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Synthesis, Characterization and Biological Activity of Organotin Derivatives of 2-Thionaphthalene, Including the Crystal Structures of (Naphthalenethiolato-*S*)-triphenyltin(IV) and Bis(naphthalene-thiolato-*S*)dimethyltin(IV)

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A series of di- and tri-organotin complexes of 2-thionaphthalene of general formula $RR'R''SnL$ ($R = R' = R'' = C_6H_5$, CH_3, n-C_4H_9, C_6H_{11}, $C_6H_5CH_2$; $R = R' = C_6H_5CH_2$, $R'' = Cl$; $R = R' = Me$, $R'' = C_{10}H_7S$ and $L = 2$-thionaphthalene, $C_{10}H_7S$) have been prepared by the reaction of di-or tri-organotin chloride(s) with 2-thionaphthalene. All compounds have been characterized by elemental analysis, IR, MS, NMR (^1H, ^{13}C, ^{119}Sn) and ^{119}Sn Mössbauer spectroscopies. X-ray crystal structures of the representative compounds $(C_6H_5)_3SnL$ and $(CH_3)_2SnL_2$ confirm a tetrahydral geometry about tin. The biological activities of these compounds against various bacteria and fungi have been investigated. © 1997 by John Wiley & Sons, Ltd.

Keywords: organotin; 2-thionaphthalene; synthesis; crystal structure; biological activity

INTRODUCTION

Metallomercaptans have a variety of industrial and biological applications. Zinc complexes of mercaptobenzothiazone have been used in the acceleration of rubber vulcanization[1–3] and its rhenium and ruthenium complexes have been reported as corrosion inhibitors.[4–6] Most of the metallo-organic mercaptans are known for their fungicidal activities,[7,8] while organotins in general are known for their toxicity and widespread biological activity.[9,10]

Tetraorganotin compounds react with thiols and thiophenols to cleave the Sn–C bond with the formation of Sn–S bonds[11–13] The products obtained by such reactions are non-uniform and yields are only moderate. Sn–S heterocycles are formed when the thiolysis of diorganotin dihalides is carried out with 1 mol of dithiol instead of 2 mol of monothiol.[14] In the recent work we report the synthesis and characterization of various 2-thionaphthyltin(IV) derivatives. The crystal structures of (naphthalenethiolato-*S*)triphenyltin(IV) and bis(naphthalenethiolato-*S*)dimethyltin(IV) along with the biological activities of these compounds are also reported.

EXPERIMENTAL

All reagents were of analytical grade and were used without further purification. R_3SnCl (R = Me, n-Bu, C_6H_{11} and Ph) were of commercial origin; $(PhCH_2)_nSnCl_{4-n}$ ($n = 1, 2$) were prepared by literature methods.[15] Solvents were dried by standard procedures.[16] Spectra were recorded on the following instruments: JEOL GX270 (^1H, ^{13}C NMR), and GX400 (^{119}Sn NMR), Hitachi model 270–50 spectrometer (IR;

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as = asymmetric; sm = symmetric; s = strong; sh = sharp; shd = shoulder; m = medium; w = weak; v = very), MAT 8500 (70 eV EI mass spectra, courtesy of the University of Bayreuth, Germany; quoted fragments are based on ^{120}Sn). NMR spectra were recorded in $CDCl_3$ unless indicated otherwise. Analytical data were determined on a Carlo Erber Elemental Analyser model 1106 at the University of Bath. Details of the Mössbauer spectrometer and related procedures are given elsewhere.[17]

LD_{50} values were determined by a brine-shrimp assay method.[18, 19] Antibacterial studies were carried out by Muller Hinton agar and agar-well diffusion methods.[20–24] One loopful of 24 h old culture containing ca 10^4–10^6 colony-forming units (cfu) was spread on the surface of Muller Hinton agar (MHA) plates. Wells were created in the medium using a sterile metallic borer and stock solutions of the samples were added. Tobramycin and ampicilin were used as standards. The minimum inhibitory concentration (MIC) is defined as the lowest concentration of active compound which prevents the growth of the test organism under optimal concentration. MIC values were determined by the broth dilution method using nutrient broth: 0.1 ml at 10^4–10^6 cells ml^{-1} of the sensitive bacterial culture was added to tubes containing 1 ml of different concentrations of compound and 1 ml of nutrient broth. Results were observed after 24 h of incubation at 37 °C.

Antifungal behaviour was determined by the agar tube diffusion method. Test tubes containing sterile Sabour and dextrose agar were inoculated with the test compound at different concentrations and kept in a standing position at room temperature to solidification. Test fungal cultures were inoculated on the slant, and growth inhibition was observed after an incubation period of seven days. Griseofulvin and nystatin were used as standards and MIC values were determined as above.[21, 25, 26]

Syntheses

The synthesis of (naphthalenethiolato-*S*)triphenyltin(IV) is reported as typical of the general procedure used to prepare compounds **1**–**6**.

(Naphthalenethiolato-*S*)triphenyltin(IV) (1)
2-Thionaphthalene (1.60 g, 10 mmol) in tetrahydrofuran (30 ml) was added to triethylamine (2.2 ml, 10 mmol) in a three-necked flask with reflux condenser. Triphenyltin chloride (3.85 g, 10 mmol) in tetrahydrofuran (20 ml) was added dropwise with constant stirring. The reaction mixture turned cloudy and was left for overnight stirring. The mixture was filtered and tetrahydrofuran was removed under vacuum. The residue obtained was crystallized from petroleum ether (40–60 °C) to obtain **1** as a colourless crystalline compound (50%, m.p. 66 °C).

Analysis: Found (calcd for $C_{28}H_{22}SSn$): C, 65.7 (66.0); H, 4.26 (4.23)%.
IR data (cm^{-1}): 3040 m, ν(C—H); 1578 s, shd, ν(C=C); 660 b, ν(S—C); 400 shd, m, ν(Sn—S).
Mössbauer data: IS=1.31, QS = 1.46, Γ = 1.10, 1.00 mm s^{-1}
^{1}H NMR: 7.0–7.2 ppm (complex, 22H, C_6H_5, $C_{10}H_7$).
^{13}C NMR: 137.4, 136.6, 133.5, 132.4, 129.7, 129.6, 128.7, 127.8, 127.3, 126.8, 126.0, 125.4 ppm ($C_{10}H_7S$, C_6H_5).
^{119}Sn NMR: −64.9 ppm. 70 eV EI monoisotropic mass spectra (*m/z*): 510 [27%, $C_{10}H_7SSn(C_6H_5)_3$], 351 [100%, $Sn(C_6H_5)_3$], 197 [20%, SnC_6H_5], 159 [6%, $C_{10}H_7S$], 115 [7% C_9H_7].

The following compounds were prepared by analogous procedures.

$(CH_3)_3Sn(SC_{10}H_7)$ (2)
Yield 60%, liquid.

Analysis: Found (calcd for $C_{13}H_{16}SSn$): C, 49.1 (48.2); H, 5.00 (4.90)%.
IR data (cm^{-1}): 2986 m, ν(C—H); 1581 s, sh, ν(C=C); 650 b, shd, ν(S—C); 550 s, ν(Sn—C); 510 s, ν(Sn—C); 365 vs, ν(Sn—S).
Mössbauer data: IS = 1.25, QS = 2.09, Γ = 0.95, 0.96 mm s^{-1}.
^{1}H NMR ($CDCl_3$): 7.40–8.00 (complex, 7H, $C_{10}H_7$), 0.49 ppm (s, 9H, CH_3) [^2J(^{1}H–^{119}Sn) = 55.0 Hz].
^{13}C NMR: −4.7, [^1J(^{13}C–$^{117,\,119}$Sn) = 336.4, 353.0 Hz], 133.5, 132.6, 132.4, 131.9, 131.4, 127.7, 127.4, 126.7, 126.0, 125.2 ppm ($C_{10}H_7S$).
^{119}Sn NMR: 96.7 ppm.
70 eV monoisotropic mass spectra (*m/z*): 324 [8%, $C_{10}H_7SSn(CH_3)_3$], 309 [30%, $C_{10}H_7SSn(CH_3)_2$], 279 [35%, $C_{10}H_7SSn$], 159 [75%, $C_{10}H_7S$], 115 [100%, C_9H_7].

$(n\text{-}C_4H_9)_3Sn(SC_{10}H_7)$ (3)
Yield 60%, liquid, b.p. 89 °C/0.5 mm Hg.

Analysis: Found (calcd for $C_{22}H_{34}SSn$): C, 58.2

(58.7); H, 7.73 (7.50)%.
IR data (cm^{-1}): 3053 m, ν(C—H); 1589 s, sh, ν(C=C); 660 b, shd, ν(S—C); 445, vs, ν(Sn—C).
Mössbauer data: IS = 1.40, QS = 2.15, Γ = 0.97, 0.95 mm s^{-1}.
^{1}H NMR ($CDCl_3$): 7.41–8.00 (complex, 7H, $C_{10}H_7$), 0.94 (t, 9H, CH_3) [$^2J(^1H–^1H)$ = 7 Hz], 1.21 (m, 6H, CH_2), 1.37 (m, 6H, CH_2), 1.62 ppm (m, 6H, CH_2).
^{13}C NMR: 13.4, 14.3 [$^1J(^{13}C–^{117,\,119}Sn)$ = 310.7, 325.4 Hz], 26.8 [$^3J(^{13}C–^{117,\,119}Sn)$ = 62.5 Hz], 28.4 ppm [$^2J(^{13}C–^{117,\,119}Sn)$ = 20.2 Hz] (γ, α, δ, β-C_4H_9, respectively), 133.6, 132.7, 132.6, 132.4, 131.4, 127.5, 127.4, 126.6, 126.0, 125.16 ppm ($C_{10}H_7S$).
^{119}Sn NMR: 84.0 ppm.
70 eV monoisotropic mass spectra (*m/z*): 393 [45%, $C_{10}H_7SSn(C_4H_9)_2$], 336[2%, $C_{10}H_7$ SSn (C_4H_9)], 279 [35%, $C_{10}H_7SSn$], 291 [35%, $Sn(C_4H_9)_3$], 179 [95% $H_2Sn(C_4H_9)$].

$(C_6H_{11})_3Sn(SC_{10}H_7)$ (4)
Yield 45%, crystallization solvent light petroleum, m.p. 45–47 °C.

Analysis: Found (calcd for $C_{28}H_{40}SSn$): C, 63.5 (63.8), H, 7.59 (7.59)%.
IR data (cm^{-1}): 3053 m, ν(C—H); 1575 sh, ν(C=C); 675 b, ν(S–C); 390 m, shd, ν(Sn—S).
Mössbauer data: IS = 1.49, QS = 1.88, Γ = 1.06, 1.06 mm s^{-1}.
^{1}H NMR ($CDCl_3$): 7.17–7.85 (complex, 7H, $C_{10}H_7$), 1.14–1.84 ppm (complex, 33H, C_6H_{11}).
^{13}C NMR: 26.9, 29.0, 31.9 (γ, δ, β-CH_2, respectively) [$^3J(^{13}C–^{119}Sn)$ = 62.0; $^2J(^{13}C–^{119}Sn)$ = 16.6 Hz], 133.7, 132.9, 132.7, 131.4, 127.5, 126.7, 126.1, 125.2 ppm ($C_{10}H_7S$).
^{119}Sn NMR: 10.1 ppm.
70 eV EI monoisotropic mass spectra (*m/z*): 528 [8%, $C_{10}H_7SSn(C_6H_{11})_3$], 445 [3%, $C_{10}H_7SSn(C_6H_{11})_2$], 401 [1%, $SSn(C_6H_{11})_3$], 159 [28%, $C_{10}H_7S$], 127 [5%, $C_{10}H_7$], 115 [100%, C_9H_7].

$(C_6H_5CH_2)_3Sn(SC_{10}H_7)$ (5)
Yield 50%, crystallization solvent light petroleum.

Analysis: Found (calcd for $C_{31}H_{28}SSn$): C, 67.8 (67.5), H, 5.08 (5.08)%.
IR data (cm^{-1}): 3052 m, ν(C—H): 1575 sh, ν(C=C); 675 b, w, ν(S—C); 390 m, sh, ν(Sn–S).
Mössbauer data: IS = 1.50, QS = 1.69, Γ = 0.99, 0.93 mm s^{-1}.
^{1}H NMR ($CDCl_3$): 7.02–8.03 (complex, 22H, C_6H_5, $C_{10}H_7$); 2.76 ppm (s, 6H, CH_2Sn) [$^2J(^1H–^{119}Sn)$ = 62.2 Hz].
^{13}C NMR: 22.4 (CH_2Sn) [$^1J(^{13}C–^{117,\,119}Sn)$ = 262.9, 273.9 Hz], 139.1, 133.6, 133.1, 132.4, 128.6, 128.5, 128.0, 127.7, 127.8, 127.4, 126.6, 126.2, 125.5, 124.2 ppm ($C_{10}H_7S$, C_6H_5).
^{119}Sn NMR: 18.0 ppm.
70 eV EI monoisotropic mass spectra (*m/z*): 552 [2%, $C_{10}H_7SSn(C_6H_5CH_2)_3$], 461 [25%, $C_{10}H_7SSn(C_6H_5CH_2)_2$], 393 [2%, $Sn(CH_2C_6H_5)_3]_3$, 279 [100%, $C_{10}H_7SSn$].

$(CH_3)_2Sn(SC_{10}H_7)_2$ (6)
Yield 80%, recrystallization solvent petroleum ether (40–60 °C).

Analysis: Found (calcd for $C_{22}H_{20}S_2Sn$): C, 56.8 (56.4), H, 4.30 (4.20)%.
IR data (cm^{-1}): 2914 m, ν(C—H); 1581 s, sh, ν(C=C); 695 b, shd, ν(S—C); 395 vs, ν(Sn—S).
Mössbauer data: IS = 1.37, QS = 1.73, Γ = 0.82, 0.82 mm s^{-1}.
^{1}H NMR ($CDCl_3$): 7.40–7.80 (complex, 14H, $C_{10}H_7$), 0.57 ppm (s, 6H, CH_3) [$^2J(^1H–^{117,\,119}Sn)$ = 56.4, 59.0 Hz].
^{13}C NMR: −1.5 [$^1J(^{13}C–^{117,\,119}Sn)$ = 368.7, 387.9 Hz], 133.6, 132.5, 131.9, 129.7, 128.2, 127.6, 127.1, 126.4, 125.9 ppm ($C_{10}H_7S$).
^{119}Sn NMR: 126.1 ppm.
70 eV monoisotropic mass spectra (*m/z*): 468 [18%, $(C_{10}H_7S)_2Sn(CH_3)_2$], 453 [3%, $(C_{10}H_7S)_2Sn(CH_3)$], 309 [12%, $C_{10}H_7SSn(CH_3)_2$], 279 [55%, $C_{10}H_7SSn$], 127 [100%, $C_{10}H_7$].

$(C_6H_5CH_2)_2SnCl(SC_{10}H_7)$ (7)
2-Thionaphthalene (3.20 g, 20 mmol) in tetrahydrofuran (20 ml) was added to triethylamine (20 mmol) in the same solvent (5 ml) in a three-necked flask fitted with reflex condenser. Dibenzyltin dichloride (5.77 g, 20 mmol), also in tetrahydrofuran (40 ml), was added dropwise and the mixture was stirred overnight. After filtration and solvent evaporation the residue was washed several times with petroleum ether (40–60 °C) and subsequently recrystallized from the same solvent. Yield 55%, m.p. 88 °C.

Analysis: Found (calcd for $C_{24}H_{21}ClSSn$): C, 58.1 (58.1), H, 4.23 (4.23)%.
IR data (cm^{-1}):3022 m, ν(C—H); 1596 s, sh, ν(C=C); 670 b, w, ν(S—C); 387 sh, m, ν(Sn—S); 340 m, sh, ν(Sn—Cl).

Mössbauer data: IS = 1.12, QS = 2.29, Γ = 1.06, 1.06 mm s^{-1}.
^{1}H NMR ($CDCl_3$): 6.80–8.00 (complex, 17H, C_6H_5, $C_{10}H_7$); 2.27 ppm (s, 4H, CH_2Sn) [$^{2}J(^{1}H–^{119}Sn)$ = 59.4 Hz].
^{13}C NMR: 26.1 (CH_2Sn), 134.3, 134.2, 133.0, 128.9, 128.7, 128.5, 128.4, 128.0, 127.6, 126.7, 126.1, 125.2 ppm (C_6H_5, $C_{10}H_7$).
^{119}Sn NMR: 53.0 ppm.
70 eV EI monoisotropic mass spectra (*m/z*): 496 [1%, $C_{10}H_7SSn(CH_2C_6H_5)_2Cl$], 370 [12%, $C_{10}H_7SSnCH_2C_6H_5$], 279 [100%, $C_{10}H_7SSn$], 247 [1%, $C_{10}H_7Sn$], 212 [8%, $HSnCH_2C_6H_5$], 159 [3%, $C_{10}H_7S$], 127 [34%, $C_{10}H_7$].

Crystal and molecular structures

(Naphthalenethiolato-*S*)triphenyltin(IV) (1)

A crystal of approximate dimensions 0.2 mm × 0.2 mm × 0.2 mm, grown from a petroleum ether (40–60 °C) solution, was used for data collection.

Crystal data: $C_{28}H_{22}SSn$, M = 509.2 monoclinic, a = 14.107(4), b = 9.845(1), c = 17.814(4) Å, β = 106.81(2), U = 2368.3 Å^3, space group $P2_1/c$, Z = 4, D_c = 1.43 g ml^{-1}, μ(Mo-K_α) = 10.74 cm^{-1}, F(000) = 1024.

Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2 \leqslant \theta \leqslant 24°$; 4146 reflections were collected, of which 2557 were unique with $I \geqslant 3\sigma(I)$. Data were corrected for Lortentz and polarization effects but not for absorption. The structure was solved by Patterson methods and refined using the SHELX suite of programs.[27, 28] In the final least-squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions. Final residuals after ten cycles of least squares were R = 0.0507, R_w = 0.0529, for a weighting scheme of $w = 2.4368/[\sigma^2(F) + 0.002017(F)^2]$. Maximum final shift/ESD was 0.033. The maximum and minimum residual densities were 0.27 and −0.31 e Å^{-3} respectively. Final fractional atomic coordinates are given in Table 1. The asymmetric unit is shown in Fig. 1, alongwith the labelling scheme used.

Bis(naphthalenethiolato-*S*)dimethyltin(IV) (6)

A crystal of approximate dimensions 0.2 mm × 0.2 mm × 0.3 mm, crystallized from petroleum ether (40–60 °C), was used for data collection.

Crystal data: $C_{22}H_{20}S_2Sn$, M = 467.2, monoclinic, a = 16.625(2), b = 5.9501(7), c = 21.665(3) Å, β = 107.74(1)°, U = 2041.2 Å^3, space group $P2_1/n$, Z = 2, D_c = 1.52 g ml^{-1}, μ(Mo-K_α) = 12.4 cm^{-1}, F(000) = 936.

Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2 \leqslant \theta \leqslant 22°$; 2919 reflections were collected, of which 1858 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by Patterson methods and refined using the SHELX[27, 28] suite of programs. In the final least-squares cycles all were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions. Final residuals after ten cycles of least squares were R = 0.0296, R_w = 0.0286, for a weighting

Table 1 Fractional atomic coordinates (× 10^4) for (naphthalenethiolato-*S*)-triphenyltin(IV) (**1**)

Atom	*x*	y	z
Sn (1)	3199.5 (2)	1122.9 (3)	402.1 (2)
S(1)	1883.9 (10)	1990.1 (14)	887.4 (7)
C(1)	996 (3)	2220 (5)	− 52 (3)
C(2)	577 (4)	1082 (5)	− 513 (3)
C(3)	− 79 (4)	1270 (6)	− 1243 (3)
C(4)	− 343 (4)	2577 (6)	− 1546 (3)
C(5)	− 986 (4)	2808 (8)	− 2319 (4)
C(6)	− 1204 (5)	4073 (10)	− 2584 (4)
C(7)	− 819 (5)	5216 (9)	− 2123 (4)
C(8)	− 178 (4)	5045 (6)	− 1386 (3)
C(9)	66 (4)	3707 (5)	− 1082 (3)
C(10)	733 (3)	3498 (5)	− 328 (3)
C(11)	4529 (3)	1145 (4)	1355 (2)
C(12)	5050 (4)	− 52 (5)	1557 (3)
C(13)	5926 (4)	− 91 (6)	2157 (3)
C(14)	6287 (4)	1077 (7)	2565 (3)
C(15)	5775 (5)	2256 (6)	2379 (3)
C(16)	4901 (4)	2312 (5)	1768 (3)
C(17)	2861 (3)	− 947 (4)	70 (3)
C(18)	2365 (4)	− 1750 (5)	482 (3)
C(19)	2210 (4)	− 3127 (5)	303 (3)
C(20)	2550 (4)	− 3682 (5)	− 282 (4)
C(21)	3028 (4)	− 2910 (5)	− 688 (3)
C(22)	3194 (4)	− 1544 (5)	− 512 (3)
C(23)	3336 (4)	2377 (4)	− 540 (3)
C(24)	4240 (4)	3018 (5)	− 460 (3)
C(25)	4377 (6)	3801 (5)	− 1064 (5)
C(26)	3627 (6)	3957 (5)	− 1736 (4)
C(27)	2714 (5)	3342 (6)	− 1832 (3)
C(28)	2572 (4)	2541 (5)	− 1232 (3)

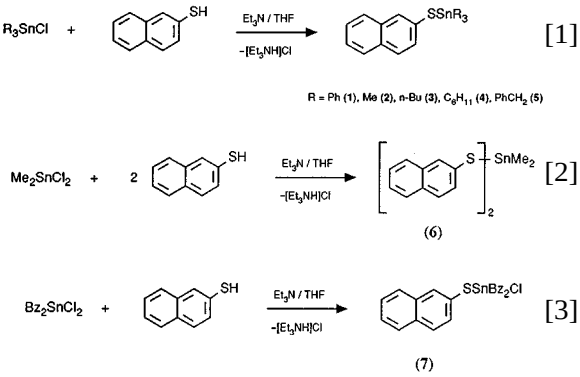
scheme of $w=2.6005/[\sigma^2(F)+0.000371(F)2]$. Maximum final shift/ESD was 0.001. The maximum and minimum residual densities were 0.67 and $-0.32\ e\ \text{Å}^{-3}$, respectively. Final fractional atomic coordinates are given in Table 2. The asymmetric unit is shown in Fig. 2, along with the labelling scheme used.

For both **1** and **6**, tables of anisotropic temperature factors, hydrogen atom positions and a complete listing of geometric parameters are available as supplementary data.

DISCUSSION

Synthesis, spectroscopy and structures

Five new triorganotin derivatives of 2-thionaphthalene have been synthesized by the reaction of the appropriate triorganotin halide and the thiol in the presence of base (Eqn [1]). A representative diorganotin derivative, $Me_2Sn(SC_{10}H_7)_2$ (**6**), has also been prepared by a similar route (Eqn [2]). We have also used the methodology of Eqn [2] to substitute $(C_6H_5CH_2)_2SnCl_2$ partially with thionaphthyl groups (to produce **7** and **8**, respectively) by control of reagent stoichiometries (Eqn [3]).



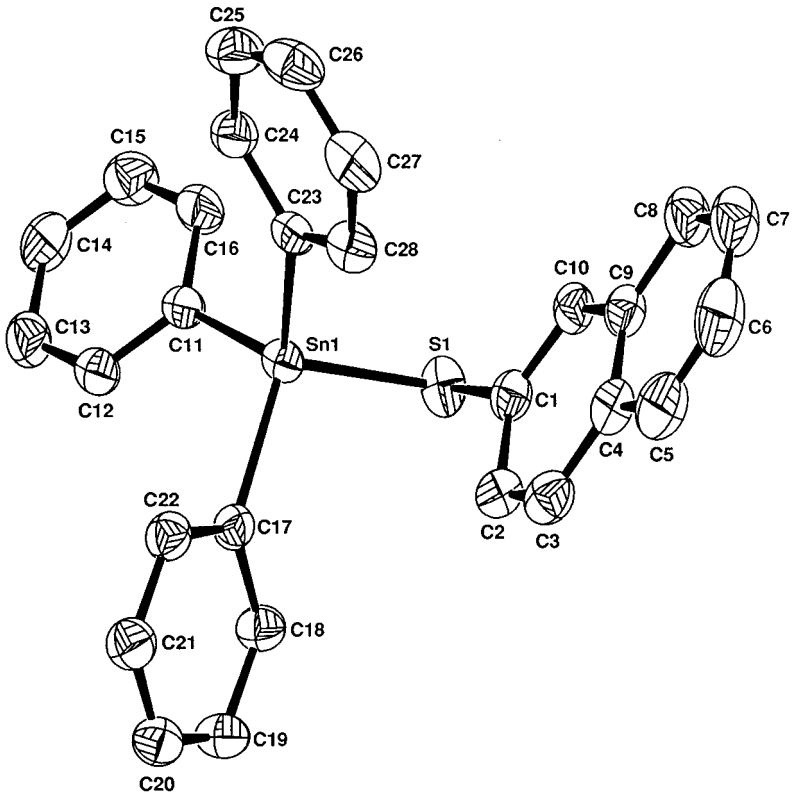


Figure 1 The asymmetric unit in **1** showing the labelling scheme used in the Tables. Important geometric data: Sn(1)–S(1) 2.418(1) Å, Sn(1)–C(11) 2.135(5) Å, Sn(1)–C(17) 2.137(4) Å, Sn(1)–C(23) 2.136(4) Å; S(1)–Sn(1)–C(11) 107.5(1)°, S(1)–Sn(1)–C(17) 107.6(1)°, S(1)–Sn(1)–C(23) 109.2(1)°, C(11)–Sn(1)–C(17) 107.7(2)°, C(11)–Sn(1)–C(23) 111.1(2)°, C(17)–Sn(10)–C(23) 113.4(2)°.

In the infrared spectra, ν(Sn—Cl) and ν(S—H) at 330 cm^{-1} and 2554 cm^{-1}, respectively, in the parent reagents are absent in the spectra of **1**–**6**. In contrast, ν(Sn—Cl) vibration in **7** is still visible at 340 cm^{-1}. For all seven compounds synthesized, ν(Sn—S) is observable in the range 380–400 cm^{-1}, in line with previous work.[8]

Table2 Fractional atomic coordinates ($\times 10^4$) for (**6**)

Atom	*x*	y	z
Sn (1)	781.3 (2)	2045 (1)	1903.4 (2)
S(1)	1038 (1)	− 385 (3)	1089 (1)
S(2)	− 403 (1)	4472 (3)	1416 (1)
C(1)	1679 (4)	1531 (9)	809 (3)
C(2)	2513 (4)	1099 (9)	914 (2)
C(3)	3035 (4)	2619 (9)	713 (2)
C(4)	3909 (4)	2227 (11)	818 (3)
C(5)	4395 (4)	3731 (14)	636 (3)
C(6)	4045 (5)	5734 (14)	330 (3)
C(7)	3210 (5)	6195 (11)	214 (3)
C(8)	2683 (4)	4650 (10)	403 (2)
C(9)	1807 (4)	5024 (11)	294 (3)
C(10)	1325 (4)	3525 (10)	480 (3)
C(11)	− 1260 (3)	2606 (9)	1365 (2)
C(12)	− 1863 (3)	3208 (9)	1641 (2)
C(13)	− 2561 (3)	1796 (9)	1596 (2)
C(14)	− 3201 (4)	2377 (10)	1877 (3)
C(15)	− 3854 (4)	981 (13)	1831 (3)
C(16)	− 3931 (4)	− 1058 (12)	1500 (3)
C(17)	− 3333 (4)	− 1663 (10)	1218 (3)
C(18)	− 2635 (3)	− 283 (9)	1260 (2)
C(19)	− 1995 (4)	− 849 (10)	986 (3)
C(20)	− 1326 (4)	532 (9)	1035 (3)
C(21)	466 (4)	− 27 (11)	2590 (3)
C(22)	1817 (3)	4288 (10)	2234 (3)

The ^{1}H NMR spectra of all seven compounds are consistent with their empirical formulae. In the cases of **2**, **5** and **6** tin satellites are readily resolved abut the $SnCH_3$ or $SnCH_2$ protons. $^2J(^1H–^{119}Sn)$ coupling are *ca* 55–59 Hz, indicating tetracoordinated tin moieties in both the tri- and di-organotin species.[29] In the ^{13}C NMR spectra of **3**, **4** and **5** resonances due to all the unique carbon atoms are visible. The situation for **1**, **7** (both 12 out of 14 aromatic carbons), **4** (8 of 10) and **6** (9 of 10 aromatic carbons) is less clear since some of the signals are obscured due to the spectral complexity, though in all these cases some signals are of sufficient intensity to suggest overlap. No attempt has been made to assign individual signals, nor to distinguish signals due to aromatic groups attached to tin from the thiol ligand in view of the very narrow range (125–133 ppm) in which all these signals occur. The $^1J(^{13}C–^{119}Sn)$ coupling constants which are observable in the spectra of **2**, **3**, **5** and **6** lie in the range 274–388 Hz and are all consistent with a tetrahedral environment about tin in these representative compounds.[24] The four-coordinate nature of **1**–**8** is also reflected in their ^{119}Sn shifts, which are − 64.9 ppm for **1**, and lie in the range 10.1–126.1 ppm for **2**–**8**. For comparison, the ^{119}Sn chemical shifts of related four-coordinate species are: Ph_3SnSMe − 69, Me_3SnSMe 90, $(Bz_3Sn)_2S$ 27, $Me_2Sn(SMe)_2$ 144, $Sn(SPh)_4$ 44 ppm.[30]

Mössbauer data for **1**–**7** are all consistent with tin in the +4 oxidation state (IS: 1.12–1.50 mm s^{-1}) while the Mössbauer QS data reflect the simple tetrahedral coordination

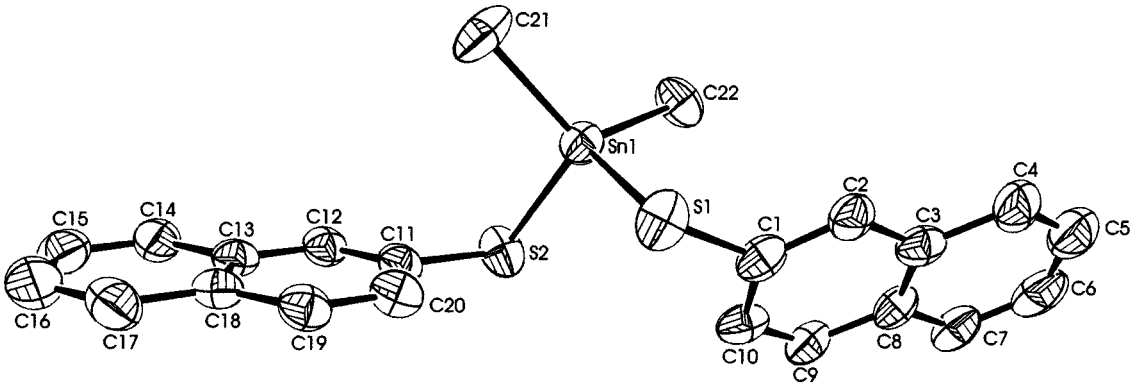


Figure 2 The asymmetric unit in **6** showing the labelling scheme used in the Tables. Important geometric data: Sn(1)–S(1) 2.418(4) Å, Sn(1)–S(2) 2.411(3) Å, Sn(1)–C(21) 2.117(7) Å, Sn(1)–C(22) 2.122(7) Å; S(1)–Sn(1)–S(2) 109.9(2)°, S(1)–Sn(1)–C(21) 107.5(3)°, S(1)–Sn(1)–C(22) 108.5(3)°, S(2)–Sn(1)–C(21) 108.2(3)°, S(2)–Sn(1)–C(22) 104.0(3)°, C(21)–Sn(1)–C(22) 118.5(4)°.

Table 3 Toxicity of compounds **1**–**7**

Compound	LD_{50} (μg ml^{-1})
1	<1
2	3
3	12
4	31
5	20
6	9
7	>100[a]
$C_{10}H_7SH$	>100[a]

[a] No activity at concentrations >100 μg ml^{-1}.

sphere about tin (1.46–2.09 mm s^{-1}).[29] The smallest QS occurs for **1** (1.46 mm s^{-1}) in which the dipole created by the four aryl groups is smaller than in the other, less symmetrical alkyltin compounds, while the largest QS (2.29 mm s^{-1}) occurs for polar **7**. Comparative data are Me_3SnSPh (QS = 1.98 mm s^{-1}),[31] Ph_3SnSPh (QS = 1.41 mm s^{-1})[32] and $Me_2Sn(SPh)_2$ (QS = 2.12 mm s^{-1}).[31]

The structural inferences from the spectroscopic data presented above are borne out by the crystal structures of **1** and **6** (Figs 1 and 2). The mean Sn–C [**1**: 2.135 Å; **6**: 2.120 Å] and Sn–S bond lengths [**1**: 2.418 Å; **6**: 2.411, 2.418 Å] are comparable with those in related structures such

Table 4 Antibacterial activity of compounds **1**–**7**

	Bacterium[a]									
Compound	1	2	3	4	5	6	7	8	9	10
1	—[b]	—	++[b]	+++[b]	—	+++	++	—	+++	+++
2	++	0[b]	+++	++	++	++	—	++	0	++
3	++	+++	+++	++	+++	+++	0	++++[b]	0	+++
4	—	—	—	—	—	—	—	—	—	++
5	—	—	++	+++	—	+++	+++	+++	++	+++
6	++	0	++	0	++	++	—	+++	0	++
7	—	—	++	++	—	+++	—	—	+++	++
$C_{10}H_7SH$	++	0	++	0	++	++	—	++	0	++

[a] Key to bacteria: 1, *Salmonella typhii*; 2, *Shigella boydii*; 3, *Corynebacterium diphtheria*; 4, *Streptococcus pyrogenes*; 5, *Escherichia coli*; 6, *Corynebacterium hoffmannii*; 7, *Streptococcus faecalis*; 8, *Klebsiella pneumonia*; 9, *Proteus vulgaris*; 10, *Staphylococcus aureus.*
[b] Key to activity: ++++, high activity (MIC < 100 μg ml^{-1}); +++, good activity (MIC < 150 μg ml^{-1}); ++, moderate activity (MIC < 200 μg ml^{-1}); — no activity; 0, not tested.

Table 5 Antifungal activity for compounds **1**–**7**

	Fungus[a]									
Compound	1	2	3	4	5	6	7	8	9	10
1	++[b]	+++[b]	+++	+++	+++	+++	—[b]	+++	+++	++
2	—	+++	+++	+++	+++	+++	+++	+++	+++	+++
3	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
4	—	+++	+++	+++	+++	+++	+++	+++	+++	++
5	—	+++	+++	+++	+++	+++	—	+++	+++	++
6	—	++	+[b]	++	+	+++	+	+	++	—
7	—	+++	+++	+++	+++	+++	—	+++	+++	+
$C_{10}H_7SH$	—	—	—	++	++	+	—	+	—	—

[a] Key for fungi: 1, *Candida albicans*; 2, *Epidermophyton floccosum*; 3, *Microsporum canis*; 4, *Pleuretus ostreatus*; 5, *Allesfcheria boydii*; 6, *Nigrospora oryzae*; 7, *Curvularia lunata*; 8, *Dreshslera rostrata*; 9, *Strachobotrys atra*; 10, *Aspergilus niger.*
[b] Key for activity: +++, high activity (100 < MIC < 200 μg ml^{-1}); ++, good activity (MIC < 400 μg ml^{-1}); +, low activity (MIC > 400 μg ml^{-1}); —, no activity.

as Ph_3SnSPh (2.138 Å; 2.421 Å),[33] $Ph_2Sn(SPh)_2$ (2.127 Å; 2.409 Å, 2.411 Å)[28] and $Ph_3SnSC_6H_4Bu^t$-4 (2.126 Å; 2.413 Å).[34] The distortions in the tetrahedral geometries of **1** and **6** also parallel those in the related pair of compounds Ph_3SnSPh and $Ph_2Sn(SPh)_2$, as evidenced by the spread of angles about the central metal. These increase from **1** (107.5–113.4°) to **6** (104.0–118.5°) while in the two thiophenyl species the spread widens from 106.4–112.4 to 102.4–119.3°.[33]

Biocidal testing

All the compounds **1**–**7** have been tested against a variety of different bacterial and fungi, and their biological activities against these species are given in Tables 3–5. LD_{50} data have been estimated through a brine-shrimp method.[18, 19] Antibacterial and antifungal activities have been measured using both Muller Hinton agar and agar–well diffusion methods, and Sabour or dextrose agar methods[20–26] respectively.

The LD_{50} values for the organotins **1**–**6** are lower than for the thiol ligand alone, while the diorganotin **7** is comparable with the ligand. The low value for **6** is, perhaps, a little surprising and probably reflects the inherent toxicity of methyltin compounds in general. The antibacterial activity maximizes for the tributyltin species (**4**) in line with other studies in this area,[30] though the activity of all the organotins species is reasonable. Compound **7** is again most like the free thiol in its level of activity. The antifungal properties of all the species including **7**, are broadly excellent, and far exceed the levels for the ligand. The influence of the metal is most clearly visible in this area.

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