text{Ph}_3\text{SnClBr}]^-$	125–126 [64]		
$\text{Ph}_3\cdot p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{P}^+[\text{Ph}_3\text{SnClBr}]^-$	161–163 [64]		
$\text{Ph}_3\cdot\text{CH}_2\text{OMe}\cdot\text{P}^+[\text{Ph}_3\text{SnCl}_2]^-$	136–138 [64]		
$\text{Ph}_3\cdot\text{CH}_2\text{OEt}\cdot\text{P}^+[\text{Ph}_3\text{SnCl}_2]^-$	117–118 [64]		
$\text{Ph}_3\cdot p\text{-C}_6\text{H}_4\text{OH}\cdot\text{P}^+[\text{Ph}_3\text{SnCl}_2]^-$	201–203 [64]		
$\text{Ph}_3\cdot p\text{-C}_6\text{H}_4\text{OH}\cdot\text{P}^+[\text{Ph}_3\text{SnClBr}]^-$	134–136 [64]		
$\text{Ph}_3\cdot p\text{-CH}_2\text{C}_6\text{H}_4\text{Cl}\cdot\text{P}^+[\text{Ph}_3\text{SnCl}_2]^-$	152–154 [64]		
$\text{Ph}_3\cdot\text{PhCH}_2\cdot\text{P}^+[\text{Et}_3\text{SnCl}_2]^-$	189–190 [77]	1.50 [16] 1.42 [17] 1.56 [60] 1.50 [60] 1.55 [60] 1.59 [60] 1.43 [60] 1.34 [60]	3.44 [16] –3.49 [17] 3.46 [60] 3.41 [60] 3.42 [60] 3.13 [60] 3.38 [60] 2.89 [60]
$\text{Ph}_3\cdot\text{PhCH}_2\cdot\text{P}^+[\text{Bu}_3\text{SnCl}_2]^-$	115–118 [77]		
$\text{Ph}_3\cdot\text{PhCH}_2\cdot\text{P}^+[\text{Pr}_3\text{SnCl}_2]^-$	117–120 [77]		
$\text{Ph}_3\cdot\text{PhCH}_2\cdot\text{P}^+[(\text{PhCH}_2)_3\text{SnCl}_2]^-$	73–75 [77]		
$\text{Ph}_3\cdot\text{PhCH}_2\cdot\text{P}^+[\text{Me}_3\text{SnCl}_2]^-$	202–203 [60]		
$\text{Ph}_3\cdot\text{PhCH}_2\cdot\text{P}^+[\text{Ph}_3\text{SnCl}_2]^-$	205–207 [64]		
$\text{Ph}_3\cdot\text{PhCH}_2\cdot\text{P}^+[\text{Ph}_3\text{SnClBr}]^-$	195–196 [64]		
$\text{Ph}_3\cdot\text{C}_{10}\text{H}_{21}\cdot\text{P}^+[\text{Ph}_3\text{SnClBr}]^-$	119 [64]		
$\text{Ph}_3\cdot\text{C}_{10}\text{H}_{21}\cdot\text{P}^+[\text{Ph}_3\text{SnCl}_2]^-$	119–120 [78]	1.23 [78]	2.87 [78]
$\text{Ph}_3\cdot\text{C}_{10}\text{H}_{21}\cdot\text{P}^+[\text{Ph}_3\text{SnCl}_2]^-$	108–110 [78]	1.29 [78]	3.27 [78]
$\text{Ph}_3\cdot\text{C}_{10}\text{H}_{21}\cdot\text{P}^+[\text{Ph}_3\text{SnBr}_2]^-$	203–205 [64]		
$\text{Ph}_4\text{P}^+[\text{Ph}_3\text{SnCl}_2]^-$	85–88 [60]	1.55 [60] 1.43 [33] 1.39 [33]	3.44 [60] 2.63 [33] 2.48 [33]
$\text{Ph}_4\text{P}^+[\text{Bu}_3\text{SnCl}_2]^-$			
$\text{Ph}_4\text{P}^+[\text{Me}_2\text{SnCl}(\text{mnt})]^-$			
$\text{Ph}_4\text{P}^+[\text{Me}_2\text{Sn}(\text{mnt})]^-$			
$[\text{Ph}_3\text{PCH}_2\text{SnMe}_3]^+[\text{Me}_3\text{SnBr}]^-$	d. above 152° [44]		
$[\text{Ph}_3\text{PCH}_2\text{Sn}(\text{Me})_2\text{CH}_2\text{PPh}_3]^{2+}[\text{Me}_2\text{SnBr}_4]^{2-}$	d. above 135° [44]		
$(\text{Ph}_3\text{MeP}^+)(\text{BuSnBr}_5)^{2-}$	116–119 [15]	1.38 [15]	1.80 [15]



$(\text{PhCH}_2)_2\text{PhMeP}^+[\text{Ph}_3\text{SnCl}]^-$	121 [64]	1.42 [16]	3.50 [16]
$\text{Ph}_4\text{As}^+[\text{Ph}_3\text{SnCl}]^-$	> 300 [79]	1.54 [16]	3.36 [16]
$\text{Ph}_4\text{As}^+[\text{Ph}_3\text{SnCl}_2]^-$	173–175 [79]	1.18 [16]	1.82 [16]
$\text{Ph}_4\text{As}^+[\text{Me}_2\text{SnCl}_3]^-$	165–166 [28]	1.20 [29]	2.75 [29]
$\text{Ph}_4\text{As}^+[\text{Et}_2\text{SnCl}_3]^-$	180–185 [28]	1.21 [29]	2.97 [29]
$\text{Ph}_4\text{As}^+[\text{EtSnCl}_4]^-$	173–175 [29]	1.41 [33]	2.47 [33]
$\text{Ph}_4\text{As}^+[\text{Ph}_3\text{Sn}(\text{N}_3)_2]^-$	157–158 [29]	1.51 [33]	2.66 [33]
$\text{Ph}_4\text{As}^+[\text{Ph}_3\text{SnN}_3\cdot\text{NCS}]^-$		1.45 [33]	2.43 [33]
$\text{Ph}_4\text{As}^+[\text{Me}_2\text{SnCl}(\text{mnt})]^-$		1.25 [33]	2.19 [33]
$\text{Ph}_4\text{As}^+[\text{Me}_2\text{SnBr}(\text{mnt})]^-$			
$\text{Ph}_4\text{As}^+[\text{Me}_2\text{Sn}(\text{mnt})]^-$			
$\text{Ph}_4\text{As}^+[\text{Ph}_2\text{SnCl}(\text{mnt})]^-$			
$\text{Ph}_4\text{As}^+[\text{BuSnCl}_4]^-$	142–143 [28]		
$\text{Ph}_4\text{As}^+[\text{PhSnCl}_4]^-$	161–162 [28]		
$\text{Ph}_4\text{As}^+[\text{Bu}_2\text{SnCl}_3]^-$	94–96 [28]		
$\text{Ph}_4\text{As}^+[\text{Ph}_2\text{SnCl}_3]^-$	225–227 [28]		
$\text{Ph}_4\text{As}^+[\text{MeSnCl}_4]^-$ [27]			
$\text{Ph}_4\text{As}^+[\text{Me}_3\text{SnCl}_2]^-$	171–172 [56]		
$\text{Ph}_4\text{As}^+[\text{Ph}_3\text{SnCl}_2]^-$	184–185 [56]		
$(\text{Ph}_4\text{As}^+)_2[\text{Me}_2\text{Sn}(\text{N}_3)_4]^{2-}$	205–206 [29]	1.23 [29]	3.61 [29]
$(\text{Ph}_4\text{As}^+)_2[\text{Ph}_2\text{Sn}(\text{N}_3)_2(\text{NCS})_2]^{2-}$	237–239 [29]	1.10 [29]	3.72 [29]
$(\text{Ph}_4\text{As}^+)_2[\text{BuSnCl}_5]^{2-}$		1.09 [25]	1.88 [25]
$(\text{Ph}_4\text{As}^+)_2[\text{PhSnCl}_5]^{2-}$		0.93 [25]	1.64 [25]
$\text{Ph}_3\text{CH}_2\text{COPh}\cdot\text{As}^+[\text{Ph}_3\text{SnCl}_2]^-$		1.43 [60]	2.88 [60]
$(\text{pyH}^+)_2[\text{Me}_2\text{SnBr}_4]^{2-}$			
$(\text{pyH}^+)_2[\text{Ph}_2\text{SnCl}_4]^{2-}$	108–112 [10]	1.44 [16]	3.80 [16]
$(\text{pyH}^+)_2[\text{PhSnCl}_5]^{2-}$		1.44 [51]	3.80 [51]
$(\text{pyH}^+)_2[\text{Me}_2\text{SnCl}_4]^{2-}$	150–153 [61]	1.01 [16]	1.72 [16]
	151 [62]	1.10 [51]	1.92 [51]
		1.59 [16]	4.32 [16]
$(\text{pyH}^+)_2[\text{MeSnCl}_5]^{2-}$ [10]			
$(\text{pyH}^+)_2[\text{Et}_2\text{SnCl}_4]^{2-}$	118–122 [10]		
$(\text{pyH}^+)_2[\text{Pr}_2\text{SnCl}_4]^{2-}$	ca. 114 [10]		
$(\text{pyH}^+)_2[\text{MeSnBr}_5]^{2-}$	165–172 [10]		
$(\text{pyH}^+)_2[\text{Et}_2\text{SnBr}_4]^{2-}$	90–99 [10]		
$(\text{pyH}^+)_2[\text{Pr}_2\text{SnBr}_4]^{2-}$	100–114 [10]		

## APPENDIX (continued)

Complex	Melting point (°C)	Mössbauer parameters	
		$\delta$ (mm sec <sup>-1</sup> )	$\Delta E_Q$ (mm sec <sup>-1</sup> )
(pyH <sup>+</sup> ) <sub>2</sub> [Ph <sub>3</sub> SnCl <sub>3</sub> ] <sup>2-</sup>	169–170 [10]		
(pyH <sup>+</sup> ) <sub>2</sub> [Ph <sub>3</sub> SnBr <sub>3</sub> ] <sup>2-</sup>	ca. 194 [10]		
QH <sup>+</sup> [Me <sub>2</sub> SnCl <sub>3</sub> ] <sup>-</sup> [55]			
(QH <sup>+</sup> ) <sub>2</sub> [Me <sub>2</sub> SnCl <sub>4</sub> ] <sup>2-</sup>	167 [10]		
(QH <sup>+</sup> ) <sub>2</sub> [Me <sub>2</sub> SnBr <sub>4</sub> ] <sup>2-</sup>	134 [10]		
(QH <sup>+</sup> ) <sub>2</sub> [Et <sub>2</sub> SnCl <sub>4</sub> ] <sup>2-</sup>	134–135 [10]		
(QH <sup>+</sup> ) <sub>2</sub> [MeSnCl <sub>3</sub> ] <sup>2-</sup>	ca. 200 [10]		
(QH <sup>+</sup> ) <sub>2</sub> [Et <sub>2</sub> SnBr <sub>4</sub> ] <sup>2-</sup>	120–124 [10]		
(QH <sup>+</sup> ) <sub>2</sub> [MeSnBr <sub>3</sub> ] <sup>2-</sup>	145 [10]		
[Mo <sub>3</sub> (η <sup>3</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> S <sub>4</sub> ] <sup>+</sup> [Me <sub>3</sub> SnCl <sub>2</sub> ] <sup>-</sup> [45]			
(Me <sub>2</sub> SnCl·terpy) <sup>+</sup> [Me <sub>2</sub> SnCl <sub>3</sub> ] <sup>-</sup> [36]			
(BuSnCl <sub>2</sub> ·terpy) <sup>+</sup> [BuSnCl <sub>3</sub> ] <sup>-</sup>			
(Me <sub>2</sub> SnBr·terpy) <sup>+</sup> [Me <sub>2</sub> SnBr <sub>3</sub> ] <sup>-</sup> [36]	1.07 [38]	1.94 [38]	
(Ph <sub>2</sub> SnBr·terpy) <sup>+</sup> [Ph <sub>2</sub> SnBr <sub>3</sub> ] <sup>-</sup> [36]			
(Ph <sub>2</sub> SnCl·terpy) <sup>+</sup> [Ph <sub>2</sub> SnCl <sub>3</sub> ] <sup>-</sup> [36]			
[Me <sub>3</sub> Sn(HMPT) <sub>2</sub> ] <sup>+</sup> [Me <sub>3</sub> SnBr <sub>2</sub> ] <sup>-</sup> [39]			
Et <sub>4</sub> N <sup>+</sup> [BuSnCl <sub>4</sub> ] <sup>-</sup> ·PBu <sub>3</sub>	1.27 [25]	2.42 [25]	
Et <sub>4</sub> N <sup>+</sup> [BuSnCl <sub>4</sub> ] <sup>-</sup> ·Ph <sub>3</sub> PO	1.07 [25]	2.10 [25]	
Et <sub>4</sub> N <sup>+</sup> [BuSnCl <sub>4</sub> ] <sup>-</sup> ·Ph <sub>3</sub> AsO	0.94 [25]	1.84 [25]	
Et <sub>4</sub> N <sup>+</sup> [BuSnCl <sub>4</sub> ] <sup>-</sup> ·DMF	1.10 [25]	1.90 [25]	
Et <sub>4</sub> N <sup>+</sup> [BuSnCl <sub>4</sub> ] <sup>-</sup> ·pyridine	1.04 [25]	1.65 [25]	
Et <sub>4</sub> N <sup>+</sup> [BuSnCl <sub>4</sub> ] <sup>-</sup> ·DMSO	0.98 [25]	1.88 [25]	
Et <sub>4</sub> N <sup>+</sup> [BuSnCl <sub>4</sub> ] <sup>-</sup> ·NMe <sub>3</sub>	0.98 [25]	1.91 [25]	
Et <sub>4</sub> N <sup>+</sup> [PhSnCl <sub>4</sub> ] <sup>-</sup> ·PBu <sub>3</sub>	0.96 [25]	2.10 [25]	
Et <sub>4</sub> N <sup>+</sup> [PhSnCl <sub>4</sub> ] <sup>-</sup> ·Ph <sub>3</sub> PO	0.81 [25]	1.81 [25]	
Et <sub>4</sub> N <sup>+</sup> [PhSnCl <sub>4</sub> ] <sup>-</sup> ·Ph <sub>3</sub> AsO	0.74 [25]	1.63 [25]	
Et <sub>4</sub> N <sup>+</sup> [PhSnCl <sub>4</sub> ] <sup>-</sup> ·DMF	0.83 [25]	1.55 [25]	
Et <sub>4</sub> N <sup>+</sup> [PhSnCl <sub>4</sub> ] <sup>-</sup> ·pyridine	0.89 [25]	1.57 [25]	
Et <sub>4</sub> N <sup>+</sup> [PhSnCl <sub>4</sub> ] <sup>-</sup> ·NMe <sub>3</sub>	0.82 [25]	1.77 [25]	

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