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Preparation, vibrational spectra and crystal structure of tris(trimethyltin) tetrathiophosphate $(Me_3SnS)_3PS$

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Abstract

Tris(trimethyltin) tetrathiophosphate $(Me_3SnS)_3PS$ has been prepared by the reaction of $(Me_3Sn)_2S$ with $PSCl_3$. Its IR and Raman spectra are reported and discussed, and ^{31}P NMR spectral data presented. A X-ray diffraction study shows that crystals of $(Me_3SnS)_3PS$ consist of discrete monomeric molecules in which both the tin and phosphorus atoms are four-coordinate and the Me_3Sn groups are covalently bonded to the sulphur.

Introduction

It was previously found that $(Me_3Sn)_2S$ reacts with Me_2PSCl and $PSBr_3$ with symmetrical cleavage of Sn–S–Sn bonds to give $(Me_2PS)_2S$ and P_4S_9. The reaction of $(Me_3Sn)_2S$ with $POCl_3$ gives mixture as a result of oxygen–sulphur exchange [1]. In contrast, unsymmetrical fission of Si–S–Si bonds takes place in the reaction of $(Me_3Si)_2S$ with POX_3 to give $Me_3SiOSPX_2$ ($X = F$ [2], Cl, Br [3]), and $P_4O_4S_6$ informed on treatment of $(Me_3Si)_2S$ with $POCl_3$ [4]. Phosphorus oxyhalides and thiohalides also cause the scission of the Sn–O bonds in $(Me_3Sn)_2O$. Thus, $Me_3SnOSPF_2$, $Me_3SnOSPRR'$ ($RR' = Me_2$, MePh, Ph_2) and $Me_3SnO_2PCl_2$ have been prepared by the reaction of $(Me_3Sn)_2O$ with PSF_3 [5], $RR'PSCl$ [6], or $POCl_3$ [1], respectively.

Solid $Me_3SnOSPMe_2$ [6] and $Me_3SnO_2PCl_2$ [7] have been shown by X-ray diffraction to have a polymeric structure involving penta-coordinate tin atoms, the $OSPMe_2$ and O_2PCl_2 groups behaving as bidentate bridge ligands.

We describe here the reaction between $(Me_3Sn)_2S$ and $PSCl_3$ and the preparation of $(Me_3SnS)_3PS$. The X-ray crystal structure and the vibrational spectra of the product are discussed.

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Results and discussion

Phosphorus thiochloride reacts with $(Me_3Sn)_2S$ to give white crystals of $(Me_3SnS)_3PS$ containing $PSCl_3$, which cannot be removed by keeping the product under vacuum.

$$3(Me_3Sn)_2S + PSCl_3 \rightarrow (Me_3SnS)_3PS + 3Me_3SnCl$$

The chloride analysis indicates that $PSCl_3$ forms 17% of the isolated material. The product is soluble in common organic solvents and undergoes a change in its properties when left for a few days at room temperature, possibly because of further reaction of $PSCl_3$ with $(Me_3SnS)_3PS$. However, if it is kept in the freezer there is no significant change even after a considerable period.

The presence of $PSCl_3$ along with the $(Me_3SnS)_3PS$ is confirmed by the IR spectrum, which shows the typical $PSCl_3$ absorption bands (ν(P=S) at 755, $\nu_{as}(PCl_3)$ at 536 and $\nu_s(PCl_3)$ at 425 cm^{-1}). Furthermore, the ^{31}P NMR spectrum of the product contains two signals, one at δ 30 ppm corresponding to $PSCl_3$ and the other at δ 79 corresponding to $(Me_3SnS)_3PS$.

The $(Me_3SnS)_3PS$ was obtained free from $PSCl_3$ by recrystallization from cyclohexane. The ^{31}P NMR spectrum of the recrystallized material shows the expected $(Me_3SnS)_3PS$ signal at 79 ppm, and the $PSCl_3$ IR bands are absent. The $(Me_3SnS)_3PS$ crystallizes as long shiny needles which seem to contain some cyclohexane since removal of cyclohexane when the needles are kept under vacuum leads to deformation and clouding of the crystals.

We reported previously that $(Me_3Sn)_2S$ reacts with $POCl_3$ with oxygen–sulphur exchange and formation of a precipitate. The ^{31}P NMR of the filtered solution shows a signal at 79 ppm, which is shown by the present study to be from $(Me_3SnS)_3PS$. This identification of the latter compound among the products, from $(Me_3Sn)_2S$ and $PSCl_3$ provides additional evidence for the suggested O/S exchange [1].

$PSCl_3$ reacts both with either an equimolar amount or an excess of $(Me_3Sn)_2S$ to give $(Me_3SnS)_3PS$. In contrast, if an excess $PSCl_3$ is used under reflux conditions the reaction gives P_4S_9 [8].

The silicon analogue of $(Me_3SnS)_3PS$, $(Me_3SiS)_3PS$, is known, and was prepared by reaction of $(Me_3Si)_2S$ with P_4S_{10} [9] and also by reaction of sulphur with $(Me_3Si)_3P$ [10]. $(Me_3Sn)_2S$ is more reactive toward phosphorus thiohalides than $(Me_3Si)_2S$. Whereas $(Me_3Si)_2S$ does not react with PSF_3 and reacts only slowly with PSF_2Br [11], $(Me_3Sn)_2S$ reacts readily with $PSCl_3$, $PSBr_3$ and Me_2PSCl [1]; $PSBr_3$ reacts more readily than $PSCl_3$ probably as a result of the greater ease of cleavage of the weaker P–Br bond.

Vibrational spectra

Table 1 lists the observed IR and Raman frequencies of the title compound, with the relative intensities and assignments.

The frequencies of Me_3Sn groups are assigned by comparison with the vibrational spectra of $(Me_3Sn)_2S$ [12] and other Me_3Sn containing compounds [6,7].

In keeping with approximate C_{3v} local symmetry of the SnC_3 skeleton, the two expected bands, $\nu_{as}(SnC_3)$ E (542 (IR), 535 cm^{-1} (Raman)) and $\nu_s(SnC_3)$ A_1 (510 (IR), 507 cm^{-1} (Raman)) appear in both the IR and Raman spectra. However, a

Table 1

IR and Raman spectral data for $(Me_3SnS)_3PS$ (cm^{-1})

IR	Raman	Assignment
2998w	2994vw	$\nu_{as}(CH_3)$
2926m	2920w	$\nu_s(CH_3)$
1194w	1185m	$\delta_{as}(CH_3)$
1188m	1178m-s	$\delta_s(CH_3)$
788vs		$\rho(CH_3)$
652s	644w	$\nu(P{=}S)$
546sh	540sh	$\nu_{as}(SnC_3)$
542s	535m	
529m	523m-s	$\nu_{as}(PS_3)$
510vs	507vs	$\nu_s(SnC_3)$
422vw	411s	$\nu_s(PS_3)$
356w	343s	$\nu(Sn{-}S)$
328m	324vw	
	242s	$\delta(SP{=}S)$
	168sh	$\delta(SnC_3)$
	152s	
	110w	

shoulder on the $\nu_{as}(SnC_3)$ band at 546 (IR) and 540 cm^{-1} (Raman) is presumably due to the deviation from the exact C_{3v} symmetry (see the description of the structure); in such a case the E mode splits into two fundamental vibrations. The band at 652 (IR) and 644 cm^{-1} (Raman) is attributed to $\nu(P{=}S)$, since no other fundamental vibrations are expected in this region; the corresponding band in $(MeS)_3PS$ is at 700 cm^{-1} [13]. IR spectra of $(MeS)_3PS$ and related compounds reveal a vibrational coupling of $\nu(P{=}S)$ with $\nu(PS_3)$ which causes a shift of $\nu(P{=}S)$ to higher frequency [14]. Correspondingly, the $\nu(P{=}S)$ band of $(Me_3SnS)_3PS$ appears at higher frequency than that of R_3PS (R = Ph (639 cm^{-1}) R = i-Pr (539 cm^{-1}), R = Et (536 cm^{-1}), R = Me (565 cm^{-1})) [15].

Structural investigation

(a) Experimental data. Table 2 lists data on the crystal used and the measurement parameters. The unit cell was determined from a set of 25 reflexions with $18° < \theta < 26°$. The structure was solved by direct methods (MULTAN80 [18]) and successive difference Fourier syntheses, with refinements by least squares. The structure determination showed the space group to be *Cc*. In the final stage of refinement the hydrogen atoms were introduced located at the corners of ideal tetrahedra with C–H 108 pm and all angles 109.28°. Anisotropic treatment of all atoms but hydrogen gave a final *R*-value of 0.024. Atomic coordinates and equivalent temperature factors for the non-hydrogen atoms are listed in Table 3. Lists of observed and calculated structure factors are available from the authors.

(b) The structure. From the stereoscopic view (Fig. 1) it can be seen that the compound is not ionic but consists of covalently-bonded molecules in which the tin atom is coordinated by three methyl groups and one sulfur atom in tetrahedral geometry. The angles at the single bonded sulfur atoms S(1) to S(3) are all bent towards S(4), and the $SnMe_3$ groups are arranged to surround S(4) with six methyl

Table 2

Crystal data, details of intensity measurement and structure development

Crystal dimensions	$0.276 \times 0.082 \times 0.874$ mm
Cell constants	a 1004.8(1), b 3189.9(5), c 698.0(1) pm β 95.28(1)°
Volume	V 2227.8×10^6 pm^2
Formula units per Unit cell	$Z = 4$
Crystal system, Space group	monoclinic, Cc
Diffractometer	CAD4, Enraf–Nonius
Radiation	Mo-K_α (graphite-monochromatized)
Temperature during measurement	20 °C
Scan range and mode	$1° < \theta < 26°$, ω-scans
Measured reflexions	3310
independent	2369
unobserved	110 ($F_o < 3\sigma(F_o)$)
Corrections	Lorentz- and polarisation factor, absorption corr. with μ 35.0 cm^{-1}
Restrictions	methyl groups rigid with C–H = 108 pm and H–C–H 109°28′, same isotropic temperature factor for hydrogens of one methyl group
Atomic scattering factors	[16,17]
Used computer programs	MULTAN80 [18], STRUX [19], SHELX76 [20], ORTEP [21]
R-value	$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert = 0.024$

groups (group 1 and 2 of each tin atom) resembling a chair-configurated hexagon. This suggests, hydrogen bridging to S(4), but the S–H distances, ranging from 284 pm (H(211)) to 337 pm (H(221)) do not confirm this. Comparison of the tetrahedral

Table 3

Atomic coordinates for the non-hydrogen atoms of $(Me_3SnS)_3PS$ with equivalent thermal parameters ($U_{eq} = 1/3 \Sigma_i \Sigma_j U_{ij} \cdot a_i^\star \cdot a_j^\star \cdot \mathbf{a_i} \cdot \mathbf{a_j}$)

Atom	x	y	z	U_{eq}
Sn(1)	0.000	0.0748(0)	0.0000	0.0479(3)
Sn(2)	0.2151(1)	0.2447(0)	0.8181(1)	0.0462(3)
Sn(3)	0.4892(1)	0.0955(0)	0.5668(1)	0.0454(2)
S(1)	0.0571(2)	0.0872(1)	0.6682(3)	0.0515(9)
S(2)	0.0648(2)	0.1894(1)	0.6758(3)	0.0488(9)
S(3)	0.2888(2)	0.1367(1)	0.4583(3)	0.0475(9)
S(4)	0.3054(2)	0.1360(1)	0.9450(3)	0.0495(9)
P	0.1891(2)	0.1373(1)	0.7058(3)	0.0385(8)
C(11)	0.157(1)	0.0396(3)	1.147(2)	0.068(5)
C(12)	−0.0537(9)	0.1322(3)	1.127(1)	0.064(5)
C(13)	−0.170(1)	0.0344(4)	0.937(2)	0.079(6)
C(21)	0.2425(9)	0.2399(3)	1.124(1)	0.062(5)
C(22)	0.3971(9)	0.2426(3)	0.683(2)	0.072(5)
C(23)	0.106(1)	0.3001(3)	0.733(2)	0.073(5)
C(31)	0.6290(9)	0.1349(3)	0.729(2)	0.066(5)
C(32)	0.437(1)	0.0406(3)	0.713(2)	0.070(5)
C(33)	0.562(1)	0.0791(3)	0.297(2)	0.069(5)

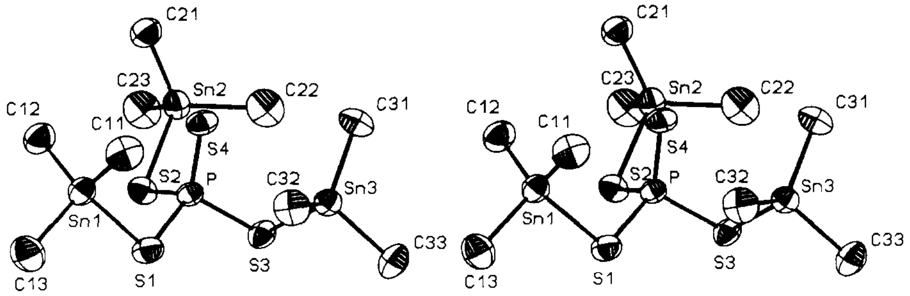

Fig. 1. Stereoscopic view of a molecule of $(Me_3SnS)_3PS$. ORTEP [21] plot with 50% thermal ellipsoids determined at 20 ° C.

angles (Table 4) at the tin atom (in particular S–Sn–C) shows that the SnC_3 groups are bent away slightly from S(4), indicating steric hindrance.

Whereas in the ionic tetrathiophosphates the P–S bond lengths range from 202 to 206 pm [22,23], covalent species exhibit distances of 205 to 207 pm for single-bonded

Table 4

Bond lengths (pm) and bond angles (°) in $(Me_3SnS)_3PS$

P–S(1)	208.0(2)	S(4)–P–S(1)	114.7(1)
P–S(2)	207.8(2)	S(4)–P–S(2)	114.3(1)
P–S(3)	207.6(2)	S(4)–P–S(3)	114.6(1)
P–S(4)	194.8(2)		
		S(1)–P–S(2)	103.4(1)
Sn(1)–S(1)	246.9(2)	S(2)–P–S(3)	104.8(1)
Sn(2)–S(2)	247.1(2)	S(3)–P–S(1)	103.8(1)
Sn(3)–S(3)	246.5(2)		
		P–S(1)–Sn(1)	101.8(1)
Sn(1)–C(11)	212.4(9)	P–S(2)–Sn(2)	101.0(1)
Sn(1)–C(12)	212.7(8)	P–S(3)–Sn(3)	101.1(1)
Sn(1)–C(13)	215.6(9)		
		Sn(1)–Sn(1)–C(11)	108.1(3)
Sn(2)–C(21)	213.1(9)	S(1)–Sn(1)–C(12)	110.1(3)
Sn(2)–C(22)	213.4(8)	S(1)–Sn(1)–C(13)	98.8(3)
Sn(2)–C(23)	213.7(9)		
		C(11)–Sn(1)–C(12)	117.3(4)
Sn(3)–C(31)	213.2(8)	C(12)–Sn(1)–C(13)	111.9(4)
Sn(3)–C(32)	212.0(8)	C(13)–Sn(1)–C(11)	108.9(4)
Sn(3)–C(33)	214.8(9)		
		S(2)–Sn(2)–C(21)	111.7(2)
		S(2)–Sn(2)–C(22)	108.5(3)
		S(2)–Sn(2)–C(23)	101.3(3)
		C(21)–Sn(2)–C(22)	113.7(4)
		C(22)–Sn(2)–C(23)	110.1(4)
		C(23)–Sn(2)–C(21)	111.9(4)
		S(3)–Sn(3)–C(31)	109.3(3)
		S(3)–Sn(3)–C(32)	110.8(3)
		S(3)–Sn(3)–C(33)	101.2(3)
		C(31)–Sn(3)–C(32)	114.4(4)
		C(32)–Sn(3)–C(33)	109.9(4)
		C(33)–Sn(3)–C(31)	110.4(4)

sulfur and 193 to 199 pm when π-overlap is thought to occur [24–26]. Comparison of the bond length P–S(4) (195 pm) with those P–S bonds in similar environments [6,24–28] shows that most of those bonds to which π-bond character is attributed are longer than 196 pm. In some cases the sulfur atom of the short P–S bond is weakly coordinated to an electrophilic center. An explanation for the apparent high proportion of π-bonding in $(Me_3SnS)_3PS$ may lie in the complete inability of the S(4) atom to take part in coordination because of complete shielding by the six methyl groups. As a consequence of π-bonding, the bond angles at the phosphorus atom radiating away from the S(4)–P bond are significantly larger (114.2–114.8°) than the other S–P–S angles (103.4–104.8°).

Experimental

The IR spectra were obtained with a Perkin–Elmer 577 spectrophotometer equipped with CsBr windows; Nujol or Hostaflon mulls were used. Raman spectra were recorded with a Cary 83 instrument with laser excitation. The ^{31}P NMR spectra were obtained for C_6D_6 solutions with a Varian XL 100 spectrometer, 85% H_3PO_4 was used as external standard. The experiments were carried out under anhydrous conditions.

$(Me_3Sn)_2S$ was prepared by a published method [29], and $PSCl_3$ was by treating PCl_3 with sulfur in the presence of $AlCl_3$ [30].

Preparation of $(Me_3SnS)_3PS$

Phosphorus thiochloride (4.6 g, 27 mmol) was added to (10 g, 27.7 mmol) $(Me_3Sn)_2S$ at room temperature. The reaction was slightly exothermic. The mixture was kept at 80 °C for 45 min then set aside overnight. The crystalline precipitate was filtered off, washed with cyclohexane, and dried in vacuum. The yield of $(Me_3SnS)_3PS$ containing $PSCl_3$ was 4.6 g. The product (1.8 g) was recrystallized from 7 ml cyclohexane to give $(Me_3SnS)_3PS$ (1.1 g), m.p. 81 °C.

$(Me_3SnS)_3PS$ is readily soluble in common organic solvents such as benzene, ether, CH_2Cl_2 and toluene. The single crystals suitable for intensity measurement were obtained by evaporation of an ether solution of the recrystallized substance at room temperature; the flask used in this process was equipped with a drying tube. Analysis: Found: C, 17.10; H, 4.15; P, 4.82; Sn, 51.11. $C_9H_{27}PSn_3S_4$ calc: C, 16.59; H, 4.14; P, 4.76; Sn, 54.84%.

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