Coordination Chemistry Reviews, , 135/136 (1994) 809–843

The chemistry and applications of organotin(IV) complexes of phosphorus-based acids

Vimal K. Jain

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

(Received 31 December 1993; accepted 13 March 1994)

CONTENTS

ABSTRACT

Synthesis, reactivity, structural aspects and applications of organotin(IV) complexes with phosphorus-based acids are reviewed. Complexes are classified according to the number of organic groups on tin and the nature of the donor atoms (oxygen and/or sulphur) on phosphorus. In general, organotin complexes of these acids are synthesized either by the reaction of organotin oxide with a free ligand or by treating the organotin halide with the alkali metal salt of an acid. Reactions of monoorganotin oxides with phosphorus-based acids proceed in a stepwise manner involving a variety of organotin clusters, some of which are now fully characterized. The structure of the organotin complexes of these ligands is influenced by the number of R groups on tin and the donor set of phosphorus ($>PO_2$, >POS, $>PS_2$). The $>PO_2$-type ligands usually prefer bidentate bridging or a chelating bonding mode, while $>PS_2$-type ligands bind an organotin moiety in a monodentate or chelating (asymmetric or symmetric) fashion. The application of these complexes as catalysts, corrosion inhibitors and biocides is discussed.

Correspondence to: V.K. Jain, Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

0010-8545/94/$26.00
SSDI 0010-8545(94)01113-P

1. INTRODUCTION

During the last four decades or so the chemistry of organotin(IV) complexes of phosphorus-based acids has been the subject of considerable research. Much of the earlier work was reported in the patent literature and primarily describes their synthesis and applications as biocides. In the late 1970s structural aspects of these complexes began to emerge and an interesting field of organotin cluster chemistry came into being in the late 1980s. There are now several review articles that cover some of the aspects of these complexes [1–6]. It may be noted that the article by Molloy and Zuckerman [3] published in 1983 presents an account solely of their own work. Considerable research and novel advances in the chemistry of organotin(IV) complexes of phosphorus-based acids have been reported since Molloy and Zuckerman's publication. It is the intention of this review to cover synthesis, spectroscopic, structural aspects and applications of these complexes. Structural features of these complexes are markedly influenced by the number of R groups on tin and the nature of the donor atoms (O and/or S) attached to phosphorus. The chemistry of these complexes is discussed in this review according to the number of R groups on tin and the donor set of atoms attached to phosphorus.

2. TRIORGANOTIN(IV) COMPLEXES

2.1. *With* $>PO_2$*-type ligands*

Triorganotin(IV) complexes of oxyphosphorus acids have been prepared by the reactions of triorganotin oxides, hydroxides, halides or hydrides with phosphorus oxy acids (eqns. (1)–(3)) [7–15]. In addition to this general synthetic method, there are several other less commonly employed procedures for the preparation of these complexes [16–19]. These include: reaction of triphenyltin diphenylphosphine ($Ph_3Sn{-}PPh_2$) with oxygen or hydrogen peroxide to yield $Ph_3SnOOPPh_2$ (eqn. (4)) [16]; treatment of tributyltin oxide with $F_2P(O){-}O{-}P(O)F_2$ to give $Bu_3SnOOPF_2$ (eqn. (5)) [17]; reaction of triphenyltin oxide with phosphorus oxyhalides (POX_3) to yield $Ph_3Sn(OOPX_2)$ ($X \equiv Cl$ or Br) [19]. The trimethyltin analogues of the latter can be obtained readily by the reaction of Me_3SnNEt_2 with X_2POOH ($X \equiv Cl$ or Me) in dichloromethane (eqn. (6)) [18]. The reactions of triorganotin oxides with diorganophosphine oxides (R'_2POH) yield $R_3SnOOPR'_2$ and triorganotin hydride [9].

$$Ph_3SnOH + (PhO)_2POOH \rightarrow [Ph_3SnOOP(OPh)_2] + H_2O \quad (1)$$

$$R_3SnCl + (R'O)_2POOH \rightarrow [R_3SnOOP(OR')_2] + HCl \quad (2)$$

$$R_3SnH + R'_2POOH \rightarrow [R_3SnOOPR'_2] + H_2 \quad (3)$$

$$Ph_3SnPPh_2 + \tfrac{1}{2}O_2 \rightarrow [Ph_3SnOPPh_2] \xrightarrow{\frac{1}{2}O_2} [Ph_3SnOOPPh_2] \quad (4)$$

$$(Bu_3Sn)_2O + F_2P(O)OP(O)F_2 \rightarrow 2[Bu_3SnOOPF_2] \quad (5)$$

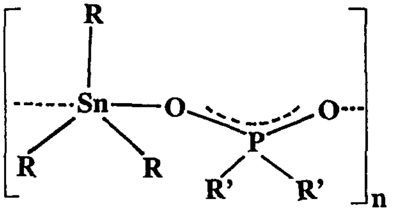
$$Me_3SnNEt_2 + Me_2POOH \rightarrow [Me_3SnOOPMe_2] + Et_2NH \quad (6)$$

The reaction of triorganotin hydroxides with $(R'O)_2POH$ affords triorganotin phosphonate complexes of the type $[R_3Sn\{OP(O)H(OR')\}]$ ($R \equiv$ Bu, *c*-Hx, Ph; $R' \equiv$ Me, Et, ^{i}Pr, Bu) [20]. The latter complexes can also be obtained by treatment of triorganotin chloride ($R \equiv$ Me, Bu, Ph) with $NaOP(O)H(OR')$ in benzene (eqn. (7)) [21]. The reaction of phenylphosphinic acid with trimethyltin chloride or acetate in water yields α-$[Me_3SnOP(O)(OH)Ph]$ (eqn. (8)) [22,23].

$$R_3SnCl + NaOP(O)H(OR') \rightarrow [R_3SnOOP(H)(OR')] + NaCl \quad (7)$$

$$\left.\begin{array}{l} Me_3SnCl + PhP(O)(OH)_2 \xrightarrow{-HCl} \\ Me_3SnOAc + PhP(O)(OH)_2 \xrightarrow{-AcOH} \end{array}\right] \longrightarrow \alpha\text{-}[Me_3SnOOP(OH)Ph] \quad (8)$$

Triorganotin complexes with $>PO_2$-type ligands are colourless oils or solids. Molecular weight measurements on a number of triorganotin(IV) complexes containing oxyphosphorus acids show them to be oligomeric (**1**) in solution at low concentration, with the degree of association varying between 6.6 and 1.8 [10,13]. Similar conclusions have been drawn from IR and Raman spectroscopic data [10,13,19]. The C_3Sn symmetrical stretching mode at 500 cm^{-1} in the Raman spectrum of $Me_3SnOOPMe_2$ has been attributed to the equatorial methyl groups in a trigonal bipyramidal plane [10].



1

The ^{119}Sn Mössbauer spectra of a large number of triorganotin phosphates have been recorded [10–12,22,23] and the large *QS* (quadrupole splitting) values (3.72–4.1 mm s^{-1} for trialkyltin and 3.54 mm s^{-1} for triphenyltin) have been interpreted in terms of polymeric structures in which tin adopts a trigonal bipyramidal geometry with bridging O–P–O linkage. The $^2J(^{119}Sn\text{–}^1H)$ (about 73 Hz) and $^1J(^{119}Sn\text{–}^{13}C)$ (460–550 Hz) values and ^{119}Sn nuclear magnetic resonance (NMR) chemical shifts (−32 to −61 ppm) of triorganotin dialkylphosphates $[R_3SnOOP(OR')_2]$ (where $R \equiv R' \equiv$ Me, Bu) indicate that the tin atom is pentacoordinated in these complexes [11,21,24]. Variable-temperature ^{31}P NMR data of $[R_3Sn\{OP(O)H(OR')\}]$ suggest that open-chain as well as cyclic structures exist in solution [21]. The *P,P'*-dialkylphosphates appear to be much weaker ligands than the dialkylphosphates, since the ^{119}Sn NMR chemical shift of $[(Bu_3Sn)_2\{OP(O)(OBu)\}_2O]$ (94 ppm) lies in a four-coordinate region [24]. The ^{119}Sn NMR spectra of $[(Bu_3SnO)_3P(O)]$ (88.2, -106.0 ppm) and $[(Bu_3SnO)_2P(O)Ph]$ (104.0, -85.8 ppm) display two resonances which at -50°C split into a doublet (down field signal) and a triplet (high field signal) owing to phosphorus coupling and are assigned to the presence of both four- and five-coordinate tin in the molecules. The variable-temperature data indicate that there is exchange between four- and five-coordinate sites [23].

The polymeric structures suggested for these complexes on the basis of spectroscopic data were confirmed by X-ray structural analyses of a number of triorganotin complexes [14,18,22,25]. The molecular unit of $[Ph_3Sn\{OOP(OPh)_2\}]$ (Fig. 1) consists of a centrosymmetric cyclic hexamer in which planar triphenyltin groups are axially bridged by O–P–O linkages [25]. The 24-atom ring of the hexamer (**2**) is moderately puckered into a chair conformation. The tin atom is in a trigonal bipyramidal configuration. The structures of $[Me_3SnOOPX_2]$ ($X \equiv Cl$ or Me) consist of polymeric chains of Me_3Sn groups and O_2PX_2 units (**3**) [18]. The phosphinate chains ($X \equiv Me$) form vast helixes whereas the dichlorophosphate ($X \equiv Cl$) forms almost planar chains. The molecular structure of $[Me_3SnOOP(OH)Ph]$ consists of an infinite, one-dimensional helical polymer. The chains are bent through tetrahedrally coordinated phosphorus atoms. The adjacent helixes turn in opposite directions and are cross-linked by a network of hydrogen bonds to form two-dimensional

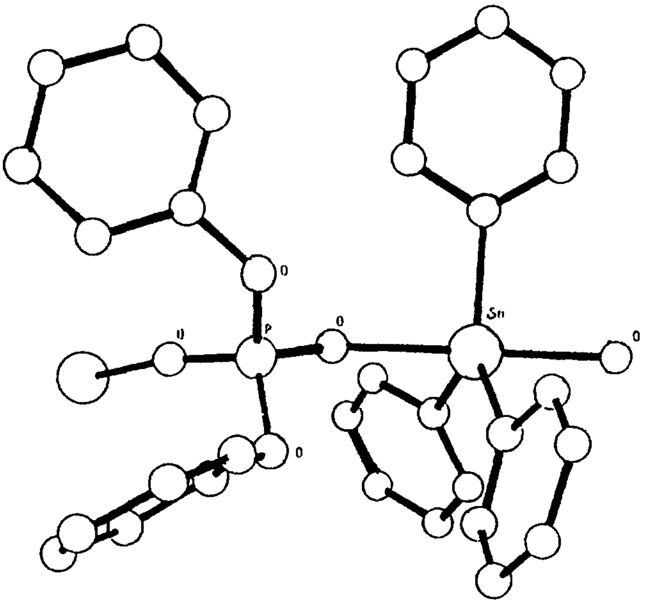
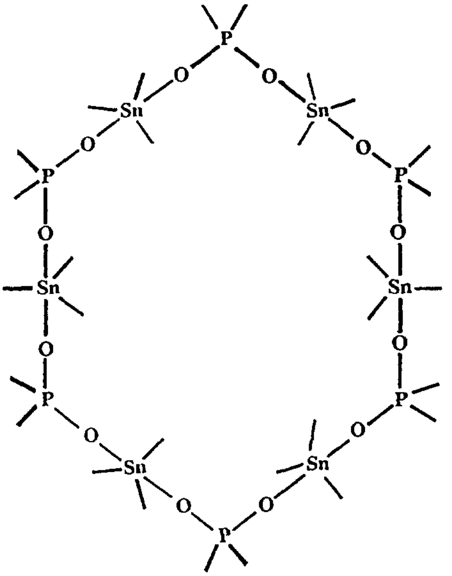
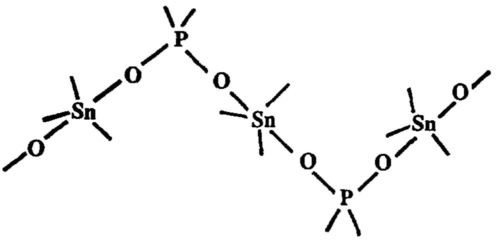


Fig. 1. Crystal structure of $[Ph_3Sn\{OOP(OPh)_2\}]$. (From ref. 25, reproduced with the permission of the American Chemical Society.)



2



3

sheets (**4**) [22]. The trimethyltin units are axially bridged by an O–P–O linkage with a tin atom in a trigonal bipyramidal configuration.

2.2. With >POS-type ligands

Triorganotin monothiophosphates and phosphinates can be prepared by a variety of reaction routes [26–33]. They have been prepared conveniently by the reaction of triorganotin halides with the sodium salt of the acid (eqn. (9)) [27–29,31]. Oxidation of $Bu_3SnOPBu_2$ with sulphur and $R_3SnSP(OEt)_2$ with oxygen readily yields $Bu_3SnOSPBu_2$ and $R_3SnOSP(OEt)_2$ respectively (eqn. (10)) [26,33]. Treatment of $(Me_3Sn)_2O$ with R'_2PSCl ($R'_2 \equiv Me_2$, MePh, Ph_2) affords $Me_3SnOSPR'_2$ (eqn. (11)) [32]. Reaction of trimethyltin hydride with various phosphorus–sulphur compounds such as $(Me_2PS)_2O$, $(RO)_2P(O)SR$ or $(RO)_2P(O)SSR$, via the trimethyltin radical, yields $Me_3SnOSPX_2$ ($X \equiv Me$ or OR) (eqns. (12) and (13)) [30].

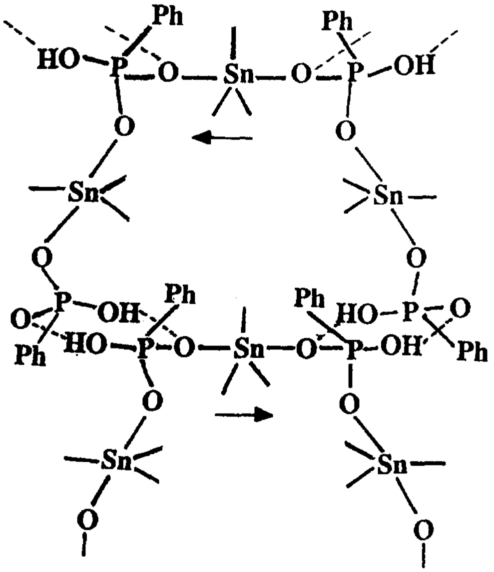
$$R_3SnCl + NaOSP(OR')_2 \rightarrow [R_3SnOSP(OR')_2] + NaCl \quad (9)$$

$$8R_3SnOPR'_2 + S_8 \rightarrow 8[R_3SnOSPR'_2] \quad (10)$$

$$(Me_3Sn)_2O + R'RPSCl \rightarrow [Me_3SnOSPRR'] + Me_3SnCl \quad (11)$$

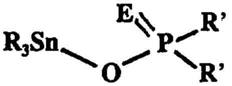
$$Me_3SnH + (R'O)_2POSR'' \rightarrow [Me_3SnOSP(OR')_2] + R''H \quad (12)$$

$$3Me_3SnH + (Me_2PS)_2O \rightarrow [Me_3SnOSPMe_2] + (Me_3Sn)_2S + Me_2PH + H_2 \quad (13)$$

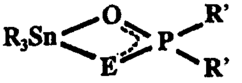


4

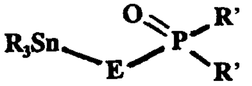
Spectroscopic data (IR, NMR and Mössbauer) obtained for a number of complexes give mixed results regarding the coordination number of tin. The absence of νP=O absorption at ca. 1250 cm^{-1} and the presence of νP=S at 770 cm^{-1} in the IR spectra of [$R_3SnOSP(O^iPr)_2$] (R ≡ Me or Ph) have indicated the formation of an O-bonded four-coordinate structure (5) [27]. The $^2J(^{119}Sn–^1H)$ value for the trimethyltin complex (63 Hz) is in accordance with a four-coordinate structure. Interestingly, the magnitude of $^2J(^{119}Sn–^1H)$ (74 Hz) for [$Me_3SnOSP(OMe)_2$] revealed a higher coordination number for tin [31]. Similar conclusions were drawn from ^{31}P NMR data of [$R_3Sn\{OSP(O^iPr)_2\}$] (R ≡ Me or Ph) (6) [28], although these authors [27] initially assigned the ^{31}P chemical shift to an O-bonded ligand moiety. Contrary to this finding, the ^{119}Sn NMR chemical shift for [$Bu_3SnOSP(OMe)_2$] (68.4 ppm) is in the range of four-coordinate tin compounds (5 or 7) [31]. A similar four-coordinate structure has been suggested for [$Ph_3SnOSeP(O^iPr)_2$] with Se–Sn bonding on the basis of ^{31}P NMR data [28]. The large *IS* (isomer shift) and *QS* values in the Mössbauer spectra of



5



6



7

(E ≡ S or Se; R′ ≡ alkyl or alkoxyl)

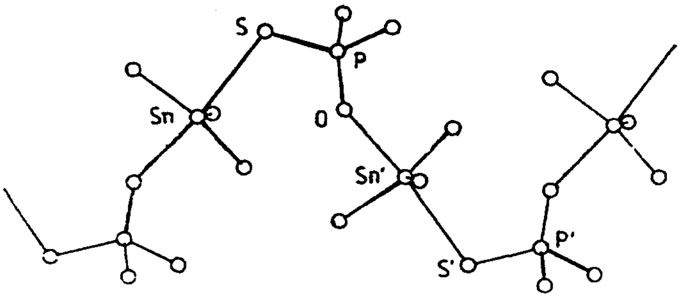


Fig. 2. Molecular structure of [$Me_3Sn(OSPMe_2)$]. (From ref. 32, reproduced with the permission of Elsevier.)

[$R_3Sn\{OSP(OR')_2\}$] (where R ≡ Me, Bu, Ph, Bz; R' ≡ Me, ^{i}Pr, Ph), except for tribenzyltin complexes, have been assigned to a tin coordination number greater than four [31]. The *IS* and *QS* values (1.81 and 2.97 mm s^{-1} respectively) for [$Bz_3SnOSP(OPh)_2$] have been attributed to four-coordinate tin [31]. This structural ambiguity has been resolved by the X-ray structure determination of one complex, trimethyltin dimethylthiophosphinate, [$Me_3SnOSPMe_2$] [32]. This complex has a five-coordinate tin atom and consists of chains in which planar Me_3Sn units and tetrahedral Me_2POS groups are linked by the O and S atoms of the thiophosphinate group (Fig. 2) [32].

2.3. *With >PS_2-type ligands*

Triorganotin(IV) complexes with diorganodithiophosphoric acids and diorganodithiophosphinic acids have been prepared by the reactions of triorganotin oxides (hydroxides) with free acids or by treatment of triorganotin chloride with the sodium, ammonium or lead salt of the acids (eqns. (14) and (15)) [34–41]. Reaction of tetraethyltin with dithiophosphorus acids leads to the formation of triethyltin dithiophosphate complexes with the elimination of ethane [36].

$$(R_3Sn)_2O + 2R'_2PSSH \rightarrow 2[R_3SnSSPR'_2] + H_2O \qquad (14)$$

$$R_3SnCl + MSSP(OR')_2 \rightarrow [R_3SnSSP(OR')_2] + MCl \qquad (15)$$

($M \equiv Na$ or NH_4)

Unlike oxygen derivatives, triorganotin dialkyldithiophosphates are monomeric in benzene [38]. Infrared spectra of these complexes are not informative in distinguishing various structural possibilities [38,39]. The magnitudes of ^2J(Sn–H) (57 Hz) and ^1J(Sn–C) (about 360 Hz) for trimethyltin complexes [39–41] have shown that the tin atom in these complexes is four coordinated. However, the Mössbauer data (*IS* and *QS*) suggest five-coordinate structures for trialkyltin dialkyldithiophosphates

[39,40] but a four-coordinate geometry for tricyclohexyl- and triphenyltin complexes [39]. The solid state ^{119}Sn NMR shift for [$Ph_3SnSSP(OEt)_2$] [42] has been attributed to four-coordinate tin as inferred from Mössbauer data. The ^{119}Sn NMR chemical shifts for triorganotin dialkyldithiophosphates in solution (less than 100 ppm), in contrast with the Mössbauer data, lie in the range of four-coordinate tin compounds [40]. This conflicting situation may be attributed to inter- or intramolecular bond rupture on dissolution. The variable-temperature ^{119}Sn NMR spectra of [$Me_3Sn\{SSP(OEt)_2\}$] [43] have revealed a rapid intermolecular dithiophosphate group exchange. The coordination number of tin did not change on lowering the temperature; at −100°C a doublet resonance (^2J(Sn–P) = 31 Hz) has been observed with little change in the chemical shift. It may be noted that HeI and HeII photoelectron spectra of [$Me_3SnSSPMe_2$] have been interpreted in terms of a distorted trigonal bipyramidal configuration with both sulphur atoms bonded to tin [44].

Conclusions drawn from the NMR data were further supported by the X-ray structural analyses of [$Ph_3SnSSP(OEt)_2$] (Fig. 3) [45] and [$Ph_3Sn\{SSP(OCMe_2CMe_2O)\}$] [46]. Both phosphorus and tin atoms in these complexes adopt a distorted tetrahedral geometry. However, the structure of a complex [$R_2Sn\{CH_2CH_2P(S)(Ph)S\}(HMPT)$] formed by sulphur oxidation of [$R_2SnH(CH_2CH_2P(H)Ph)$] (R ≡ Me, ^{t}Bu) in HMPT (eqn. (16)) exhibited a slightly distorted trigonal bipyramidal geometry [47].

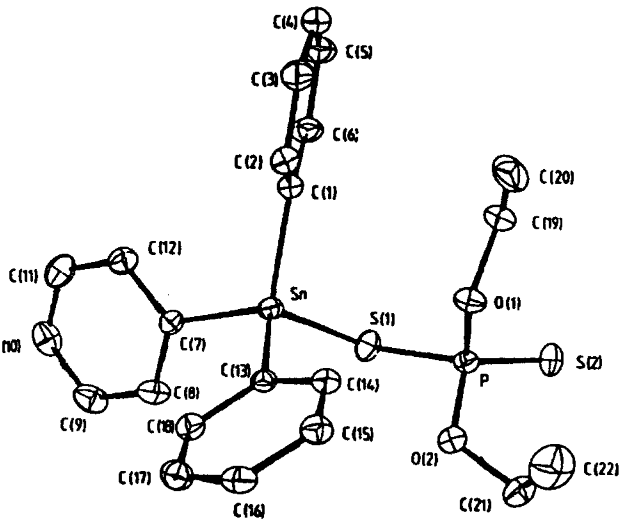


Fig. 3. Crystal structure of [$Ph_3Sn\{SSP(OEt)_2\}$]. (From ref. 45, reproduced with the permission of the American Chemical Society.)

$$\begin{tikzcd} {[R_2Sn(H)CH_2CH_2P(H)Ph]} \arrow[r, "S_8"] & {[R_2SnCH_2CH_2P(S)S(Ph)]} \arrow[d, "HMPT"] \\ & {[R_2SnCH_2CH_2P(S)S(Ph)\cdot HMPT]} \end{tikzcd} \quad (16)$$

$(R \equiv Me$ or ${}^tBu$; $HMPT \equiv (Me_2N)_3PO)$

3. DIORGANOTIN(IV) COMPLEXES

3.1. *With >PO$_2$-type ligands*

A number of diorganotin(IV) complexes with diorganophosphoric and -phosphinic acids [10–13,24,48–51], organophosphonic acid ($RP(O)(OH)_2$) [10,52–54] and phenylphosphoric acid ($(PhO)P(O)(OH)_2$) [48] have been synthesized (eqns. (17)–(21)). They can be obtained conveniently by the reaction of diorganotin oxide with free acid or by treatment of diorganotin dichloride with the sodium salt of the acid in an inert solvent. Reaction of diorganotin oxide with dibutylphosphoric acid in a 1:1 stoichiometric ratio affords tetraorganodistannoxanes (eqn. (22)) [49]. Treatment of $[R_2Sn\{OOP(O^nBu)_2\}_2]$ with diorganotin dichloride readily gives monochlorotin complexes $[R_2Sn(Cl)\{OOP(O^nBu)_2\}]$ [49]. Diorganotin bis(*o*-alkylphosphonates) $[R_2Sn\{OOP(H)(OR')\}_2]$ ($R \equiv Me$, ${}^nBu$, ${}^tBu$, Oct, Bz; $R' \equiv Me$, Et, ${}^iPr$) have been prepared by the reaction of diorganotin dichloride with $(R'O)_2POH$ in polar solvents of high boiling point [55].

$$R_2SnCl_2 + 2(PhO)_2POOH \xrightarrow{methanol} [R_2Sn\{OOP(OPh)_2\}_2] + 2HCl \quad (17)$$

$$R_2SnO + 2R'_2POOH \xrightarrow{benzene} [R_2Sn(OOPR'_2)_2] + H_2O \quad (18)$$

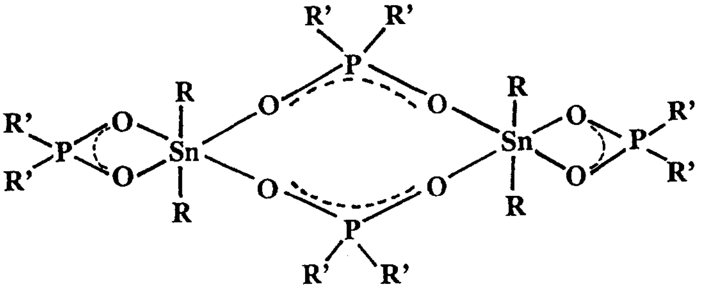
$$R_2SnCl_2 + Na_2O_3P(OPh) \xrightarrow{water} [R_2Sn\{O_3P(OPh)\}] + 2NaCl \quad (19)$$

$$R_2SnCl_2 + NaO_2P(OH)Ph \xrightarrow{methanol} \alpha\text{-}[R_2Sn(O_3PPh)] + NaCl + HCl \quad (20)$$

$$\begin{tikzcd} R_2SnCl_2 + Na_2O_3PPh \arrow[r] & {[R_2Sn(O_3PPh)]\cdot H_2O + 2NaCl} \arrow[d, "heat in vacuo"] \\ & {\beta\text{-}[R_2Sn(O_3PPh)]} \end{tikzcd} \quad (21)$$

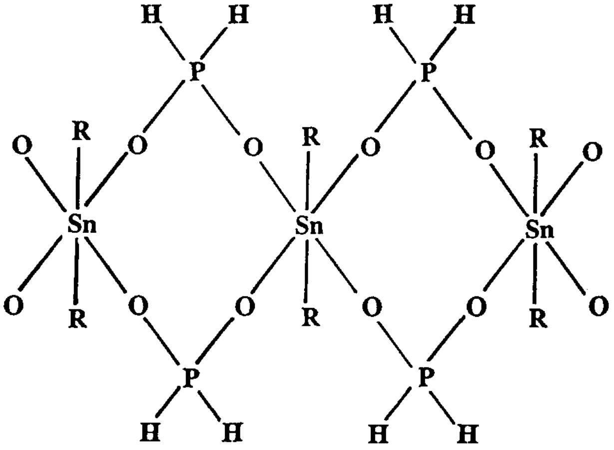
$$4R_2SnO + 4(BuO)_2POOH \rightarrow [(R_2Sn\{OOP(OBu)_2\})_2O]_2 + 2HO \quad (22)$$

Osmometric molecular weight measurements on diorganotin(IV) complexes of organophosphoric acids revealed their oligomeric nature [10]. However, diorganotin bis(diorganophosphinates) are dimeric in nature and a structure with two bridging and one chelating phosphorus acid moiety has been suggested (**8**) [10]



8

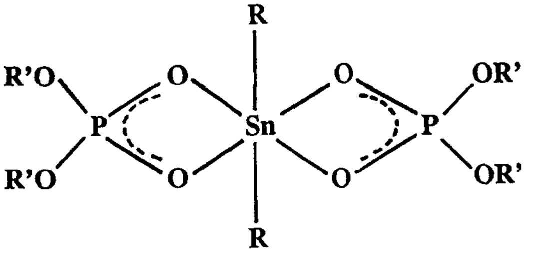
The high *QS* values (3.84–4.91 mm s^{-1}) of diorganotin bis(diphenylphosphates) [11], bis(diorganophosphinates) [10,50] and bis(phenylphosphoric phenylester) [12] have been attributed to an octahedral configuration with a trans R_2Sn arrangement. Observation of a strong Mössbauer spectrum at room temperature has been ascribed to a lattice consisting of intermolecularly associated units propagating in at least one dimension [11,48]. A similar sheet-like structure has been proposed for hypophosphite analogues $[R_2Sn(O_2PH_2)_2]$ (**9**) [56]. Variable-temperature



9

Mössbauer data suggest that $[Ph_2Sn(O_3PPh)]$ consists of infinite chains whereas α-$[Me_2Sn(O_3PPh)]$ has a more associated three-dimensional network in which tin is in a slightly distorted octahedral site [54]. The β-$[Me_2Sn(O_3PPh)]$ has been suggested to contain four- or five-coordinate tin, since the *IS* and *QS* values are smaller than for the α form (e.g. *IS* and *QS* values for α and β forms are 1.11, 3.55 and 0.94, 3.06 mm s^{-1} respectively). The α and β forms differ in the extent of association of their lattices.

In contrast with the Mössbauer results, the ^{119}Sn NMR results on diorganotin(IV) bis(dialkylphosphates) show that the ligand coordinates with the tin atom in a chelating manner (**10**) [24,29]. The solid state structure is retained in solution, since the ^{119}Sn (Fig. 4) and ^{31}P NMR chemical shifts of [$Me_2Sn\{OOP(O^nBu)_2\}_2$] did not change significantly in the solid state [51]. A linear trans arrangement of the alkyl groups on tin has been suggested from the estimated C–Sn–C angle in [$Me_2Sn\{OOP(O^nBu)_2\}_2$] (179.4°) using ^1J(Sn–C) values [49]. The $^2J(^{119}Sn–^{31}P)$ value (about 200 Hz) observed at lower temperatures is much larger than for the corresponding dithio acid complexes, indicating the presence of a strongly chelating phosphate group [49]. The ^{31}P NMR spectrum of [$^nBu_2Sn(O_3POct)$] shows a single resonance with two different values of $^2J(^{119}Sn–^{31}P)$ (144 and 172 Hz). This has been assigned to a bridging phosphinate group (**8**) [10].



10

Pentacoordinate tin in [$R_2Sn(Cl)\{OOP(O^nBu)_2\}$] has been suggested on the basis of NMR (^{13}C, ^{31}P and ^{119}Sn) data [49]. The complexes [$(R_2Sn\{OOP(O^nBu)_2\})_2O]_2$ display two ^{119}Sn NMR resonances and two ^{13}C NMR signals for R–Sn carbons. The ^{31}P NMR spectra in solution, however, show a single resonance at room temperature, but at lower temperatures the signal is flanked by ^{119}Sn satellites (92 and 59 Hz). The solid state ^{31}P NMR spectrum of [$(Bu_2Sn\{OOP(O^nBu)_2\})_2O]_2$ exhibits two separate signals (−3.3 and −8.6 ppm) and a structure similar to dicarboxylato tetraorganodistannoxanes has been suggested [49].

The Mössbauer spectrum of tris(dimethyltin) bis(orthophosphate)octahydrate, [$(Me_2Sn)_3(PO_4)_2$]·$8H_2O$, suggests the presence of only one type of tin atom which is in an octahedral environment [57]. However, the X-ray structural analysis shows that the molecule consists of infinite ribbons in which there are two different types of tin atoms in an octahedral configuration. The coordination environment around one tin atom (inner) is almost regular octahedral comprising two trans methyl groups (C–Sn–C angle 178.1(14)°) and four oxygen atoms from four bridging phosphate

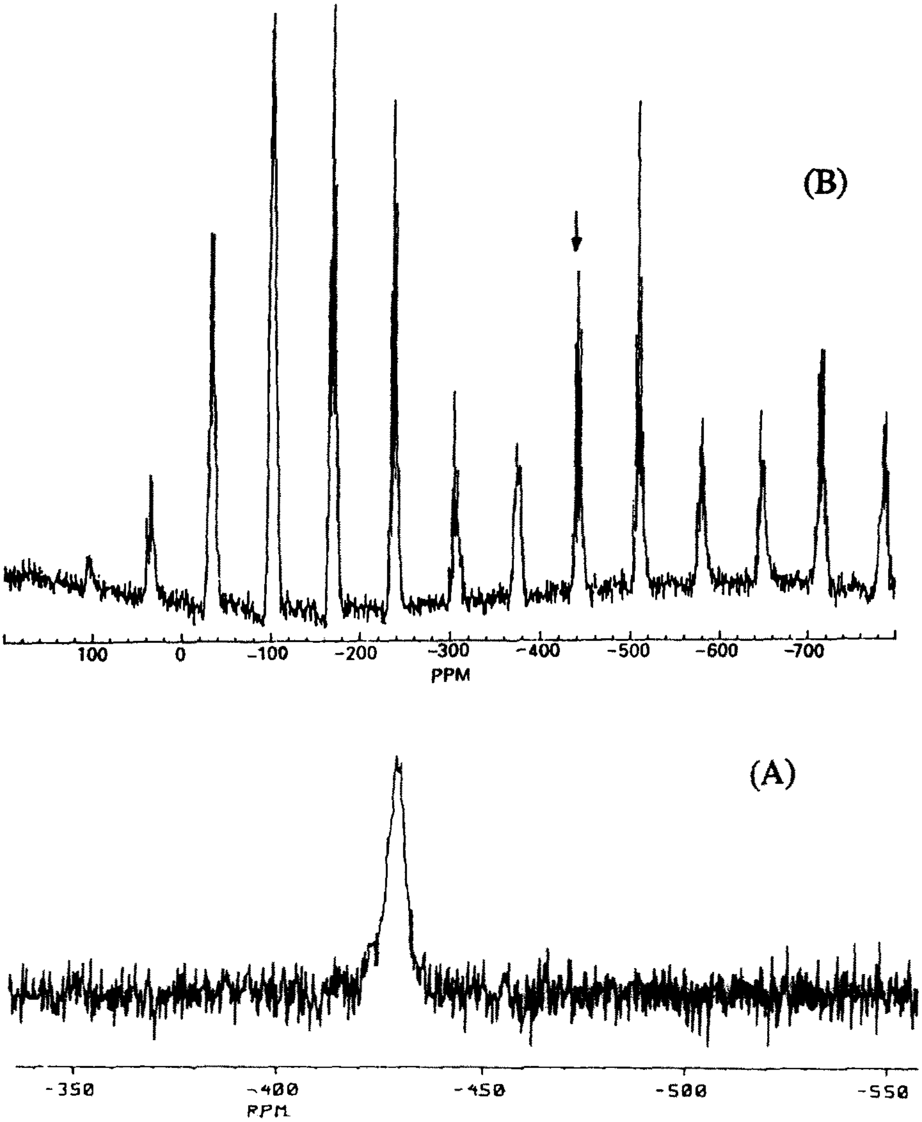
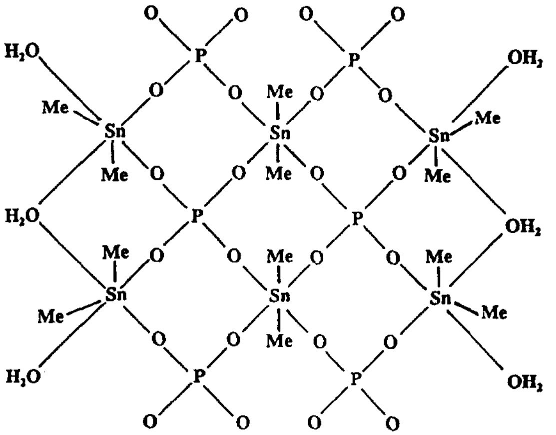


Fig. 4. ^{119}Sn NMR spectra of $[Me_2Sn\{OOP(O^nBu)_2\}_2]$ (A) in CD_2Cl_2 solution and (B) in the solid state. (From ref. 51, reproduced with the permission of Pergamon Press.)

groups. The configuration of the other two tin atoms (outer) is severely distorted octahedral formed by two skewed methyl groups (C–Sn–C angles 145.4(16)°, 151.1(15)°), two oxygen atoms of bridging phosphate groups and two cis water molecules. The tin atoms are linked by phosphate tetrahedra, leading to eight-membered rings in chair conformations (**11**) [57]. Solid state ^{13}C NMR spectra of microcrystalline polymeric dimethyltin hydrogenphosphate, $[Me_2Sn(O_4PH)]_n$, dis-



11

play three resonances for methyltin carbon atoms. The Me–Sn–Me angles estimated from ^1J(Sn–C) values are in the range 143°–147°. The data have been interpreted in terms of linear polymeric chains [58].

3.2. *With >POS-type ligands*

Diorganotin bis(dialkylthiophosphates) have been synthesized by the reaction of diorganotin dichloride with the sodium or ammonium salt of the ligand (eqns. (23) and (24)) [28,31,51,59–61].

$$R_2SnCl_2 + 2NH_4OSP(OR')_2 \xrightarrow{\text{benzene}} [R_2Sn\{OSP(OR')_2\}_2] + 2NH_4Cl \qquad (23)$$

$$R_2SnCl_2 + [R_2Sn\{OSP(OR')_2\}_2] \rightarrow 2[R_2Sn(Cl)\{OSP(OR')_2\}] \qquad (24)$$

The Mössbauer data for the dioctyltin complex $[Oct_2Sn\{OSP(OMe)_2\}_2]$ ($IS = 1.81$ mm s^{-1} and $QS = 2.97$ mm s^{-1}) are typical of four-coordinate tin complexes [31]. On the other hand, very large *IS* and *QS* values observed for $[R_2Sn\{OSP(OR')_2\}_2]$ (R ≡ Me, Et, ^{n}Bu, Ph) suggest six-coordinate tin with trans diorganotin groups and bridging ligand moieties bonded through the oxygen atom only [31]. The ^{31}P NMR spectra of these complexes showed one to four peaks in $CDCl_3$ solution [31]. However, the ^{31}P NMR shift for $[Ph_2Sn\{OSP(O^iPr)_2\}_2]$ (34.97 ppm) has been assigned to a chelating ligand moiety [28]. Extensive NMR studies in the author's laboratory, however, suggests a largely anisobidentate mode of bonding of the dialkylmonothiophosphate group [51,60,61]; the C–Sn–C angle (130.1°) for $[Me_2Sn\{OSP(O^nBu)_2\}_2]$ (estimated from ^1J(Sn–C)) and ^{119}Sn NMR chemical shifts have been assigned to a distorted octahedral geometry. The observation of a broad ^{119}Sn NMR signal for di-*n*-alkyltin complexes and a triplet due to

${}^2J(^{119}\mathrm{Sn}-^{31}\mathrm{P})$ (about 85 Hz) for di-*t*-butyltin derivatives at room temperature has been ascribed to a dynamic stereochemistry for the former and a rigid structure for the latter [60].

Unlike diorganotin(IV) complexes with dialkyldithiophosphoric acids (Section 3.3) or dialkylphosphoric acids (Section 3.1), the monothiophosphates are sensitive to atmospheric moisture and readily give intermediate hydrolysis products [60–62]. The structure of the latter depends on the nature of the R groups on the tin and phosphorus atoms. Both hydroxo- $[\mathrm{R_2Sn}(\mu\text{-OH})\{\mathrm{SSP(OR')_2}\}]_2$ (eqn. (25)) and tetraorganodistannoxanes $[(\mathrm{R_2Sn}\{\mathrm{OSP(OR')_2}\})_2\mathrm{O}]_2$ (eqn. (26)) are formed which contain oxygen-bonded ligand moieties. The hydroxo-bridged [60,62] complexes (Fig. 5) are centrosymmetric dimers with a planar $\mathrm{Sn_2O_2}$ ring. The tin–sulphur distances do not show any dative interactions and the tin atom is best described as being five coordinated. In the case of $[\mathrm{Ph_2Sn}(\mu\text{-OH})\{\mathrm{OSP(OPh)_2}\}]_2$ the sulphur and hydroxyl oxygen atoms within each molecular unit are brought together at 3.121(2) Å by a hydrogen bond interaction [62]. The molecule $[(\mathrm{Me_2Sn}\{\mathrm{OSP(OEt)_2}\})_2\mathrm{O}]_2$ is centrosymmetric about a central $\mathrm{Sn_2O_2}$ core with two independent tin atoms. Each of the two exocyclic tin atoms are connected to the central core via an oxygen atom. The thiophosphate moiety coordinates exclusively through the oxygen atom and also bridges the endocyclic tin [60] (Fig. 6). This is evident from the ^{119}Sn NMR spectra, where the exocyclic tin showed a triplet pattern while the endocyclic tin gave a broad singlet (Fig. 7).

$$2[{}^t\mathrm{Bu_2Sn}\{\mathrm{OSP(OR')_2}\}_2] + \mathrm{H_2O} \rightarrow [{}^t\mathrm{Bu_2Sn}(\mu\text{-OH})\{\mathrm{OSP(OR')_2}\}]_2 + 2(\mathrm{R'O})_2\mathrm{POSH} \qquad (25)$$

$$4[\mathrm{Me_2Sn}\{\mathrm{OSP(OEt)_2}\}_2] + 2\mathrm{H_2O} \rightarrow [(\mathrm{Me_2Sn}\{\mathrm{OSP(OEt)_2}\})_2\mathrm{O}]_2 + 4(\mathrm{EtO})_2\mathrm{POSH} \qquad (26)$$

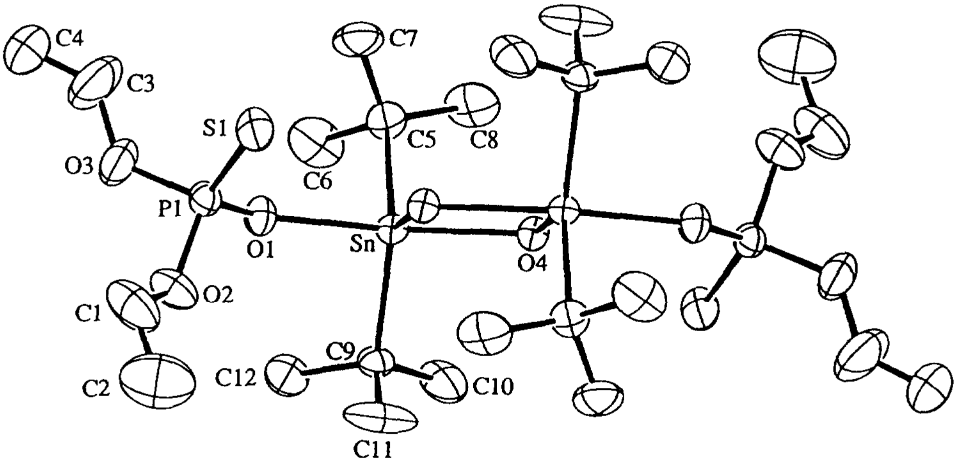


Fig. 5. Crystal structure of $[{}^t\mathrm{Bu_2Sn}(\mu\text{-OH})\{\mathrm{SOP(OEt)_2}\}]_2$.

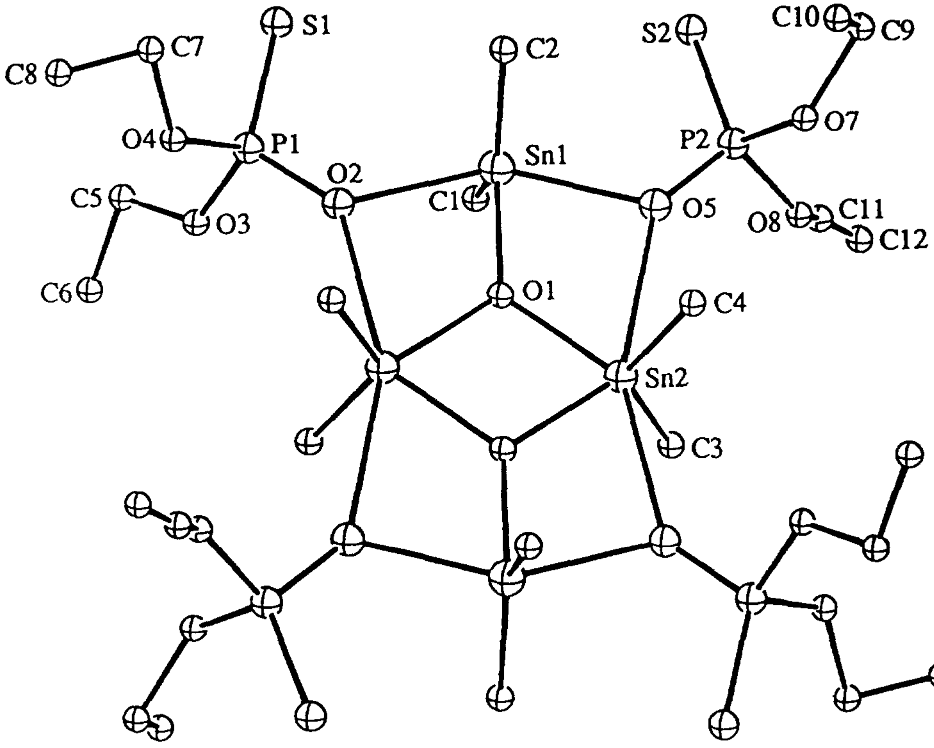


Fig. 6. Crystal structure of $[(Me_2Sn\{SOP(OEt)_2\})_2O]_2$.

3.3. *With >PS_2-type ligands*

Diorganotin(IV) bis(dialkyldithiophosphates) [40,59,63–67] and diorganophosphinates [35,41,68–71] have been synthesized conveniently by the reactions of diorganotin oxides with free acid or diorganotin halides with the sodium or ammonium salt of the acid in 1:2 stoichiometry (eqns. (27) and (28)). The latter reactions [43] in 1:1 stoichiometry (eqn. (29)) yield monochlorotin complexes $[R_2Sn(Cl)\{SSP(OR)_2\}]$ which can also be obtained by treatment of $[R_2Sn\{SSP(OR)_2\}_2]$ with R_2SnCl_2 [67].

$$R_2SnO + 2R'_2PSSH \rightarrow [R_2Sn(SSPR'_2)_2] + H_2O \qquad (27)$$

$$R_2SnCl_2 + 2NH_4SSP(OR')_2 \rightarrow [R_2Sn\{SSP(OR')_2\}_2] + 2NH_4Cl \qquad (28)$$

$$R_2SnCl_2 + NH_4SSP(OR')_2 \rightarrow [R_2Sn(Cl)\{SSP(OR')_2\}] + NH_4Cl \qquad (29)$$

Molecular weight measurements [64] and mass spectral data [65] are indicative of a monomeric nature. On the basis of ^{31}P NMR chemical shifts, monodentate bonding of the dialkyldithiophosphate has been suggested (**12**) [64]. Subsequent studies, however, established a bidentate mode of bonding (**13**). The $^2J(^{119}Sn–^1H)$

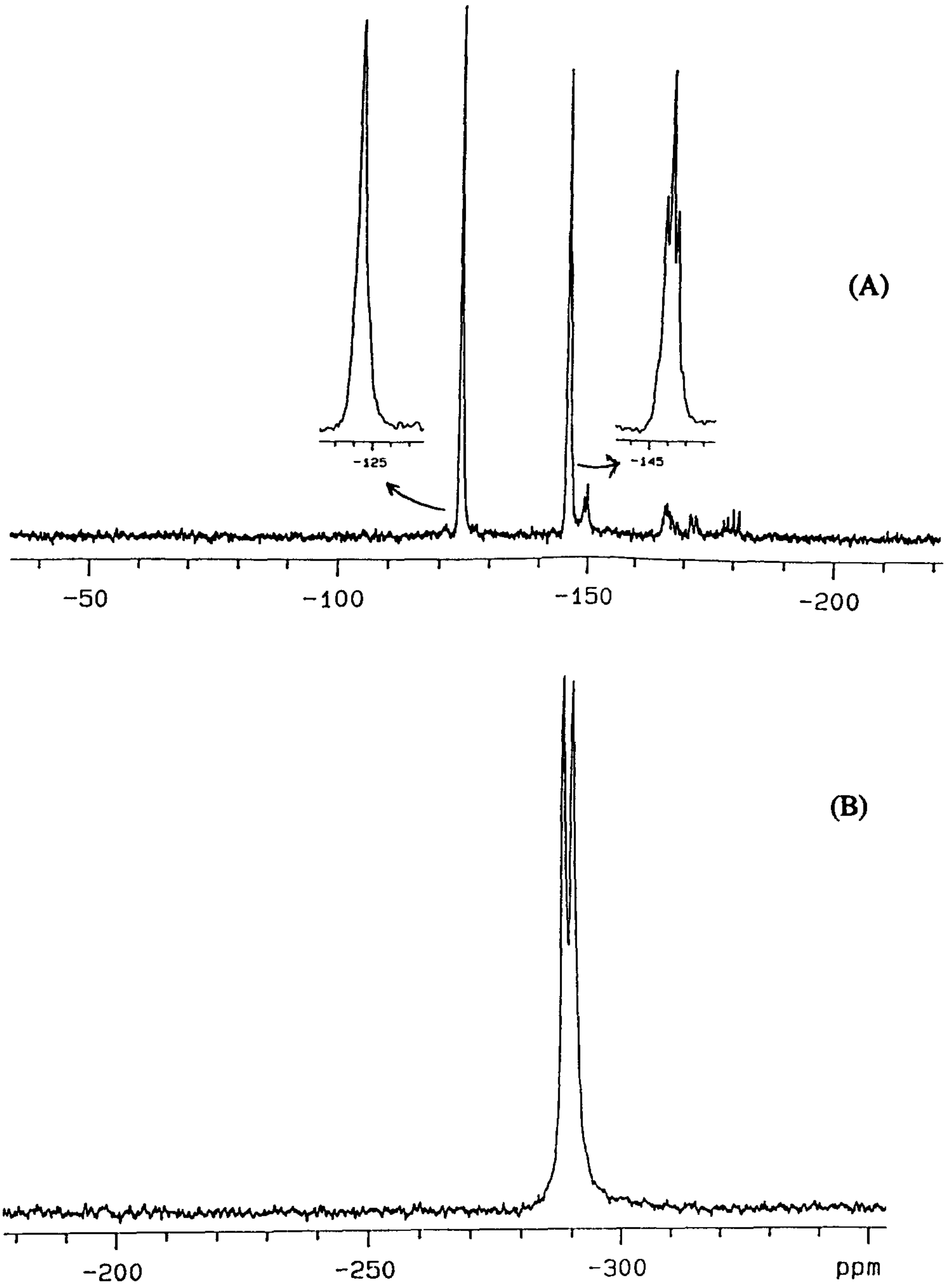
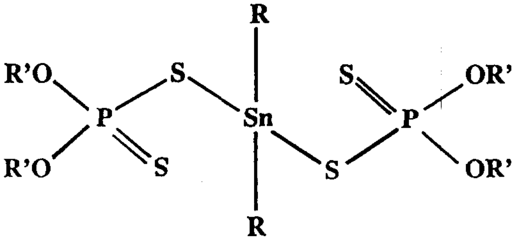
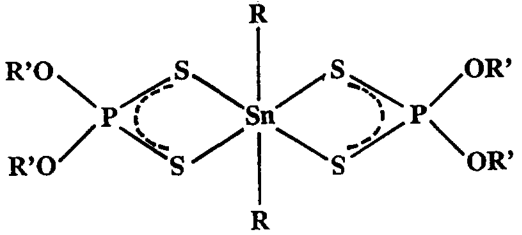


Fig. 7. $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR spectra of (A) $[(\mathrm{Me_2Sn\{SOP(OEt)_2\}})_2\mathrm{O}]_2$ and (B) $[{}^{t}\mathrm{Bu_2Sn}(\mu\text{-OH})\{\mathrm{SOP(OEt)_2}\}]_2$ in $\mathrm{CDCl_3}$.



12



13

(76–80 Hz) and $^1J(^{119}Sn–^{13}C)$ values for dithiophosphate complexes are greater than expected for four-coordinate tin compounds. The C–Sn–C angle estimated from $^1J(Sn–C)$ couplings in solution for the dimethyltin complex $[Me_2Sn\{SSP(O^nBu)_2\}_2]$ (125.5°) revealed an anisobidentate mode of bonding of the dithio ligand moieties [51]. The ^{119}Sn NMR chemical shifts (−154 to −268 ppm) [40,43,66,67] have been assigned to six-coordinate tin. The ^{119}Sn NMR shifts in solution do not vary noticeably with changes in the structure (anisobidentate or symmetrical chelating). The observed variation in the shifts has been assigned to electronic and steric effects of the groups attached to tin and phosphorus atoms. The ligand moieties behave in an anisobidentate fashion in solution [51,67]; upon lowering the temperature, the signal moves to lower frequency (shielding by less than 64 ppm) and occurs in the region for six-coordinate tin compounds [43]. The tin chemical shift for $[Me_2Sn\{SSP(OCMe_2CMe_2O)\}_2]$ (−206.8 [66], −210 ppm [72]) in dichloromethane solution and in the solid state (−257 ppm [72]) varies by about 50 ppm. Such changes have been attributed to minor changes in the molecular geometry rather than to an increase in the coordination number of tin [72]. Variable-temperature NMR (^{31}P and ^{119}Sn) has revealed a dynamic stereochemistry of these molecules, because on lowering the temperature to −40°C, $^2J(^{119}Sn–^{31}P)$ (about 40 Hz) is resolved; the process is intramolecular (monodentate$\rightleftharpoons$bidentate exchange equilibrium) in nature [43]. However, the monochlorotin complexes $[R_2Sn(Cl)\{SSP(OR')_2\}]$ have a rigid stereochemistry at room temperature, since $^2J(^{119}Sn–^{31}P)$ 36–54 Hz) can be observed [43,67]. The ^{119}Sn NMR chemical shifts

TABLE 1

Structures of organotin(IV) complexes with phosphorus-based acids

Complex	Comments	Ref.
$[Me_3SnOOPMe_2]$	Polymeric chains of $SnMe_3$ units; tin in trigonal bipyramidal configuration	[18]
$[Me_3SnOOPCl_2]$	Planar chains; bridging phosphate groups; tin in trigonal bipyramidal configuration	[18]
$[Ph_3SnOOP(OPh)_2]$	Centrosymmetric cyclic hexaner; tin in trigonal bipyramidal configuration	[25]
$[Ph_3SnOOP(OMe)Me]$	Planar triphenyltin groups axially bridged by O–P–O linkage to give cyclic hexamer	[14]
α-$[Me_3SnOOP(OH)Ph]$	Infinite one-dimensional polymer with planar Me_3Sn units	[22]
$[Me_3SnOSPMe_2]$	Infinite chains formed by planar Me_3Sn groups and bridging tetrahedral Me_2POS; tin in trigonal bipyramidal configuration	[32]
$[Ph_3SnSSP(OCMe_2CMe_2O)]$	Intermediate between tetrahedral and TBP (Sn–S lengths 2.436(3), 3.411(3) Å)	[46]
$[Ph_3SnSSP(OEt)_2]$	Four-coordinate tin with monodentate thio ligand (Sn–S lengths 2.4582(9) (bonding), 5.326 Å (non-bonding)	[45]
$[Me_2Sn\{CH_2CH_2P(S)(Ph)S\}(HMPT)]$	Tin in TBP configuration; monodentate dithio ligand	[47]
$[{}^tBu_2Sn\{CH_2CH_2P(S)(Ph)S\}(HMPT)]$	Tin in TBP configuration; monodentate dithio ligand	[47]
$[(Me_2Sn)_3(PO_4)_2] \cdot 8H_2O$	Infinite ribbon; contains one regular octahedral and two distorted octahedral tin atoms	[57]
$[Ph_2Sn(\mu\text{-}OH)\{OSP(OPh)_2\}]_2$	Centrosymmetric dimer with planar Sn_2O_2 ring; sulphur and hydroxyl proton are intramolecularly hydrogen bonded (OH $\cdots$ SP length 3.121(2) Å)	[62]
$[{}^tBu_2Sn(\mu\text{-}OH)\{OSP(OEt)_2\}]_2$	Tin in trigonal bipyramidal geometry; ligand is monodentate	[60]
$[(Me_2Sn\{OSP(OEt)_2\})_2O]_2$	Exocyclic tin is five coordinated while endocyclic tin is six coordinated; ligand is monodentate bonded through oxygen	[60]
$[Me_2Sn(SSPMe_2)_2]$	Distorted octahedral tin (C–Sn–C angle 122.6(8)°); ligand is anisobidentate (Sn–S lengths 2.482(2), 3.334(2) Å)	[75]

TABLE 1 (*continued*)

$[Me_2Sn(SSPEt_2)_2]$	Anisobidentate ligand (Sn–S lengths 2.476(2), 3.336(2) Å)	[70]
$[Ph_2Sn\{SSP(OEt)_2\}_2]$	Distorted octahedral tin (Sn–S lengths ca. 2.5, ca. 3.2 Å)	[73]
$[Ph_2Sn\{SSP(O^iPr)_2\}_2]$	Regular octahedral tin: symmetrical bidentate ligand (Sn–S lengths 2.689(1), 2.678(1) Å)	[74]
$[BuSn(O)(OOP^tBu_2)]_4$	Cubic cluster; hexacoordinated tin	[84]
$[BuSn(O)(OOPBz_2)]_4$	Cubic cluster; hexacoordinated tin	[84]
$[BuSn(O)(OOPHx_2)]_4$	Cubic cluster; hexacoordinated tin	[82]
$[BuSn(O)\{OOP(OPh)_2\}]_6$	Cyclic hexamer; drum	[83]
$[BuSn(OH)(OOPHx_2)_2]_2$	Dimeric molecule; contains two hydroxo, two phosphinate bridges and two monodentate phosphinate ligands	[84]
$[(BuSn)_2OH(OOPPh_2)_3(OSPPh_2)]_2$	Extended cluster	[85]
$[Me_2Sn(OH)\{OOP(OPh)_2\}_3\{O_3P(OPh)\}]_2$	Tetranuclear crown	[78]
$[Bu_2Sn_2(O)\{OOP(OH)^tBu\}_4]_2$	Tetranuclear crown	[78]
$[\{MeSn(O)(OAc)\}\{MeSn(O)(OOP^tBu_2)\}]_3$	Drum structure	[83]
$[\{BuSn(OH)(OOPPh_2)\}_3O][OOPPh_2]$	Oxygen-capped cluster	[81]
$[\{BuSn(S)(OOPPh_2)\}_3O]_2Sn$	Heptanuclear double-cube cluster	[86]
$[\{BuSn(O)(OOP^tBu_2)\}\{BuSn(OH)_2(OOP^tBu_2)\}][H][OOP^tBu_2]$	Cyclic dimer; crown cluster	[85]
$[\{MeSn(O)(OOP^tBu_2)\}\{MeSn(OH)(OMe)OOP^tBu_2)\}]_2[H][OOP^tBu_2]\cdot 4MeOH\cdot 2H_2O$	Cyclic dimer; crown cluster	[85]
$[\{BuSn(OH)(OOPHx_2)\}_3O][\{BuSnCl_2(OOPHx_2)\}_2OH]$	Oxygen-capped cluster	[89]
$[\{BuSn(OH)(OOP^tBu_2)\}_4O_2][H][Cl][BuSn(OH)Cl(OOP^tBu_2)]_2$	Crown butterfly cluster	[89]
$[Bu_2Sn_2Cl_2(OH)(OOPPh_2)_3]_2\cdot 2CH_2Cl_2$	Centrosymmetric dimer	[89]

(−71 to −248 ppm) lie in the range expected for five-coordinate tin complexes [43,67].

The ^{119}Sn Mössbauer data for a number of diorganotin(IV) dialkyldithiophosphates and phosphinates have been reported [40,65,69]. The *IS* (1.35–1.56 mm s^{-1}) and *QS* (3.07–3.67 mm s^{-1}) values suggest a six-coordinate trans octahedral geometry for these complexes. The C–Sn–C angles have been estimated employing *QS* values from a point charge approach ($QS = 4\{R\}(1\text{-}3\sin^2\theta\cos^2\theta)^{1/2}$, where $\{R\}$ is the partial quadrupole splitting for group R) and lie in the range 135–180° [65].

Both a symmetrical chelating and an anisobidentate mode of bonding of the dithio ligand have been established by X-ray structural analyses of a number of complexes (Table 1) [70,73–75]. The structures of the dimethyltin bis(dialkyldithiophosphinates) $[Me_2Sn(SSPR_2)_2]$ ($R \equiv Me$ [75], Et [70]) showed a distorted octahedral configuration with a trans dimethyl group. The ligands are severely anisobidentate, the two Sn–S distances being 2.482(2) ($R \equiv Me$), 2.476(2) ($R \equiv Et$) and 3.334(2) (Me), 3.336(2) Å (Et). A similar structure is adopted by $[Ph_2Sn\{SSP(OEt)_2\}_2]$ (Fig. 8) [73]. Each ligand has one normal covalent Sn–S bond of about 2.5 Å, while the other is significantly longer (about 3.2 Å). All the sulphur atoms lie approximately in an equatorial plane around Sn. Interestingly, the dithio ligand in $[Ph_2Sn\{SSP(O^iPr)_2\}_2]$ is symmetrically chelated (Fig. 9), the Sn–S distances being 2.689(1) and 2.678(1) Å [74].

Although these complexes are stable indefinitely in moist air, under certain conditions intermediate hydrolysis products can be isolated. Thus the reaction of bis(arylhydroxydialkylstannoic)oxide with the anhydride of dithiophosphoric acid in chlorobenzene yields tetraorganodistannoxane, $[(R_2Sn\{SSPR'(OAr)_2\})_2O]$ ($R' \equiv$ alkyl, aryl or alkoxy group; $R \equiv$ alkyl group; $Ar \equiv$ substituted or unsubstituted aryl group) [76]. These products have not been fully characterized. Treatment

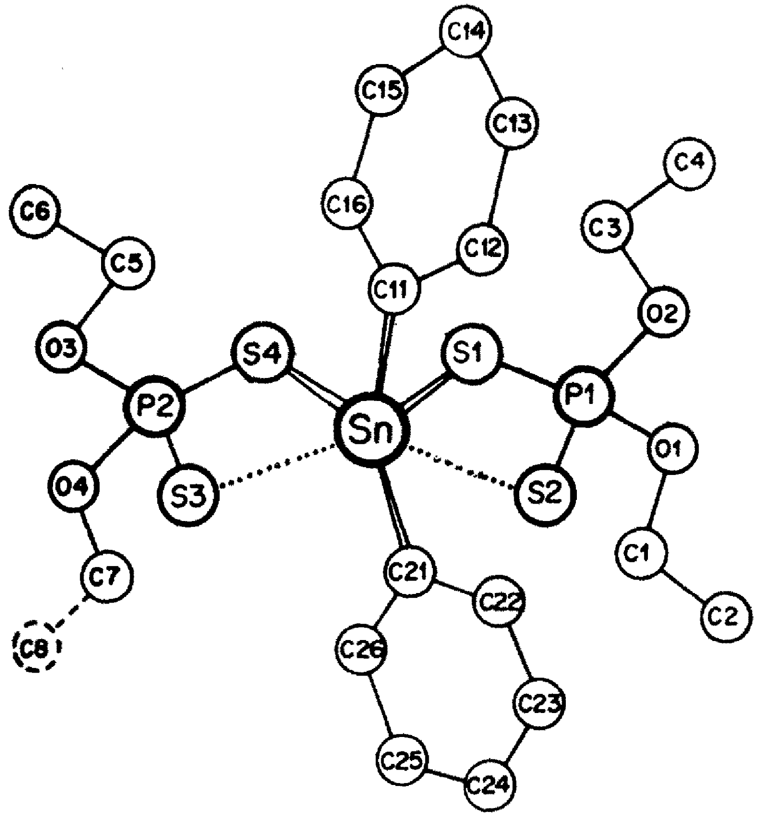


Fig. 8. Crystal structure of $[Ph_2Sn\{SSP(OEt)_2\}_2]$. (From ref. 73, reproduced with the permission of the International Union of Crystallography.)

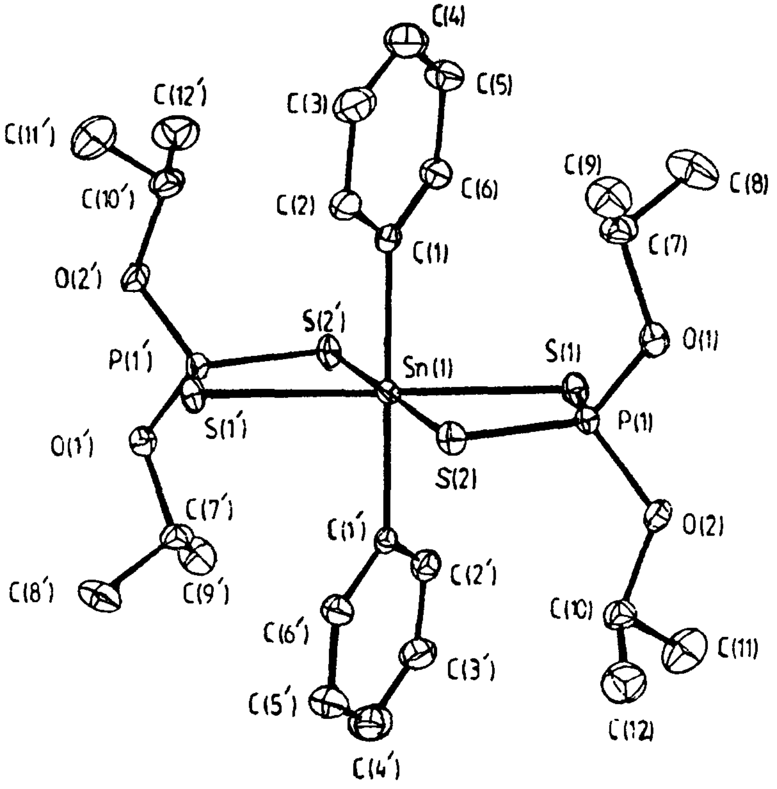


Fig. 9. Molecular structure of [$Ph_2Sn\{SSP(O^iPr)_2\}_2$]. (From ref. 74, reproduced with the permission of the American Chemical Society.)

of diorganotin oxides with dialkyldithiophosphoric acids in a 1 : 1 stoichiometry at room temperature in benzene affords hydroxo complexes [$R_2Sn(\mu\text{-}OH)\{SSP(OR')_2\}]_2$ [77]. The IR spectra show ν(Sn)–OH vibration in the region 3360–3470 cm^{-1}. In the ^{31}P NMR spectra two overlapping broad resonances which can be resolved to sharp peaks at −30°C have been observed, where one of the peaks is characterized by a $^2J(^{119}Sn\text{–}^{31}P)$ value of about 50 Hz (Fig. 10). The high field signal has been attributed to five-coordinate monomeric species, while the low field signal has been assigned to a hydroxo-bridged molecule. In solution a dynamic equilibrium exists between two species (eqn. (30)) [77].

$$2[R_2Sn(OH)\{SSP(OR')_2\}] \rightleftharpoons [R_2Sn(\mu\text{-}OH)\{SSP(OR')_2\}]_2 \qquad (30)$$

4. MONOORGANOTIN(IV) COMPLEXES

The chemistry of monoorganotin(IV) complexes with phosphorus-based acids has not been explored in much detail. Reaction of [$MeSn(O)(OAc)]_6$ with diphenyl-

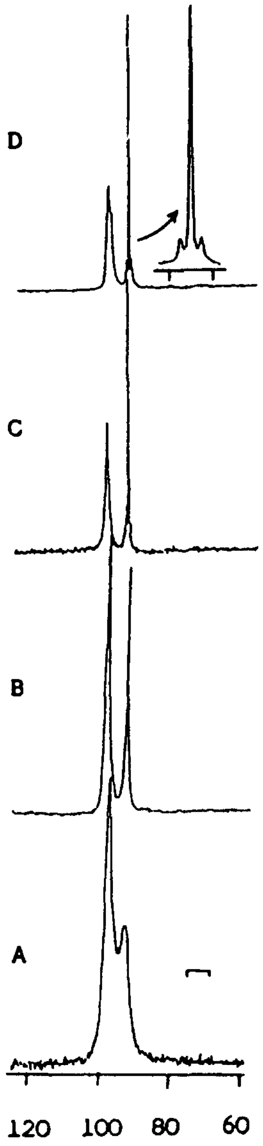


Fig. 10. Variable-temperature ^{31}P NMR spectra of $[Bu_2Sn(OH)\{SSP(O^iPr)_2\}]$ in $CDCl_3$: (A) at room temperature, bar represents 200 Hz; (B) at −15°C; (C) at −25°C; (D) at −35°C, inset scale 100 Hz.

phosphoric acid affords $[MeSn\{OOP(OPh)_2\}_3]$ in quantitative yield (eqn. (31)) [78]. Monobutyltin phosphate and pyrophosphate, $[BuSn\{OOP(O^nBu)_2\}_3]$ and $[BuSn\{OP(O)(OBu)–O–P(O)(OBu)–O\}_{3/2}]$, have been obtained by the reactions of butyltin oxide with the corresponding free acid [24]. Unlike di- and triorganotin derivatives, monobutyltin complexes are discrete monomeric units. The ^{119}Sn NMR chemical shifts (−648.5 ppm (br) for [$MeSn\{OOP(OPh)_2\}_3$] [78] and −631 ppm for [$BuSn\{OOP(O^nBu)_2\}_3$] [24]) are in the region expected for seven-coordinate tin(IV) complexes.

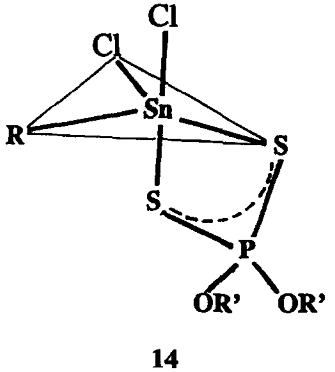
$$[MeSn(OAc)O]_6 + 18(PhO)_2POOH \rightarrow 6[MeSn\{OOP(OPh)_2\}_3] + 6H_2O + 6AcOH \quad (31)$$

The complexes [$PhSn\{SOP(O^iPr)_2\}_3$] [28] and [$PhSn\{SeOP(O^iPr)_2\}_3$] [28,29] have been prepared by the reaction of $PhSnCl_3$ with the corresponding sodium salt of the acid (eqn. (32)) and a bidentate mode of ligand bonding has been suggested on the basis of ^{31}P NMR chemical shifts.

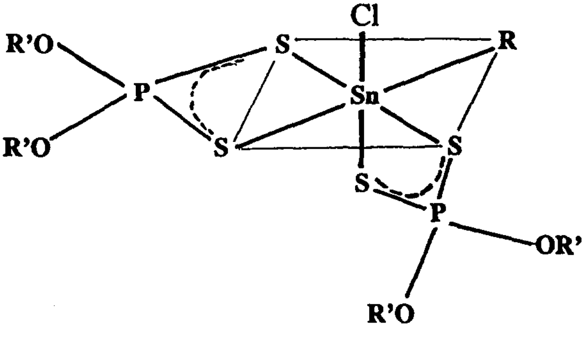
$$PhSnCl_3 + 3NaOEP(O^iPr)_2 \rightarrow [PhSn\{OPE(O^iPr)_2\}_3] + 3NaCl \quad (32)$$

($E \equiv S$ or Se)

A number of monoorganotin(IV) dialkyldithiophosphates of the types [$RSn\{SSP(OR')_2\}_3$], [$RSn(Cl)\{SSP(OR')_2\}_2$] and [$RSnCl_2\{SSP(OR')_2\}$] ($R \equiv$ Me, Et, Bu or Ph; $(OR')_2 \equiv (OEt)_2$, $(O^iPr)_2$, $(OPh)_2$, $OCMe_2CMe_2O$, $OCH_2CMe_2CH_2O$ or $OCMe_2CH_2CH(Me)O$) have been synthesized (eqns. (33) and (34)) [40,79,80]. All these complexes are monomeric in nature in refluxing benzene [79]. The magnitude of $^2J(^{119}Sn-^1H)$ (97 Hz) for methyltin complexes is indicative of a coordination number for tin greater than four. The ^{119}Sn NMR chemical shifts fall in the region for five-coordinate tin complexes [40]. Variable-temperature ^{31}P NMR data show that all ligands are equivalent even at −90°C [40]. These observations have established that the ligand moiety is weakly coordinated. The quadrupole splitting ($QS = 2.00\ mm\ s^{-1}$) for [$MeSn\{SSP(O^iPr)_3\}_3$] in the Mössbauer spectrum also suggests a higher coordination number for tin and is in agreement with the proposed seven-coordinate geometry for tin with a severe anisobidentate mode of ligand bonding [40]. Spectroscopic data (IR, ^{31}P and ^{119}Sn NMR) for the chlorotin complexes have



14



15

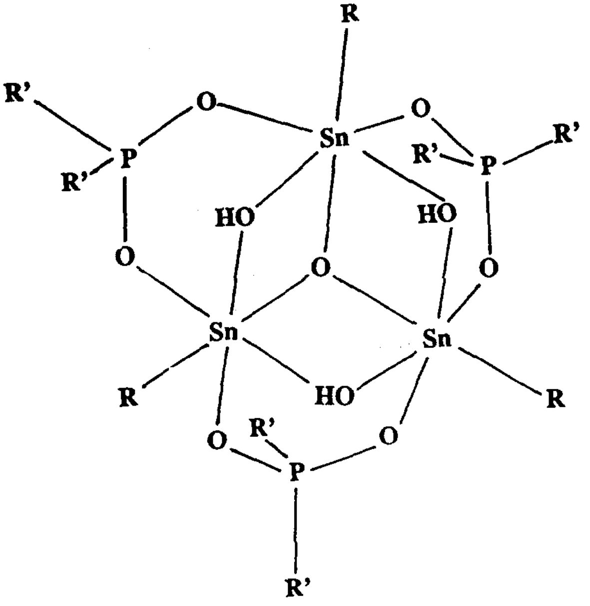
been interpreted in terms of chelating ligand bonding and structures **14** and **15** have been suggested [79,80].

$$RSnCl_3 + nMSSP(OR')_2 \rightarrow [RSn\{SSP(OR')_2\}_nCl_{3-n}] + nMCl \quad (33)$$
$$(M \equiv Na \text{ or } NH_4;\ n = 1\text{–}3;\ R \equiv Me, Et, {}^nBu, Ph)$$

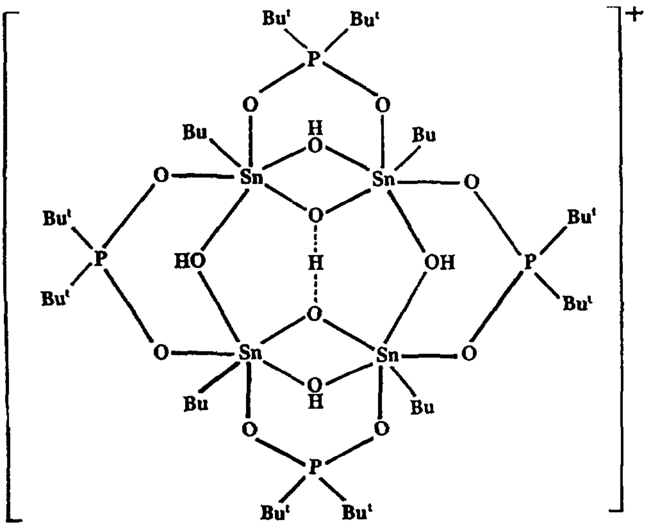
$$2BuSnO_{1.5} + 6(R'O)_2PSSH \rightarrow 2[BuSn\{SSP(OR')_2\}_3] + 3H_2O \quad (34)$$

5. MONOORGANOTIN(IV) CLUSTERS

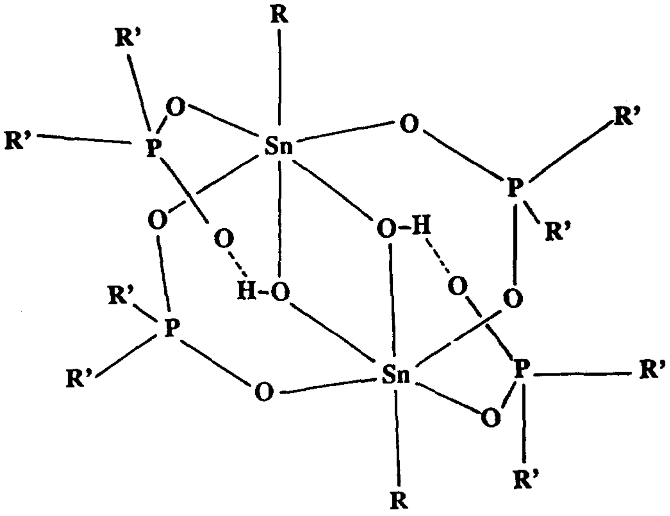
A number of monoorganotin clusters derived from phosphorus-based acids have been reported recently by Holmes and coworkers [78,81–89]. Clusters varying in nuclearity between 2 and seven have been isolated, mostly by the reactions of monoorganotin oxides or butyl(dihydroxo)tin chloride with phosphorus-based acids in various stoichiometries (eqns. (35)–(44)). The cluster geometry, i.e. cube [81,82,84,85], drum [83], oxygen capped (**16**) [81,83,84], crown cluster (**17**) [84], butterfly (**18**) [84] or cage (**19**), is determined by the type of phosphorus ligand and the groups attached to it. The tin atom is usually hexacoordinated in these clusters and a phosphorus ligand bridges adjacent tin atoms.



16



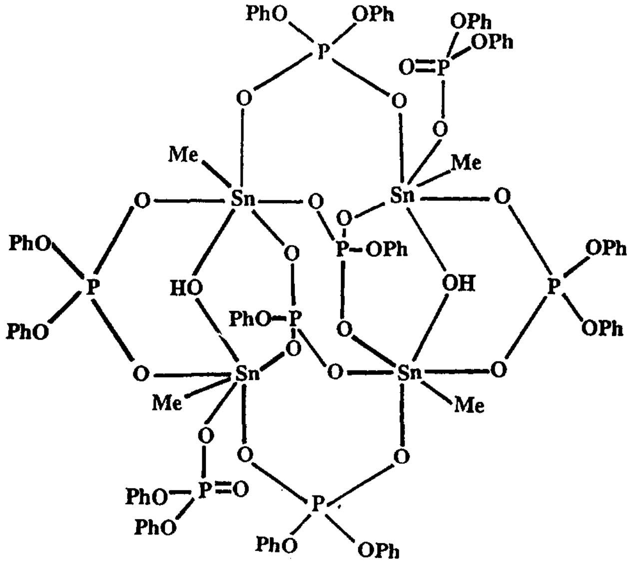
17



18

$$\begin{aligned}&2\mathrm{BuSnOOH} + 4\mathrm{Hx_2POOH}\\&\quad\rightarrow [\mathrm{BuSn(OH)\{OOPHx_2\}_2}]_2 + [\mathrm{BuSn(O)(OOPHx_2)}]_4 + \mathrm{H_2O}\end{aligned} \tag{35}$$

$$\begin{aligned}&3[\mathrm{BuSn(OH)(OOPHx_2)_2}]_2 + 2\mathrm{H_2O} \rightarrow\\&\quad \underset{\text{oxygen-capped cluster}}{[\{\mathrm{BuSn(OH)(OOPHx_2)}\}_3\mathrm{O}][\mathrm{OOPHx_2}]} + 4\mathrm{Hx_2POOH}\end{aligned} \tag{36}$$



19

$$[\{RSn(OH)(OOPR'_2)\}_3O][OOPR'_2]$$

$$\rightleftharpoons [RSn(O)(OOPR'_2)]_6 + 2R'_2POOH + H_2O \qquad (37)$$

$$4BuSnOOH + 5{}^tBu_2POOH \xrightarrow[-2H_2O]{} $$

$$[BuSn(O)(OOP{}^tBu_2)\{BuSn(OH)_2(OOP{}^tBu_2)\}]_2[H][OOP{}^tBu_2]$$

$$\text{crown cluster} \qquad (38)$$

$$\tfrac{2}{3}[BuSn(O)(OAc)]_6 + 5{}^tBu_2POOH + 2H_2O \xrightarrow[-4AcOH]{}$$

$$[MeSn\{OOP(OPh)_2\}_3] + 4H_2O \longrightarrow$$

$$[Me_2Sn_2(OH)\{OOP(OPh)_2\}_3\{O_3P(OPh)\}]_2 + PhOH + 4(PhO)_2POOH$$

$$\text{cage} \qquad \downarrow 4H_2O$$

$$[MeSn(O)\{OOP(OPh)_2\}\{MeSn(OH)_2OOP(OPh)_2\}]_2[H][OOP(OPh)_2]$$

$$+ (PhO)_2POOH + 2(PhO)P(O)(OH)_2 \qquad (39)$$

$$4BuSnOOH + 8RP(O)(OH)_2 \rightarrow [Bu_2Sn_2(O)\{OOP(OH)R\}_4]_2 + 6H_2O \qquad (40)$$

$$28BuSnOOH + 24Ph_2POH + 3S_8$$

$$\rightarrow 4[\{BuSnS(OOPPh_2)\}_3O]_2Sn + 24H_2O + 4BuH \qquad (41)$$

$$5BuSn(OH)_2Cl + 5Hx_2POOH \rightarrow [\{BuSn(OH)(OOPHx_2\}_3O][\{BuSnCl_2(OOPHx_2\}_2OH] + 5H_2O + HCl \quad (42)$$

$$6BuSn(OH)_2Cl + 6Ph_2POOH \xrightarrow{CH_2Cl_2} [Bu_2Sn_2Cl_2(OH)(OOPPh_2)_3]_2 \cdot 2CH_2Cl_2 \quad (43)$$

$$3BuSn(OH)_2Cl + 3Mes_2POOH \rightarrow [\{BuSn(OH)(OOPMes_2)\}_3O]Cl + 2H_2O + 2HCl \quad (44)$$

The reactions of butylstannoic acid with diorganophosphoric and -phosphinic acids proceed in a stepwise manner, e.g. reactions with dicyclohexylphosphinic acid in 1:1 stoichiometry afford a dimeric butterfly cluster $[BuSn(\mu\text{-}OH)(OOP\text{–}Hx_2)]_2$ (eqn. (35)) (**18**) (^{119}Sn −547.5 ppm, d, t, $^2J(Sn\text{–}P) = 128$ (bridging), 182 Hz (dangling)) an oxygen-capped cluster $[\{BuSn(OH)(OOP\text{–}Hx_2)\}_3O][OOP\text{–}Hx_2]$ (eqn. (36)) (**16**) (^{119}Sn −499.5 ppm, $^2J(Sn\text{–}P) = 132$ Hz) and a tetrameric cubic cluster $[BuSn(O)(OOP\text{–}Hx_2)]_4$ [84] (Fig. 11). The intermediate dimeric butterfly and oxygen-capped clusters have not been isolated in every case. However, in the reaction of butylstannoic acid with diphenylphosphoric acid the oxygen-capped cluster $[\{BuSn(OH)(OOP(OPh)_2)\}_3O][OOP(OPh)_2]$ (^{119}Sn −508.8 ppm, $^2J(Sn\text{–}P) =$ 189.2 Hz) is formed at room temperature, but in refluxing solvent a hexameric drum-oxo-tin cluster $[BuSn(O)\{OOP(OPh)_2\}]_6$ (Fig. 12) is isolated (eqn. (37)) [83]. With

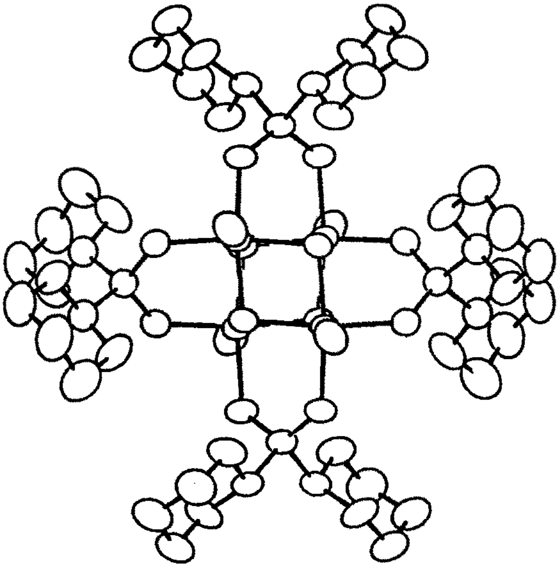


Fig. 11. Crystal structure of $[BuSn(O)\{OOP(c\text{-}Hx)_2\}]_4$. (From ref. 82, reproduced with the permission of the American Chemical Society.)

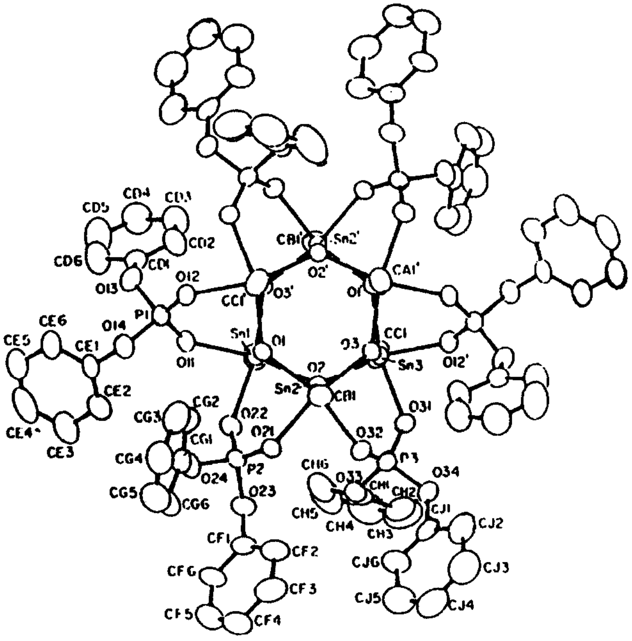


Fig. 12. Crystal structure of $[BuSn(O)\{OOP(OPh)_2\}]_6$. (From ref. 83, reproduced with the permission of the American Chemical Society.)

the exception of nuclearity, the drum and cube have the same empirical formula; the cube geometry is preferred by the ligands with greater steric demands, whereas the drum formulation is adopted by the less bulky ligands. In the cubic geometry each face is defined by a four-membered Sn_2O_2 stannoxane ring. The top and bottom faces of the cube are open, whereas each of the remaining four sides is spanned diagonally by a phosphinate bridge between two tin atoms. In the drum configuration the sides consist of six four-membered Sn_2O_2 stannoxane rings, each of which is spanned by a ligand group that forms a bridge between two tin atoms. The molecular structure of oxygen-capped clusters consists of a tristannoxane ring in a cyclohexane chair arrangement with hydroxyl oxygen atoms as part of the ring. A triconnective oxygen atom caps one side of this framework and the phosphorus acid moiety bridges adjacent tin atoms. In general the oxygen-capped clusters resemble a cube with one corner missing. Both cube and drum forms yield oxygen-capped clusters on hydrolysis, which on heating revert back to the parent cluster geometry.

Treatment of butylstannoic acid with dephenylthiophosphinic acid in 1:1 stoichiometry in refluxing benzene gives mainly $[BuSn(O)SOPPh_2]_n$, which is either cube or drum, and a small amount (about 3%) of an extended cluster $[(BuSn)_2OH(OOPPh_2)_3(OSPPh_2)_2]_2$ (Fig. 13) (^{119}Sn two multiplets at −575.0 and −614.0 ppm) [85]. The latter molecule is an open dimer in which all the tin atoms are hexacoordinated. There are two types of phosphate bridges, each one bridging

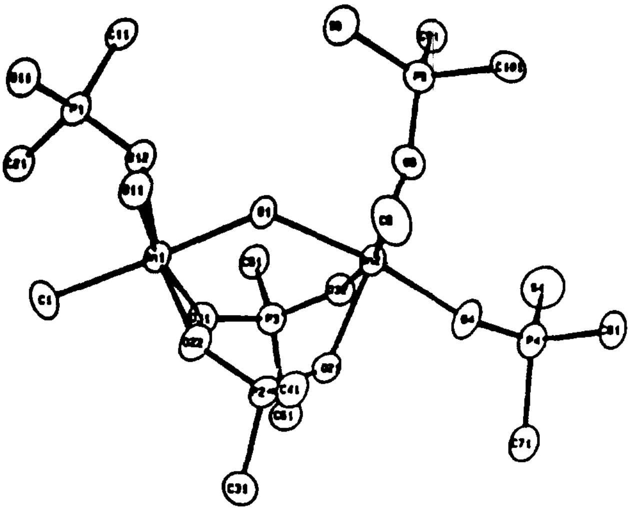


Fig. 13. Crystal structure of $[(BuSn)_2OH(OOPPh_2)_3(OSPPh_2)_2]_2$. (From ref. 85, reproduced with the permission of the American Chemical Society.)

adjacent tin atoms. Each terminal tin atom is bonded to two monodentate thiophosphinate groups through an oxygen atom. If the reaction conditions are varied, a new structural form results, e.g. when butylstannoic acid is heated with diphenylphosphine oxide in the presence of sulphur, a heptanuclear sulphur-containing cluster $[\{BuSn(S)(OOPPh_2)\}_3O]_2Sn$ (^{119}Sn −467.7 ppm, t, $^2J(Sn–P) = 132$ Hz) is obtained (eqn. (41)) [86]. The X-ray structure (Fig. 14) reveals a double cube connected at the corners occupied by Sn atoms. The four-membered Sn_2S_2 rings are nearly planar.

When butyl(hydroxy)tin chloride is used in place of butylstannoic acid, new cluster geometries are obtained (eqns. (42)–(44)). Thus reactions of butyl(dihydroxy)tin chloride with phosphinic acid in 1:1 stoichiometry readily afford a series of chloro(oxo)tin clusters in which the nuclearity varies between two and four depending on the nature of the R group on phosphorus [89]. Accordingly, the oxygen-capped clusters $[\{BuSn(OH)(OOP–Hx_2)\}_3O\{BuSnCl_2(OH)(OOP–Hx_2)\}]$ and $[\{BuSn(OH)(OOPMes_2)\}_3O]Cl$ (Mes ≡ mesityl), the extended tetranuclear cluster $[(BuSn)_2Cl_2(OH)(OOPPh_2)_3]_2$ and the crown butterfly cluster $[\{BuSn(OH)(OOP^{t}Bu_2)\}_4O_2][H][Cl][BuSn(OH)(Cl)(OOP^{t}Bu_2)]_2$ have been isolated and all have a hexacoordinated tin atom and hydroxy bridges [89].

6. APPLICATIONS OF ORGANOTIN(IV) COMPLEXES OF PHOSPHORUS-BASED ACIDS

6.1. *Catalyst and corrosion inhibitors*

Organotin compounds with phosphorus-based acids have been used as polymerization catalysts [24,90] or stabilizers of polyolefins against heat and light

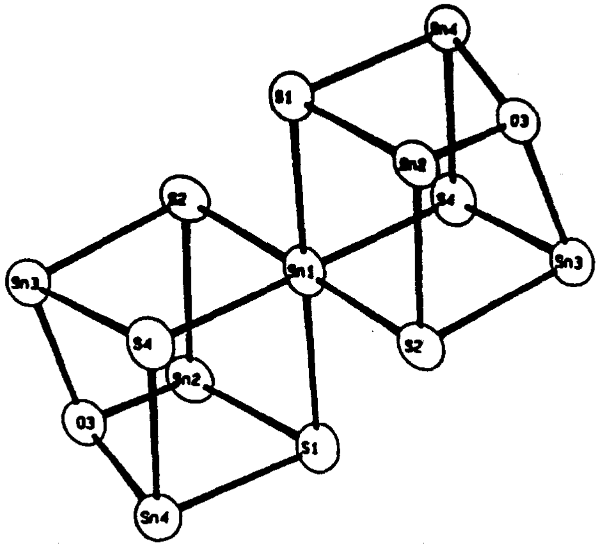


Fig. 14. ORTEP plot showing tin–sulphur–oxygen core of $[\{BuSn(S)(OOPPh_2)\}_3]_2Sn$. (From ref. 86, reproduced with the permission of the American Chemical Society.)

[91–93]. Organotin phosphates and pyrophosphates are effective catalysts for polymerization of epoxides [24]. These studies have indicated that monobutylpyrophosphate, $BuSn[\{OP(O)(OBu)\}_2O]_{3/2}$, is an active species which is formed by pyrolysis of various organotin phosphate complexes in the catalytic process. These complexes have an advantage over organomagnesium and zinc catalysts in that they can be handled in air and afford polymers of high crystallinity. Polymerization with organotin phosphate complexes is therefore highly stereospecific in nature.

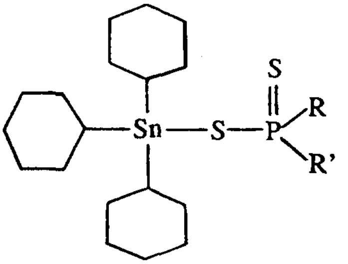
Poly(ethylterephthalate) can be readily obtained from bis(hydroxyethyl)terephthalate in the presence of $[Bu_2Sn\{SSP(OR)_2\}_2]$ ($R \equiv Me$ or Et) [90]. Polyethylene, polypropene and polybutene can be stabilized against oxidation and UV degradation when $[R_{4-n}Sn(XYPR'_2)_n]$ ($n = 1$ or 2; $R \equiv Bu$, Oct, Ph; $R' \equiv OEt$, Ph; $X,Y \equiv O,S$ or S,S) is added in amounts of 0.05%–5.0% to polyolefin [91–93], e.g. polypropylene with $[Bu_2Sn(SSPPh_2)_2]$ (0.5%) was brittle after 1 month in an Atlas Weather Ometer at 60°C [93].

Diorganotin bis(dialkyldithiophosphates) $[R_2Sn\{SSP(OR')_2\}_2]$ ($R \equiv C_4H_9$, $C_{11}H_{23}$ or $C_{12}H_{25}$; $R' \equiv {}^iPr$, $C_6H_{10}OMe$-4, C_6H_4-C_8H_{17}-4) have been used as corrosion inhibitors for lubricating oils [94,95]. Addition of $[Bu_2Sn\{SSP(Odecyl)_2\}_2]$ (0.001–1.0 wt.%) to water-based drilling mud reduces the tendency of the drill pipe to become stuck during drilling [96].

6.2. Biocides

The parent species, organotin(IV) residue and organophosphorus ligands, are known to be highly effective biocides. A combination of these species into a single molecule may result in a much stronger biocide. With this goal in mind, a number of organotin compounds with phosphorus-based acids have been synthesized and their biocidal activities have been assessed [37,52,97–114]. Tri-, di- and monoorganotin(IV) complexes with phosphorus-based acids are effective fungicides, bactericides, antimicrobial, acaricides, miticides, insecticides and herbicides. They also inhibit germination of plant seeds [100]. The dibutyltin compounds $[\mathrm{Bu_2Sn\{SSP(OR)_2\}_2}]$ ($\mathrm{R \equiv C_8H_{15}}$ or $\mathrm{C_6H_{10}Me}$-4) are effective fungicides with low phytotoxicity [97]. Introduction of diphenylphosphine grouping into tin compounds reduces phytotoxicity considerably [99].

The insecticidal activity of organotin phosphates and dithiophosphates increases with increasing solubility in organic solvents [99], the latter molecules being more effective. Of the organotin dithiophosphates, triorganotin, particularly tricyclohexyltin(IV) (**20**), compounds are very effective miticides and insecticides



20

(X ≡ O or S; R ≡ R′ ≡ OMe, OEt, $\mathrm{O^{n}Pr}$, $\mathrm{O^{i}Pr}$, OHx, SR; R ≡ Et; R′ ≡ $\mathrm{O^{i}Pr}$, amino or SR group)

[37,104–110]. For example, LD_{50} values for $[\mathrm{Hx_3Sn\{SSP(O^{n}Pr)_2\}}]$ are 0.05 for *Lygus* bugs, 0.01 for bean aphids and 0.1 for salt-marsh caterpillars [105], whereas LD_{50} values for $[\mathrm{Hx_3Sn(SSPRR')}]$ are 50–100 μg against house flies, 0.001%–0.008% against spotted mites and 0.03%–0.008% against their eggs [37].

ACKNOWLEDGEMENT

Thanks are expressed to Dr. Mark A. Keane for helpful discussions.

REFERENCES

1 P.G. Harrison, Chemistry of Tin, Blackie, Glasgow, 1989.
2 I. Haiduc, Rev. Inorg. Chem., 3 (1981) 353.
3 K.C. Molloy and J.J. Zuckerman, Acc. Chem. Res., 16 (1983) 386.
4 R.C. Mehrotra, G. Srivastva and B.P.S. Chauhan, Coord. Chem. Rev., 55 (1984) 207;

R.C. Mehrotra, J. Indian Chem. Soc., 64 (1987) 265; Silicon, Germanium, Tin and Lead Comp., 9 (1986) 185.
5 R.R. Holmes, ACS Symp. Ser., 360 (1988) 469; Main Group Met. Chem., 12 (1989) 291; V. Chandrasekhar and M.G. Muralidhar, Curr. Sci., 60 (1991) 158.
6 R.R. Holmes, Acc. Chem. Res., 22 (1989) 190.
7 I.G.M. Campbell, G.W.A. Fowels and L.V. Nixon, J. Chem. Soc., (1964) 1389.
8 A.A. Muritova, Dokl. Akad. Nauk SSSR, 158 (1964) 419; Chem. Abstr., 62 (1965) 11 646f.
9 K. Issleib and B. Walther, J. Organomet. Chem., 10 (1967) 177.
10 R.E. Ridenour and E.E. Flagg, J. Organomet. Chem., 16 (1969) 393.
11 K.C. Molloy, F.A. Nasser and J.J. Zuckerman, Inorg. Chem., 21 (1982) 1711; University of Oklahoma Rep. TR-33, 1981; Chem. Abstr., 96 (1982) 104423.
12 D. Cunningham, L.A. Kelly, K.C. Molloy and J.J. Zuckerman, Inorg. Chem., 21 (1982) 1416.
13 C. Silvestru, F. Ilies and I. Haiduc, Stud. Univ. Babes-Bolyai Chem., 34 (1989) 93; Chem. Abstr., 114 (1991) 164–364v.
14 J.G. Masters, F.A.K. Nasser, M.B. Hossain, A.P. Hagen, D. van der Helm and J.J. Zuckerman, J. Organomet. Chem., 385 (1990) 39.
15 K.C. Molloy and T.G. Purcell, J. Organomet. Chem., 312 (1986) 167.
16 H. Schumann, P. Jutzi, A. Roth, P. Schwabe and E. Schauer, J. Organomet. Chem., 10 (1967) 71.
17 H.W. Roesky, Chem. Ber., 100 (1967) 2147.
18 F. Waller and A.F. Shihada, J. Organomet. Chem., 322 (1987) 185.
19 A.F. Shihada, Z. Naturforsch., Teil B, Chem. Sci., 47 (1992) 553.
20 F. Nietjschmann and K. Kellner, Phosphorus, Sulfur, Silicon, 55 (1991) 73.
21 J.N. Pandey and G. Srivastava, J. Organomet. Chem., 354 (1988) 301.
22 K.C. Molloy, M.B. Hossain, D. van der Helm, D. Cunningham and J.J. Zuckerman, Inorg. Chem., 20 (1981) 2402.
23 S.J. Blunden, R. Hill and D.G. Gillies, J. Organomet. Chem., 270 (1984) 39.
24 J. Otera, T. Yano, E. Kunimoto and T. Nakata, Organometallics, 3 (1984) 426.
25 K.C. Molloy, F.A.K. Nasser, C.L. Barens, D. van der Helm and J.J. Zuckerman, Inorg. Chem., 21 (1982) 960.
26 K. Issleib and B. Walther, J. Organomet. Chem., 22 (1970) 375.
27 I.A. Duncan and C. Glidwell, J. Organomet. Chem., 97 (1975) 51.
28 C. Glidwell, Inorg. Chim. Acta, 24 (1977) 255.
29 C. Glidwell and E.J. Leslie, J. Chem. Soc., Dalton Trans., (1977) 527.
30 G. Avar and W.P. Neumann, J. Organomet. Chem., 131 (1977) 207, 215.
31 F.A.K. Nasser and J.J. Zuckerman, J. Organomet. Chem., 244 (1983) 17.
32 A.F. Shihada, I.J. Jassim and W.F. Amie, J. Organomet. Chem., 268 (1984) 125.
33 P.N. Nagar, Phosphorus, Sulfur Relat. Comp., 40 (1988) 177.
34 N.K. Bliznyuk, P.S. Khokhlov and Yu.A. Andrianov, USSR Patent 181 103, 1966; Chem. Abstr., 65 (1966) 8962e.
35 F. Bonati, S. Cenini and R. Ugo, J. Organomet. Chem., 9 (1967) 395.
36 A.N. Pudovik, R.A. Cherkasov, I.V. Bykova, G.I. Evstaf'ev, Z.I. Zemskaya and M.N. Nazypov, Zh. Obsch. Khim., 42 (1972) 76; Vysokomol Soedin Ser. B, 13 (1971) 907.
37 D.R. Baker (Stauffer Chemical Co.), S. Afr. Patent 7 202 699, 1972; Chem. Abstr., 79 (1979) 78 964t.
38 B.P. Singh, G. Srivastava and R.C. Mehrotra, J. Organomet. Chem., 171 (1979) 35.
39 J.L. Lefferts, K.C. Molloy, J.J. Zuckerman, I. Haiduc, C. Guta and D. Ruse, Inorg. Chem., 19 (1980) 1662.

40 H.C. Clark, V.K. Jain, R.C. Mehrotra, B.P. Singh, G. Srivastva and T. Birchall, J. Organomet. Chem., 279 (1985) 385.
41 C. Silvestru and I. Haiduc, J. Organomet. Chem., 365 (1989) 83.
42 K.C. Molloy, Inorg. Chim. Acta, 141 (1988) 151.
43 D. Dakternieks, H. Zhu, D. Masi and C. Mealli, Inorg. Chem., 31 (1992) 3601.
44 C. Cauletti, G. Nicotra and M.V. Piancastelli, J. Organomet. Chem., 190 (1980) 147.
45 K.C. Molloy, M.B. Hossain, D. van der Helm, J.J. Zuckerman and I. Haiduc, Inorg. Chem., 18 (1979) 3507.
46 H. Prent, V.D. Ngo and F. Huber, Acta Crystallogr. C, 43 (1987) 164.
47 H. Weichmann, J. Meunier-Piret and M. van Meerssche, J. Organomet. Chem., 309 (1986) 273.
48 R. Barbieri, G. Alonzo and R.H. Herber, J. Chem. Soc., Dalton Trans., (1987) 789.
49 C. Vatsa, V.K. Jain and T.K. Das, Main Group Met. Chem., 13 (1990) 279.
50 A. Shihada and H.R. Yosuif, Z. Naturforsch., Teil B, Chem. Sci., 46 (1991) 1568.
51 V.K. Jain, T.K. Das, C. Vatsa and M.E. Smith, Spectrochim. Acta, Part A, 48 (1992) 1583.
52 S. Freireich, D. Gertner and A. Zilkha, J. Organomet. Chem., 25 (1970) 111.
53 D. Seyferth and F.G.A. Stone, J. Am. Chem. Soc., 79 (1957) 515.
54 D. Cunningham, P. Firtear, K.C. Molloy and J.J. Zuckerman, J. Chem. Soc., Dalton Trans., (1983) 1523.
55 K. Kellner, L. Rodewald and K. Schenzel, Phosphorus, Sulfur, Silicon Relat. Elements, 55 (1991) 65.
56 T. Chivers, J.H. van Roode, J.N.R. Ruddick and J.R. Sames, Can. J. Chem., 51 (1973) 3702.
57 J.P. Ashmore, T. Chivers, K.A. Kerr and J.H.G. van Roode, Inorg. Chem., 16 (1977) 191; J. Chem. Soc., Chem. Commun., (1974) 653.
58 T.P. Lockhart and W.F. Manders, Inorg. Chem., 25 (1986) 1068.
59 G.A. Lapitski, L.S. Granenkina, P.S. Khokhlov and N.K. Bliznyuk, Zh. Obsch. Khim., 38 (1968) 2787; Chem. Abstr., 70 (1969) 78 100x.
60 V.B. Mokal, V.K. Jain and E.R.T. Tiekink, J. Organomet. Chem., 471 (1994) 53.
61 V.K. Jain and V.B. Mokal, unpublished results, 1994.
62 F.A.K. Nasser, M.B. Hossain, D. van der Helm and J.J. Zuckerman, Inorg. Chem., 22 (1983) 3107.
63 G.A. Lapitskii, L.S. Granenkina, P.S. Khokhlov and N.K. Bliznyuk, USSR Patent 228 027, 1968; Chem. Abstr., 70 (1969) 58 022v.
64 B.P. Singh, G. Srivastava and R.C. Mehrotra, Synth. React. Inorg. Met. Org. Chem., 10 (1980) 359.
65 J.L. Lefferts, K.C. Molloy, J.J. Zuckerman, I. Haiduc, M. Curtui, C. Guta and D. Ruse, Inorg. Chem., 19 (1980) 2861.
66 R.J. Rao, G. Srivastava, R.C. Mehrotra, B.S. Saraswat and J. Mason, Polyhedron, 3 (1984) 485.
67 R. Visalakshi, V.K. Jain and G.S. Rao, Spectrochim. Acta, Part A, 43 (1987) 1235.
68 W. Kuchen, A. Jadat and J. Metten, Chem. Ber., 98 (1965) 3981.
69 F.P. Mullins, J. Inorg. Nucl. Chem., 41 (1979) 633.
70 C. Silvestru, I. Haiduc, K. Simona, U. Thewalt, M. Gielen and J.J. Zuckerman, J. Organomet. Chem., 327 (1987) 181.
71 C. Silvestru, F. Ilies, I. Haiduc, M. Gielen and J.J. Zuckerman, J. Organomet. Chem., 330 (1987) 315.
72 R.K. Harris, A. Sebald, D. Furlani and G. Tagliavini, Organometallics, 7 (1988) 388.
73 B.W. Liebich and M. Tomassini, Acta Crystallogr., Sect. B, 34 (1978) 944.
74 K.C. Molloy, M.B. Hossain, D. van der Helm, J.J. Zuckerman and I. Haiduc, Inorg. Chem., 19 (1980) 2041.

75 K.C. Molloy, M.B. Hossain, D. van der Helm, J.J. Zuckerman and F.P. Mullins, Inorg. Chem., 20 (1981) 2172.
76 N.K. Bliznyuk, L.D. Protasova and Z.N. Kvasha, USSR Patent 248 673, 1969; Chem. Abstr., 72 (1970) 100 889b.
77 C.S. Parulekar, V.K. Jain and T.K. Das, Phosphorus, Sulfur and Silicon, 46 (1989) 145.
78 K.C. Kumar Swamy, C.G. Schmid, R.O. Day and R.R. Holmes, J. Am. Chem. Soc., 112 (1990) 223.
79 B.P. Singh, G. Srivastava and R.C. Mehrotra, Synth. React. Inorg. Met. Org. Chem., 13 (1983) 963.
80 R.J. Rao, G. Srivastava and R.C. Mehrotra, Phosphorus and Sulfur, 25 (1985) 183.
81 R.O. Day, J.M. Holmes, V. Chandrasekhar and R.R. Holmes, J. Am. Chem. Soc., 109 (1987) 940.
82 K.C. Kumar Swamy, R.O. Day and R.R. Holmes, J. Am. Chem. Soc., 109 (1987) 5546.
83 R.O. Day, V. Chandrasekhar, K.C. Kumar Swamy, J.M. Holmes, S.D. Burton and R.R. Holmes, Inorg. Chem., 27 (1988) 2887.
84 R.R. Holmes, K.C. Kumar Swamy, C.G. Schmid and R.O. Day, J. Am. Chem. Soc., 110 (1988) 7060.
85 K.C. Kumar Swamy, C.G. Schmid, R.O. Day and R.R. Holmes, J. Am. Chem. Soc., 110 (1988) 7067.
86 K.C. Kumar Swamy, R.O. Day and R.R. Holmes, J. Am. Chem. Soc., 110 (1988) 7543.
87 C.G. Schmid, R.O. Day and R.R. Holmes, Phosphorus, Sulfur and Silicon, 41 (1989) 69.
88 K.C. Kumar Swamy, R.O. Day and R.R. Holmes, Phosphorus, Sulfur and Silicon, 41 (1989) 291.
89 K.C. Kumar Swamy, R.O. Day and R.R. Holmes, Inorg. Chem., 31 (1992) 4184.
90 T. Toda, K. Ida and K. Kimoto (Tokyo Spinning Co. Ltd.), Jpn. Patent 7 019 512, 1966; Chem. Abstr., 73 (1970) 77 830k.
91 O.A. Homberg and I. Hechenbleikner (Carlisle Chemical Works Inc.), Fr. Patent 1 365 375, 1964; Chem. Abstr., 61 (1964) 14 711d.
92 E.N. Walsh and A.F. Kopacki (Stauffer Chemical Co.), US Patent 3 296 193, 1967; Chem. Abstr., 66 (1967) 55 981.
93 E.N. Walsh and A.F. Kopacki (Stauffer Chemical Co.), US Patent 3 358 006, 1967; Chem. Abstr., 68 (1968) 30 705.
94 Esso Research and Engineering Co., Br. Patent 737 392, 1955; Chem. Abstr., 50 (1955) 9010.
95 J.P. McDermett (Esso Research and Engineering Co.), US Patent 2 786 812, 1957; Chem. Abstr., 51 (1957) 10 892e.
96 R.W. Walker and H.E. Ramsden, US Patent 3 410 797, 1968; Chem. Abstr., 70 (1969) 1592e.
97 Ethyl Corporation and Esso Research Engineering Co., Br. Patent 806 535, 1958; Chem. Abstr., 53 (1959) 13 499e.
98 C.J. Stern Jr. (Nease Chemical Co. Inc), US Patent 3 179 676, 1965, Chem. Abstr., 63 (1965) 2999g.
99 H. Kubo, Agric. Biol. Chem., 29 (1965) 43.
100 M. Nakanishi and A. Tsuda (Yoshitomi Pharmaceutical Industries Ltd.), Jpn. Patent 15 290, 1962; Chem. Abstr., 65 (1966) 20 164f.
101 Y. Nagae and K. Wakamori (Toa Agricultural Chemical Co. Ltd.), Jpn. Patent 4575, 1963; Chem. Abstr., 65 (1966) 2298h.
102 Y. Nagae and K. Wakamori (Toa Agricultural Chemical Co. Ltd.), Jpn. Patent 4576, 1963; Chem. Abstr., 65 (1966) 2298g.

103 C. Pfizer and Co. Inc., Br. Patent 1 163 738, 1969; Chem. Abstr., 72 (1970) 2550q.
104 D.R. Baker (Stauffer Chemical Co.), US Patent 3 947 461, 1972; Chem. Abstr., 85 (1976) 46 857t.
105 D.R. Baker (Stauffer Chemical Co.), US Patent 3 947 481, 1976; Chem. Abstr., 85 (1976) 46 858.
106 D.R. Baker (Stauffer Chemical Co.), US Patent 3 919 418, 1971; Chem. Abstr., 84 (1976) 85 644v.
107 D.R. Baker (Stauffer Chemical Co.), US Patent 3 917 827, 1975; Chem. Abstr., 84 (1976) 85 648z.
108 D.R. Baker (Stauffer Chemical Co.), US Patent 3 992 425, 1976; Chem. Abstr., 86 (1977) 90 031p.
109 D.R. Baker (Stauffer Chemical Co.), US Patent 4 012 421, 1977; Chem. Abstr., 87 (1978) 6201j.
110 A. Mihailovski (Stauffer Chemical Co.), US Patent 4 071 545, 1978; Chem. Abstr., 88 (1978) 170 295.
111 J. Drabck (Ciba Geigy AG.), Eur. Patent 46 730, 1982; Chem. Abstr., 97 (1982) 39 145d.
112 I. Haiduc, C. Silvestru and M. Gielen, Bull. Soc. Chem. Belg., 92 (1983) 187.
113 E. Nietzschmann, K. Kellner, J. Kalbitz, V. Otte, C. Fieseler, D. Mielke, U. Thust, C. Schmoll and D. Wilbrandt, E. Ger. Patent 240 376, 1986; Chem. Abstr., 107 (1987) 154 527s.
114 Q. Xie, N. Luo, J. Li and X. Jing, Youji Xauxue, 12 (1992) 159; Chem. Abstr., 117 (1992) 26 650w.