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Synthesis and characterization of di- and tri-organotin(IV) dimethyldithiophosphinates *

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Abstract

Di- and tri-organotin(IV) dimethyldithiophosphinates, $R_2Sn(S_2PMe_2)_2$ (R = Me, n-Bu, Bz, Ph) and $R_3SnS_2PMe_2$ (R = Me, Cy, Bz, Ph) were prepared by treating the corresponding organotin chlorides with sodium dimethyldithiophosphinate. All the compounds were characterized by infrared and ^1H NMR spectra. For two representative derivatives, i.e. $Me_2Sn(S_2PMe_2)_2$ and $Ph_3SnS_2PMe_2$, ^{119m}Sn Mössbauer spectra and mass spectra were also investigated. Monodentate coordination of the dithiophosphinato ligand and tetrahedral structures are proposed for the triorganotin derivatives. In diorganotin compounds the coordination geometry around tin is intermediate between tetrahedral (with monodentate dithiophosphinato ligands) and octahedral (with anisobidentate dithiophosphinato ligands). The C–Sn–C bond angle values calculated for $Me_2Sn(S_2PMe_2)_2$, on the basis of $^2J(^{119}Sn–C–^1H)$, i.e. 128.4°, or QS value, i.e. 126.8°, compare satisfactorily with that obtained by X-ray diffraction, i.e. 122.6°.

Introduction

Some years ago we became interested in organometallic derivatives of organothiophosphorus acids and we reported the synthesis and characterization of organolead [1] and organomercury [2] derivatives of dialkyldithiophosphoric acids (phosphorodithioic acid diesters) of general formula $R_nM[S_2P(OR')_2]_m$ (M = Pb, Hg). Following a friendly visit of J.J. Zuckerman to our laboratory, a joint research program was initiated, which resulted in a rather detailed investigation of organotin dithiophosphates, $R_nSn[S_2P(OR')_2]_{4-n}$ [3–6], later extended to organotin dithiophosphinates, $R_nSn(S_2PR'_2)_{4-n}$ [7,8]. The discovery of antitumor activity (al-

* This paper is dedicated to the memory of J.J. Zuckerman, a great friend with whom we shared the pleasure of joint research and fruitful collaboration.

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though marginal) of some organotin dithiophosphinates [9] enhanced our interest towards this class of compounds. The experience and fascination with organotin derivatives led to an extension of the study to related organoantimony compounds [10,11] and, for comparison, organometallic diorganodithioarsinates [12–16].

The dithiophosphato and -phosphinato anions are versatile ligands, able to exhibit various coordination patterns, often leading to unexpected structures [17].

We wish to report here the preparation and characterization of organotin dimethyldithiophosphinates, which completes the work already reported on diethyldithiophosphinates [7] and diphenyldithiophosphinates [8].

Results and discussion

Preparation

The organotin dimethyldithiophosphinates were prepared using the reaction between organotin chlorides and the sodium salt of dimethyldithiophosphinic acid in stoichiometric ratio:

$$R_nSnCl_{4-n} + (4-n)Me_2PS_2Na \cdot 2H_2O \rightarrow$$
$$R_nSn(S_2PMe_2)_{4-n} + (4-n)NaCl + 2(4-n)H_2O$$

Organic solvents, e.g. acetone, benzene or absolute ethanol, were generally used. Only in the case of dimethyltin derivative, distilled water was used as solvent. Organotin dimethyldithiophosphinates are crystalline, white solids, stable in air, which can be recrystallized from organic solvents. Only the trimethyltin derivative is an oil. Yields, recrystallization solvents and melting points are given in Table 1.

Table 1

Preparation of $R_nSn(S_2PMe_2)_{4-n}$ compounds

Starting materials		Product	M.p.	Recryst.
R_nSnCl_{4-n}, mol	$NaS_2PMe_2 \cdot 2H_2O$, mol	$R_nSn(S_2PMe_2)_{4-n}$ (yield (%))	(°C)	solvent
Me_2SnCl_2, 0.01 [a]	0.02 [a]	R = Me, $n = 2$ (72)	213–215 [b]	$EtOH/CHCl_3$ (1/1)
n-Bu_2SnCl_2, 0.01 [c]	0.02 [c]	R = n-Bu, $n = 2$ (67)	108–110 [d]	Me_2CO
Bz_2SnCl_2, 0.005 [e]	0.01 [e]	R = Bz, $n = 2$ (95)	184–185	Me_2CO
Ph_2SnCl_2, 0.01 [f]	0.02 [f]	R = Ph, $n = 2$ (52)	167–169 [g]	–
Me_3SnCl, 0.01 [e]	0.01 [e]	R = Me, $n = 3$ (84)	oil	–
Cy_3SnCl, 0.01 [c]	0.01 [c]	R = Cy, $n = 3$ (53)	165–167	Me_2CO
Bz_3SnCl, 0.005 [e]	0.005 [e]	R = Bz, $n = 3$ (83)	51– 53	C_6H_6
Ph_3SnCl, 0.01 [f]	0.01 [f]	R = Ph, $n = 3$ (75)	124–126	EtOH

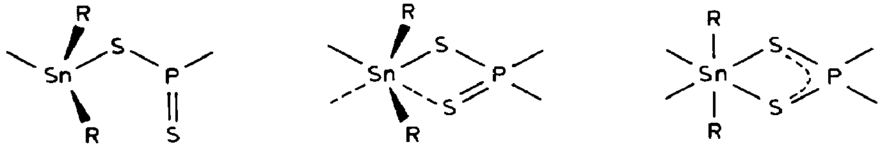
[a] In 25 ml H_2O. [b] M.p. 215–217 °C [18]. [c] In 25 ml acetone. [d] M.p. 105–107 °C [18]. [e] In 25 ml benzene. [f] In 25 ml absolute EtOH. [g] M.p. 130 °C [18].

Spectra and structure

Organotin dimethyldithiophosphinates were characterized by infrared spectra and [1]H NMR and, in part, by tin-199m Mössbauer and mass spectra.

Infrared spectra. The infrared spectra were recorded for all compounds in the range 4000–400 cm^{-1}. The PS_2 and SnC_n stretching vibrations, which can provide useful structural information [19,20], were assigned according to literature data (Me_2PS_2Me: ν(P=S) 605 cm^{-1}, ν(P–S) 465, 487 cm^{-1} [21]; $Me_2PS_2Na \cdot 2H_2O$: $\nu_{as}(PS_2)$ 600 cm^{-1}, $\nu_s(PS_2)$ 495 cm^{-1} [22]) and by comparison with the infrared spectra of the starting materials. The $\nu_{as}(SnC_2)$ and $\nu_s(SnC_2)$ for the dimethyl- and dibenzyl-tin derivatives were 555 and 525 cm^{-1}, and 442 and 430 cm^{-1}, respectively (all are weak intensity bands), thus suggesting a non-linear configuration for the R–Sn–R fragment in diorganotin derivatives. For $Me_3SnS_2PMe_2$, the presence of two bands at 540 ($\nu_{as}(SnC_3)$) and 508 cm^{-1} ($\nu_s(SnC_3)$) (weak intensity) are in agreement with a non-planar configuration of the $SnMe_3$ group, and four-coordination at the tin atom. The Sn–C stretching frequencies for phenyltin derivatives were not observed since they fall below 400 cm^{-1} [19,23], while for other alkyltin dimethyldithiophosphinates they are masked by strong frequencies of the organic groups and P–S bonds.

In monomeric compounds the dithiophosphinato ligands can, in principle, adopt one of the following coordination patterns: monodentate (**A**), anisobidentate (**B**) and isobidentate (**C**).



(**A**) (**B**) (**C**)

In **A** the tin atom is four-coordinate with tetrahedral geometry. In **C** it is six-coordinate with octahedral geometry and equivalent P–S and Sn–S bonds, while the coordination geometry in **B** is intermediate between tetrahedral and octahedral, with non-equivalent P–S and Sn–S bonds [17].

It has been suggested that the differences Δ between asymmetric and symmetric P–S stretching vibrations can be used to establish the coordination pattern of the dithiophosphinato ligands. Thus, Δ values larger than 95 cm^{-1} are observed for monodentate dithiophosphinates (type **A**) and values between 50 and 70 cm^{-1} for isobidentate dithiophosphinates (type **C**); intermediate values (70–90 cm^{-2}) would indicate anisobidentate behavior (type **B**) [20]. The Δ values for the compounds reported in this paper are listed in Table 2.

According to the criteria cited [20], these data suggest that in all of our compounds the ligand is monodentate. However, a clear difference is observed between triorganotin and diorganotin derivatives. The highest values (Δ in the range 125–128 cm^{-1}) for triorganotin dimethyldithiophosphinates suggest that these are of type **A**, with tetrahedral tin and monodentate ligand. The decrease of the Δ values (113–118 cm^{-1}) observed for diorganotin dimethyldithiophosphinates suggest that a weak Sn...S interaction occurs, the coordination becoming of type **B**. This coordination geometry can be described either as tetrahedral, if only the covalent Sn–S

Table 2

Infrared data for $R_nSn(S_2PMe_2)_{4-n}$ (cm^{-1}) [a,b]

R	n	$\nu_{as}(PS_2)$	$\nu_s(PS_2)$	Δ [c]
Me	2	600s	487s	113
n-Bu	2	599s 592s	485s	114
Bz	2	598s	483s	115
Ph	2	600s	482s	118
Me [d]	3	600s	472s	128
Cy	3	605s	480s	125
Bz	3	600s	473s	127
Ph	3	600s	475m	125

[a] m = medium, s = strong. [b] In KBr pellets. [c] In CS_2 solution. [d] $\Delta = \nu_{as}(PS_2) - \nu_s(PS_2)$.

and Sn–C bonds are considered, or as severely distorted octahedral, if the weak, nonbonding (or semibonding) Sn...S interactions (to sulfur involved in double P=S bonds), are considered. This type of coordination is confirmed by two relevant X-ray structure determinations of $Me_2Sn(S_2PMe_2)_2$ [24] and $Me_2Sn(S_2PEt_2)_2$ [7]. In both cases, two sets of tin–sulfur interatomic distances were observed: Sn–S bond distances of ca. 2.5 Å corresponding to single covalent tin–sulfur bonds, and ca. 3.3 Å, which is longer than a single tin–sulfur bond, but significantly shorter than the sum of Van der Waals radii (4 Å). Therefore, the anisobidentate structure **B** seems to be achieved by all diorganotin dialkyldithiophosphinates. Dipole moments and ^{119m}Sn Mössbauer data are also in agreement with this conclusion [18].

It is interesting to note that the only known example of symmetrical (isobidentate) dithiophosphorus ligand in an organotin derivative, with octahedral coordination around the metal has been observed so far in a dithiophosphate, $Ph_2Sn[S_2P(OPr^i)_2]_2$ [5].

^{1}H NMR spectra. Chemical shifts and coupling constants, corresponding to the organic groups bonded to tin and phosphorus atoms, are listed in Table 3. For all organotin dimethyldithiophosphinates, the ^{1}H NMR spectra contain a doublet of singlets, corresponding to the protons of the methyl groups linked to phosphorus. The splitting of this signal (13 Hz) arizes from a $^2J(^{31}P{-}C{-}^1H)$ coupling with the ^{31}P nucleus.

For $Me_2Sn(S_2PMe_2)_2$, the C–Sn–C bond angle was calculated from the ^{119}Sn–^{1}H coupling constant $^2J(^{119}Sn{-}C{-}^1H)$ of 78 Hz, according to the relation given by Lockhart [25], viz.: $\theta_{deg} = 0.0161\ |^2J|^2 - 1.32\ |^2J| + 133.4$. The values of 128.4° obtained compared satisfactorily with that calculated from Mössbauer data, i.e. 126.8° (see below), and with the value obtained by X-ray diffraction, i.e. 122.6° [24].

^{119m}Sn-Mössbauer spectra. Tin-119m Mössbauer spectra were recorded for two representative compounds, $Me_2Sn(S_2PMe_2)_2$ and $Ph_3SnS_2PMe_2$. The data, collected in Table 4, are consistent with the structures suggested by infrared spectra. For both compounds the magnitude of isomer shifts (IS) values agrees with the tin(IV) oxidation state [26]. The magnitudes of quadrupole splitting indicate a *trans*-configuration of the methyl groups bonded to the metal atom in the dimethyltin derivative [26,27], corresponding to structure **B**.

Table 3

^{1}H NMR data for $R_nSn(S_2PMe_2)_{4-n}$ [a,b,c]

R	n	Chemical shifts (ppm) and coupling constants (Hz)
Me [d]	2	1.72s (6H), $^2J(^{117}SnC^1H)$ 74, $^2J(^{119}SnC^1H)$ 78, (SnCH_3) 2.14ds (12H), $^2J(^{31}PC^1H)$ 13.5, (P–CH_3)
n-Bu [e]	2	1.00–2.18m (18H), (Sn–CH_2–CH_2–CH_2–CH_3) 2.1ds (12H), $^2J(^{31}PC^1H)$ 13, (P–CH_3)
Bz [d]	2	3.67s (4H), $^2J(^{117}SnC^1H)$, 72, $^2J(^{119}SnC^1H)$ 75, (Sn–CH_2–C_6H_5) 7.3m (10H), (Sn–CH_2–$C_6$$H_5$) 1.68s (12H), $^2J(^{31}PC^1H)$ 12, (P–CH_3)
Ph [d]	2	7.33m (6H-*meta* + *para*), 7.97m (4H-*ortho*), (Sn–$C_6$$H_5$) 1.78ds (12H), $^2J(^{31}PC^1H)$ 12, (P–CH_3)
Me [e]	3	0.6s (9H), $^2J(^{117}SnC^1H)$ 58, $^2J(^{119}SnC^1H)$ 61, (Sn–CH_3) 1.98ds (6H), $^2J(^{31}PC^1H)$ 13, (P–CH_3)
Cy [e]	3	1.27–2.11m (33H), (Sn–$C_6$$H_{11}$) 2.11ds (6H), $^2J(^{31}PC^1H)$ 13, (P–CH_3)
Bz [e]	3	2.64s (6H), $^2J(^{117}SnC^1H)$ 62, $^2J(^{119}SnC^1H)$ 68, (Sn–CH_2–C_6H_5) 6.26m (15H), (Sn–CH_2–$C_6$$H_5$) 1.97ds (6H), $^2J(^{31}PC^1H)$ 13, (P–CH_3)
Ph [e]	3	7.29m (9H-*meta* + *para*), 7.64m (6H-*ortho*), (Sn–$C_6$$H_5$) 2.11ds (6H), $^2J(^{31}PC^1H)$ 13, (P–CH_3)

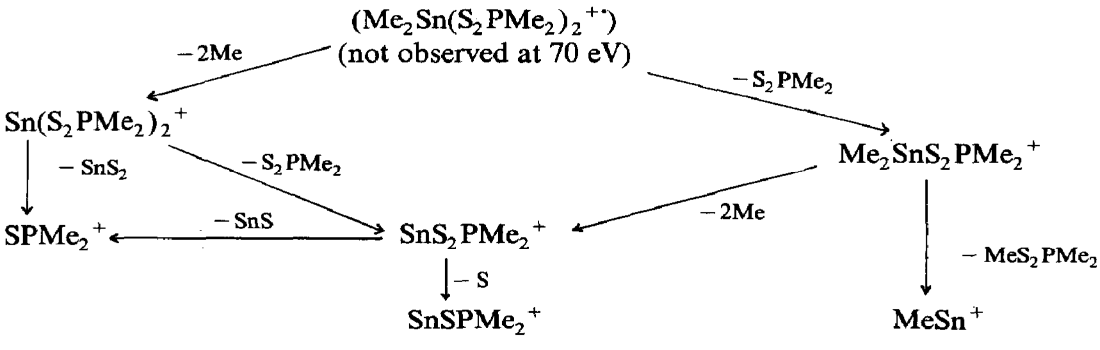
[a] TMS as internal standard. [b] s = singlet, ds = doublet of singlets, m = multiplet. [c] *ortho, meta* and *para* protons of phenyl groups linked to tin atom. [d] In $CDCl_3$ solution. [e] In CCl_4 solution.

Table 4

^{119m}Sn Mössbauer data for $R_nSn(S_2PMe_2)_{4-n}$ (at 77 K, in mm s^{-1})

R	n	IS ± 0.03	QS ± 0.06	Γ_1 ± 0.03	Γ_2 ± 0.03	ρ = QS/IS
Me	2	1.50	2.97	1.64	1.68	1.98
Ph	3	1.32	1.74	1.36	1.27	1.32

A value of 126.8° was calculated from the QS value [28], for the C–Sn–C bond angle in $Me_2Sn(S_2PMe_2)_2$. This is consistent with the X-ray diffraction value [24], and is intermediate between those corresponding to tetrahedral and octahedral geometry (closer to tetrahedral), indicating a distorted structure around tin.



Scheme 1. Fragmentation pattern of $Me_2Sn(S_2PMe_2)_2$.

Table 5

70 eV monoisotopic mass spectra of $R_nSn(S_2PMe_2)_{4-n}$ (*m/e*, (%)) [a]

	$Me_2Sn(S_2PMe_2)_2$	$Ph_3SnS_2PMe_2$
$Sn(S_2PMe_2)_2^+$	370 (2)	–
$R_2SnS_2PMe_2^+$	275 (100)	399 (100)
R_3SnS^+	197 (7)	383 (4)
$R_2SnSPMe_2^+$	–	367 (28)
R_3Sn^+	165 (7)	351 (50)
$SnS_2PMe_2^+$	245 (57)	245 (27)
$RSnS^+$	–	229 (18)
$SnPSMe_2^+$	213 (7)	213 (1)
RSn^+	135 (16)	197 (68)
Sn^+	–	120 (25)
$SPMe_2^+$	93 (57)	93 (24)

[a] The *m/e* values were computed according to H = 1, C = 12, P = 31, S = 32, Sn = 120.

The ρ value ($\rho = QS/IS$) for dimethyltin derivative is at the limit between a four-coordinated and a higher than four-coordinated configuration of the metal atom, while for the triphenyltin derivative ($\rho < 1.6$) it is consistent with a four-coordinated tin atom [26,27].

Mass spectra. The 70 eV monoisotopic mass spectra of $Me_2Sn(S_2PMe_2)_2$ and $Ph_3SnS_2PMe_2$ are listed in Table 5. The fragmentation pattern of the dimethyltin derivative is shown in Scheme 1.

Neither compound showed the molecular ion at 70 eV.

For $Me_2Sn(S_2PMe_2)_2$, one of the expected ions [29,30], of the first fragmentation, i.e. $Me_2SnS_2PMe_2^+$, is the base peak, as observed before for other diorganotin dithiophosphinates [7,8]. However, the second ion of the initial fragmentation, $MeSn(S_2PMe_2)_2^+$, is absent, like for $Ph_2Sn(S_2PPh_2)_2$ [8].

A $Sn(S_2PMe_2)_2^+$ ion, in which tin has a formal oxidation state of III, is also present in low abundance. This exception to the general rule that only fragments in which tin is in an oxidation state of II or IV are observed in the mass spectra of organotin compounds [29,30], seems to be general for diorganotin diorganodithiophosphinates, since similar ions were also observed for some diethyl- and diphenyl-dithiophosphinates [7,8].

The unusual fragment $Me_4PS_4Sn^+$ (*m/e* 339, 5%), which can be described as $Me_2PS_2Sn(SMe)_2^+$ or $Me_2PS_2Sn(Me)(SMe)S^+$, shows that a sulfur atom can be found between tin and a methyl group. An analogous interpretation is possible for another ion, $MeSn(SMe)_2^+$ or $Me_2Sn(SMe)S^+$, which is also present in an abundance of 7% of the base peak. How these ions are formed can be a mater of speculation.

The fragment ions containing three methyl groups bonded to tin, i.e. Me_3SnS^+ (*m/e* 197, 7%) and Me_3Sn^+ (*m/e* 165, 7%), may arise from some traces of $Me_3SnS_2PMe_2$ present accidentally in the sample.

Fragment ions containing two tin atoms were also observed: $MeS_2Sn_2^+$ (*m/e* 329, 2%) and $MeP_2SSn_2^+$ (or $Me_3S_2Sn_2$) (*m/e* 349, 12%).

The fragmentation pattern of $Ph_3SnS_2PMe_2$ is very similar to those described for other triorganotin dithiophosphinates [7,8]. The base peak is $Ph_2SnS_2PMe_2^+$, obtained by the cleavage of a tin–carbon bond, and only tin fragments in which the tin has an oxidation state II or IV are observed in the mass spectra.

Experimental

Organotin chlorides, R_2SnCl_2 and R_3SnCl, were commercial products or were prepared as described in previous papers [7,8]. The salt $Me_2PS_2Na \cdot 2H_2O$ was prepared by cleavage of $Me_2P(S)$–$P(S)Me_2$ with $Na_2S \cdot xH_2O$ and sulfur, according to published procedures [31]. The IR spectra were recorded on a Specord 75 IR Carl Zeiss Jena (DDR) with KBr pellets or CS_2 solutions. The ^1H NMR spectra were recorded on a Tesla B-487 spectrometer (made in Czechoslovakia), operating at 80 MHz, and mass spectra were recorded on an AEI MS-902S instrument. ^{119m}Sn-Mössbauer spectra were recorded by the late J.J. Zuckerman, at 77 K on a Ranger Engineering constant-acceleration spectrometer with $Ca^{119m}SnO_3$ (New England Nuclear Corp.) as the source and as standard reference material for zero velocity. Satisfactory elemental analyses were obtained for all new compounds prepared.

Preparation of title compounds. Stoichiometric amounts of organotin chlorides and sodium dimethyldithiophosphinate were refluxed in organic solvents (see Table 1), with stirring for 2 h. Then the NaCl precipitated was filtered off and the hot filtrate was concentrated in vacuum. The solid thus obtained was recrystallized from organic solvents, yielding white, crystalline products.

For $Me_2Sn(S_2PMe_2)_2$, distilled water was used as solvent. The white crystals of the product which separated from the reaction mixture were filtered under vacuum and recrystallized from $EtOH/CHCl_3$ mixture (1/1).

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