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Triphenyltin(IV) sulfanylpropenoates: synthesis, crystal structures and antimicrobial activities

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Three new triphenyltin(IV) sulfanylcarboxylates with the general formula [Q][$SnPh_3$(L)] (Q = di-isopropylammonium cation; L = tspa, pspa or pyspa, where t = 3-(2-thienyl)-, p = 3-(2-phenyl)-, py = 3-(2-pyridinyl)- and spa = 2-sulfanylpropenoato) have been prepared by reaction of triphenyltin(IV) hydroxide with the corresponding acid in the presence of di-isopropylamine in ethanol. The compounds have been characterized by elemental analysis and mass spectrometry and by IR, Mössbauer and NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopy. X-ray studies of the crystal structures of [Q][$SnPh_3$(pspa)] and [Q][$SnPh_3$(pyspa)] show that in both compounds the tin atom is coordinated to three phenyl C atoms and to S and one O atom of the ligand L. All three complexes are active against strains of the Gram-positive bacterium *Staphylococcus aureus*, but are inactive or only slightly active against the Gram-negative bacteria *Escherichia coli* and *Pseudomonas aeruginosa*. **Copyright © 2000 John Wiley & Sons, Ltd.**

Keywords: organotin(IV); triphenyltin(IV); sulfanylcarboxylato; synthesis; crystal structure; antimicrobial activity

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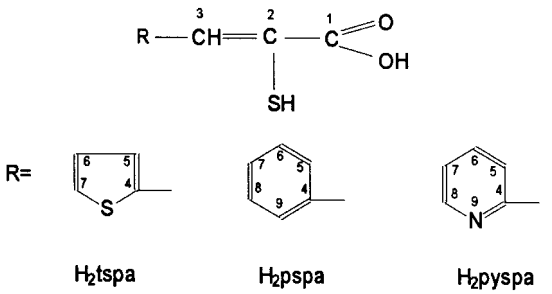
INTRODUCTION

The environmental and biological chemistry of organotin(IV) compounds is being studied with growing intensity due to their increasingly widespread use.[1] In particular, the role of the Sn–S bond in the biological and industrial applications of triphenyltin(IV) compounds has prompted considerable efforts to characterize it, especially in compounds in which an additional donor atom (D) can form Sn–D bonds of variable intensity, leading to structures ranging from tetrahedral to *cis*-trigonal bipyramidal (see Refs 2 and 3; references therein). Recently described examples of biologically active compounds belonging to these structural classes include two mercapto compounds with distorted tetrahedral structures and high *in vitro* antitumour activity,[4] and some tetrahedral and *cis*-tbp compounds with fungicidal activity.[5] Another interesting class of triphenyltin(IV) compounds comprises the carboxylates, for which both antitumour[6] and fungicidal activities[7] have been reported. For neither thiolates nor carboxylates has a clear structure–activity correlation been discovered, perhaps due in part to the instability of the Sn–S[5] and Sn–O[6] bonds in solution.

Previously we described the hydrolysis equilibrium of [$SnPh_3$(mimt)] (Hmimt = 1-methyl-2(3*H*)-imidazolinethione),[3] a thiolate in which an N donor atom slightly distorts a basically tetrahedral SnC_3S kernel. To explore further the effects of additional donor atoms on the stability of the Sn–S bond in solution and on biological activity, we have now studied the triphenyltin(IV) complexes of the diprotonic sulfanylpropenoato ligands



Scheme 1

H_2 tspa, H_2 pspa and H_2 pyspa (Scheme 1), which can coordinate via the sulfanyl S, the carboxylato group and, in principle, a donor atom belonging to the R substituent. This paper describes the preparation of these complexes in the presence of di-isopropylamine as proton capturer, their spectroscopic characterization, their antibacterial activities against *Escherichia coli* (ATCC 25992), *Staphylococcus aureus* (ATCC 292135) and *Pseudomonas aeruginosa* (ATCC 27853 and two clinical isolates), and the crystal structures of di-isopropylammonium [3-(2-phenyl)-2-sulfanylpropenoato]-triphenylstannate and di-isopropylammonium [3-(2-pyridinyl)-2-sulfanylpropenoato]triphenylstannate.

EXPERIMENTAL

Materials and methods

3-(2-Aryl)-2-sulfanylpropenoic acids were prepared by condensation of the appropriate aldehyde with rhodanine, subsequent hydrolysis in an alkaline medium and acidification with aqueous HCl.[8] Triphenyltin hydroxide (Aldrich-Chemie) and di-isopropylamine (Merck) were used as supplied. Di-isopropylammonium hydrochloride was prepared by addition of HCl to an aqueous solution of di-isopropylamine. Elemental analyses were performed with a Carlo-Erba 1108 apparatus. Melting points were determined using a Büchi apparatus. Mössbauer spectra were determined at 80.0 K in a constant acceleration apparatus with a $Ca^{119m}SnO_3$ source, and were referred to SnO_2; to minimize the effects of preferential crystallite orientations or texture, the samples were ground to a fine powder and dispersed uniformly in vaseline. IR spectra were recorded in KBr discs or Nujol mulls (the latter between NaCl windows or polyethylene sheets) on a Bruker IFS 66v FT-IR spectrophotometer, and Raman spectra of polycrystalline samples were recorded on the same spectrophotometer using an FRA-106 accessory (vs = very strong; s = strong; m = medium; w = weak). ^1H (500.13 MHz) and ^{13}C (125.78 MHz) NMR spectra were recorded in deuterated dimethyl sulphoxide (DMSO-d_6) at room temperature on a Bruker AMX 500 spectrometer and were referred to tetramethylsilane (TMS), and ^{119}Sn (186.50 MHz) NMR spectra were recorded in DMSO-d_6 and $CDCl_3$ in the same apparatus and referred to external neat tetramethyltin. Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 system and operating under electron impact (EI) conditions (direct insertion probe, 70 eV, 250 °C). Conductivities were determined with a Crison MicroCM-2202 conductivity meter.

Antibacterial activity was initially assayed by Muller–Hinton agar diffusion methods. Discs of paper 5 mm in diameter were loaded with 20 μl of a 2 mg ml^{-1} solution of the substance to be tested (ligand, complex or di-isopropylamine) in 9:1 ethanol–water; control discs were loaded with solvent alone. The discs were placed on dishes of Muller–Hinton agar inoculated with *E. coli* (ATCC 25992), *S. aureus* (ATCC 292135) or *Ps. aeruginosa* (ATCC 27853), and after 24 hours' incubation at 37 °C the diameters of the bacterial growth inhibition zones were measured. For those products which showed activity, minimum inhibitory concentrations (MICs) were calculated using serial dilutions in Muller–Hinton broth.

Syntheses

[Q][$SnPh_3$(tspa)] (1)

$SnPh_3OH$ (1.89 g, 5 mmol) was added to a solution of H_2tspa (0.93 g, 5 mmol) and di-isopropylamine (0.7 ml, 5 mmol) in absolute ethanol. The beige solid formed after stirring at room temperature and refluxing for 3 h was filtered out and vacuum-dried. Yield: 75% M.p. >300 °C. Analysis: Found: C, 58.9; H, 5.1; N, 2.3; S, 9.7; Calcd. for $C_{31}H_{34}NO_2S_2Sn$: C, 58.5; H, 5.35; N, 2.3; S, 10.0%. IR and Raman (R) (cm^{-1}): ν_{as}(COO), 1577vs; ν_{sym}(COO); 1364vs, 1364sh(R); ν(Sn–S), 342m; ν_{as}(Sn–C), ν_{sym}(Sn–C), 236s, 237w(R). Metallated fragment signals in the mass spectrum, *m/z* (%): 120 [Sn] (100); 197 [C_6H_5Sn] (55.8); 229 [C_6H_5SSn] (9.3); 351 [$C_{18}H_{15}Sn$] (11.5). Mössbauer: δ, 1.30; ΔE_Q, 1.42; Γ, 0.84 mm s^{-1}; $A_{2/1}$,

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1.04. Λ_M (CH_3CN), 68.0 S cm^2 mol^{-1}; Λ_M (DMF), 49.5 S cm^2 mol^{-1}.

[Q][SnPh$_3$(pspa)] (2)

$SnPh_3OH$ (1.89 g, 5 mmol) was added to a solution of H_2pspa (0.90 g, 5 mmol) and di-isopropylamine (0.7 ml, 5 mmol) in absolute ethanol. The white solid formed after stirring at room temperature and refluxing for 3 h was filtered out and vacuum-dried. Yield: 90%. Slow concentration of the mother liquor at room temperature afforded crystals suitable for X-ray study. M.p. 180 °C. Analysis: Found: C, 62.7; H, 5.9; N, 2.1; S, 5.6; Calcd for $C_{33}H_{37}NO_2SSn$: C, 62.8; H, 5.9; N, 2.2; S 5.1%. IR and Raman (R) (cm^{-1}): ν_{as}(COO), 1546vs; ν_{sym}(COO), 1357vs, 1356m(R); ν(Sn–S), 352m; ν_{as}(Sn–C), 273s; ν_{sym}(Sn–C), 237s, 238w(R). Metallated fragment signals in the mass spectrum, *m/z* (%): 120 [Sn] (100); 197 [C_6H_5Sn] (48.5); 229 [C_6H_5SSn] (7.5); 274 [$C_{12}H_{10}Sn$] (12.8); 351 [$C_{18}H_{15}Sn$] (8.5); 452 [$C_{21}H_{16}SO_2Sn$] (8.6). Mössbauer: δ, 1.31; ΔE_Q, 1.42; Γ, 0.79 mm s^{-1}, $A_{2/1}$, 1.19 Λ_M (CH_3CN), 56.2 S cm^2 mol^{-1}; Λ_M (DMF), 42.9 S cm^2 mol^{-1}.

[Q][SnPh$_3$(pyspa)] (3)

$SnPh_3OH$ (1.89 g, 5 mmol) was added to a solution of H_2pyspa (0.90 g, 5 mmol) and di-isopropylamine (0.7 ml, 5 mmol) in absolute ethanol. The yellowish beige solid formed after stirring at room temperature and refluxing for 3 h was filtered out and vacuum-dried. Yield: 90%. Slow concentration of the mother liquor at room temperature afforded crystals suitable for X-ray study. M.p. 189 °C. Analysis: Found: C, 60.6; H, 5.6; N, 4.1; S, 5.7; Calcd for $C_{32}H_{36}N_2O_2SSn$: C, 60.8; H, 5.7; N, 4.4; S, 5.1%. IR and Raman (R) (cm^{-1}): ν_{as}(COO), 1552vs; ν_{sym}(COO), 1360vs, 1359w(R); ν(Sn–S), 356m; ν_{as}(Sn–C), 274m; ν_{sym}(Sn–C), 237s, 239w(R). Metallated fragment signals in the mass spectrum, *m/z* (%): 120 [Sn] (86.7); 197 [C_6H_5Sn] (100); 229 [C_6H_5SSn] (18.1); 332

Table 1 Crystal and structure refinement data for [Q][SnPh$_3$(pspa)] (**2**) and [Q][SnPh$_3$(pyspa)] (**3**)

	[Q][SnPh$_3$(pspa)]	[Q][SnPh$_3$(pyspa)]
Empirical formula	$C_{33}H_{37}NO_2SSn$	$C_{32}H_{36}N_2O_2SSn$
Formula weight	630.39	631.38
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$ (no. 2)	Triclinic, $P\bar{1}$ (no. 2)
Unit cell dimensions	a = 10.3043(8) Å	a = 10.1246(8) Å
	b = 11.6837(10) Å	b = 11.7537(11) Å
	c = 13.1953(10) Å	c = 13.2948(11) Å
	α = 82.051(8) °	α = 81.178(10) °
	β = 86.621(7) °	β = 86.876(9) °
	γ = 82.808(7) °	γ = 84.304(7) °
Volume	1559.6(2) Å^3	1554.4(2) Å^3
Z, Calculated density	2, 1.342 Mg m^{-3}	2, 1.349 Mg m^{-3}
Absorption coefficient	0.914 mm^{-1}	0.918 mm^{-1}
F(000)	648	648
Crystal size	0.30 mm × 0.15 mm × 0.15 mm	0.35 mm × 0.30 mm × 0.15 mm
(θ) range for data collection	2.20–26.29 °	2.50–26.29 °
Index ranges	$-12 \le h \le 0$, $-14 \le k \le 14$, $-16 \le l \le 16$	$-12 \le h \le 0$, $-14 \le k \le 14$, $-16 \le l \le 16$
Reflections collected/unique	6703/6332 [R(int) = 0.0133]	6688/6315 [R(int) = 0.0258]
Completeness to 2θ = 26.29 °	99.9%	99.9%
Absorption correction	Ψ-scan	Ψ-scan
Max. and min. transmission	0.975 and 0.882	0.974 and 0.905
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6332/0/491	6315/0/487
Goodness-of-fit on F^2	1.048	1.013
Final R indices [$I > 2(\sigma)(I)$]	R_1 = 0.0270, wR_2 = 0.0678	R_1 = 0.0324, wR_2 = 0.0624
R indices (all data)	R_1 = 0.0419, wR_2 = 0.0725	R_1 = 0.0825, wR_2 = 0.0721
Largest diff. peak and hole	0.532 and −0.539 e-Å^{-3}	0.572 and −0.416 e-Å^{-3}

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$[C_{14}H_{11}SSn+H^+]$ (49.6); 351 $[C_{18}H_{15}Sn]$ (21.5); 376 $[C_{15}H_{11}SO_2Sn+H^+]$ (22.6); 453 $[C_{21}H_{16}SO_2Sn+H^+]$ (4.8). Mössbauer: δ, 1.31; ΔE_Q, 1.53; Γ, 0.82 mm s^{-1}; $A_{2/1}$, 1.15. Λ_M (CH_3CN), 65.7 S cm^2 mol^{-1}; Λ_M (DMF), 52.7 S cm^2 mol^{-1}.

Determination of the crystal structures of [Q][$SnPh_3$(pspa)] (2) and [Q][$SnPh_3$(pyspa)] (3)

X-ray data collection and reduction

Colourless prismatic crystals were mounted on glass fibres for data collection in an Enraf–Nonius MACH3 automatic diffractometer.[9] Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data for 25 reflections in the range $10.50 < \theta < 18.02°$ for **2** and $8.84° < \theta < 18.01°$ for **3**. Data were collected at 293 K using MoK_α radiation (λ = 0.71073 Å) and the ω scan technique, and were corrected for Lorentz and polarization effects.[10] A semi-empirical absorption correction (ψ scan) was also made.[11]

Structure solution and refinement

The structure was solved by direct methods[12] and subsequent Fourier maps, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters.[13] All the hydrogen atoms were located from difference Fourier maps and were refined isotropically. Atomic scattering factors were taken from Ref 14. Molecular graphics were generated with PLATON.[15] The crystal data, experimental details and refinement results are summarized in Table 1.

RESULTS AND DISCUSSION

X-ray studies

Structure of [Q][$SnPh_3$(pspa)]

The crystal of [Q][$SnPh_3$(pspa)] contains $SnPh_3$(pspa) anions and di-isopropylammonium cations linked by N—H···O hydrogen bonds in centrosymmetric dimeric structures. Figure 1 shows a PLATON view of the [$SnPh_3$(pspa)] anion (for the sake of clarity the di-isopropylammonium ion has been excluded). Table 2 lists positional parameters and Table 3 selected distances and angles.

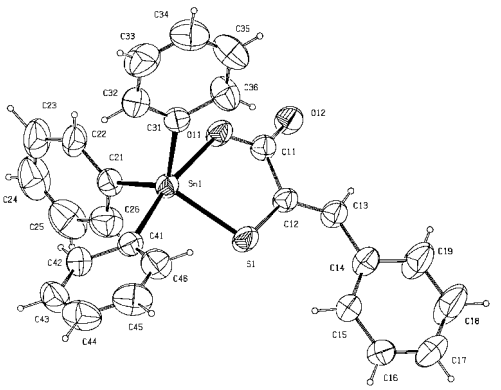

Figure 1 The crystal structure of the $SnPh_3$(pspa) anion, showing the numbering scheme.

The coordination sphere

Each tin atom is coordinated to three phenyl C atoms and to the S and O(1) atoms of a pspa ligand, creating a distorted trigonal bipyramidal *cis*-C_3SnOS kernel in which the C(41) and O(11) atoms occupy the apical positions. The apical Sn–C bond is longer than the equatorial Sn–C bonds, but all three are within the range 2.12–2.18 Å reported for other triphenyltin compounds.[16] The Sn–S bond length is close to the sum of the covalent radii of tin and sulphur (2.42 Å),[17] but within the range reported for triphenyltin thiolates (2.405–2.481 Å).[16,18–20] The Sn–O bond is longer than the sum of the covalent radii of tin and oxygen (2.13 Å).[17] The apical C-Sn-O angle [169.96(7)°] shows significant distortion with respect to the regular tbp polyhedron. In the equatorial plane, in which the angles sum 352.5 °, the greatest distortion is shown by the C-Sn-S angles. The distortions of both C-Sn-O and the C-Sn-S angles from the values obtaining in a regular trigonal bipyramid are caused by the rigidity of the sulfanylpropenoato ligand, which imposes an O(11)-Sn(1)-S(1) angle of 75.84(4)°. The general features of the tin kernel are similar to those observed in di-isopropylammonium (sulfanylethanoato-*S*,*O*)triphenylstannate(IV)[18] ([Q][$SnPh_3$(sea)]), although the Sn–O distance is shorter in [Q][$SnPh_3$(pspa)].

The pspa ligand

The pspa ligand is quasi-planar, the phenyl ring making an angle of just 11.89 ° with the least-squares plane defined by Sn(1), O(11), C(11), C(12) and S(1)$_\circ$ (rms = 0.018). The C–S bond length, 1.757(2) Å, is close to the mean for a C–S single bond in a C═C—S—C fragment.[21] The parameters

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Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [Q][$SnPh_3$(pspa)][a]

	x	*y*	*z*	*U*(eq)
Sn(1)	6803(1)	8736(1)	7054(1)	40(1)
S(1)	8242(1)	8522(1)	8486(1)	57(1)
O(11)	6302(2)	6990(2)	8080(1)	48(1)
O(12)	6534(2)	5691(2)	9444(1)	55(1)
C(11)	6848(2)	6582(2)	8900(2)	42(1)
C(12)	7924(2)	7211(2)	9229(2)	42(1)
C(13)	8574(3)	6740(2)	10068(2)	50(1)
C(14)	9588(3)	7121(2)	10623(2)	52(1)
C(15)	10033(3)	8196(3)	10439(2)	61(1)
C(16)	10966(3)	8501(3)	11036(3)	69(1)
C(17)	11460(3)	7741(3)	11837(3)	73(1)
C(18)	11081(5)	6651(4)	12008(3)	107(2)
C(19)	10152(4)	6347(4)	11415(3)	93(1)
C(21)	4780(2)	9322(2)	7349(2)	48(1)
C(22)	3827(3)	9096(3)	6727(3)	60(1)
C(23)	2524(3)	9497(3)	6898(4)	83(1)
C(24)	2166(4)	10128(4)	7679(4)	96(1)
C(25)	3070(4)	10365(4)	8306(4)	92(1)
C(26)	4392(3)	9964(3)	8140(3)	69(1)
C(31)	7331(2)	7587(2)	5932(2)	44(1)
C(32)	7039(3)	7935(3)	4920(2)	61(1)
C(33)	7419(4)	7212(4)	4177(3)	84(1)
C(34)	8091(4)	6545(3)	4431(3)	82(1)
C(35)	8407(4)	5792(3)	5419(3)	79(1)
C(36)	8029(3)	6495(3)	6166(2)	65(1)
C(41)	7507(2)	10344(2)	6319(2)	44(1)
C(42)	6633(3)	11333(2)	6037(2)	54(1)
C(43)	7079(4)	12347(3)	5521(2)	72(1)
C(44)	8392(4)	12379(3)	5295(3)	77(1)
C(45)	9263(4)	11429(3)	5582(3)	78(1)
C(46)	8823(3)	10423(3)	6085(2)	61(1)
N(1)	4039(2)	5376(2)	8585(2)	47(1)
C(1)	4886(5)	3459(4)	8163(4)	96(1)
C(2)	4128(3)	4600(3)	7768(2)	62(1)
C(3)	4690(7)	5194(6)	6770(3)	104(2)
C(4)	1840(4)	6425(4)	8135(4)	87(1)
C(5)	3230(3)	6551(2)	8388(2)	58(1)
C(6)	3265(4)	7150(3)	9316(3)	71(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

of the carboxylate group are not unusual: the O(11)-C(11)-O(12) angle, 122.3(2)°, is close to 120 °, and coordination to the tin atom does not make C(11)–O(11) [1.256(3) Å] significantly longer than C(11)–O(12) [1.246(3) Å)].

Hydrogen bonds

Each di-isopropylammonium NH_2 group forms N—H···O hydrogen bonds with the non-coordinated carboxylate O atoms of two [$SnPh_3$(pspa)] anions [N–H(1)–O(12), *d*(N–O) = 2.953(3) Å, N—H—O = 163(3)°; N–H(2)–O(12), [b] *d*(N–O) = 2.788(3) Å, N—H—O = 165(3)° (*b* = $-x + 1$, $-y + 1$, $-z + 2$)]. These bonds create [Q]$_2$[$SnPh_3$(pspa)]$_2$ dimers, as shown in Fig. 2.

Structure of [Q][$SnPh_3$(pyspa)]

The structure of [Q][$SnPh_3$(pyspa)] is isotypic to that of [Q][$SnPh_3$(pspa)]. The crystal contains [$SnPh_3$(psypa)]$^-$ anions and di-isopropylammonium cations bound by N—H…O hydrogen bonds. Figure 3 shows a PLATON view of the [$SnPh_3$(pyspa)] anion (as in Fig. 1, the di-isopropylammonium ion has been excluded for clarity). Table 4 lists positional parameters, and Table 5 selected distances and angles.

The type of coordination and the lengths of the bonds involving the tin atom are similar to those discussed above for the [$SnPh_3$(pspa]$^-$ anion. The pyspa ligand is quasi-planar [the $SnOC_2S$ ring (rms = 0.018) makes an angle of 5.95 ° with the pyridine ring] and the main distances and angles are similar to those found previously in [$SnEt_2$(pyspa)] except that the pyridine ring is *anti* with respect to the metallated ring instead of *syn*.[22] The structural parameters of the thiol and carboxylato groups and hydrogen bonds are similar to those found in the pspa derivative.

Comparison with [Q][$SnPh_3$(sea)][18]

The similarity of the planar $SnSC_2O$ rings of [Q][$SnPh_3$(pspa)] and [Q][$SnPh_3$(pyspa)] shows that replacement of the phenyl ring by the pyridine ring does not change the coordination properties of the ligand. Comparison with the $SnSC_2O$ ring of di-isopropylammonium (sulfanylethanoato-*S*,*O*)triphenylstannate(IV)[18] ([Q][$SnPh_3$(sea)]) shows that the presence of a tetrahedral carbon instead of the trigonal C(12) reduces the planarity of the ring [$\sum$angles = 525 °, vs practically 540 ° in the pspa and pyspa compounds] and lengthens the Sn–O bond (2.608(3) Å,[18] vs 2.366(2) Å in [$SnPh_3$(pyspa)] and 2.383(2) Å in [$SnPh_3$(pspa)]). These differences are in keeping with the finding[23] that metal complexes of 3-aryl-2-sulphanylpropanoates are less stable in solution than those of 3-aryl-2-sulphanylpropenoates.

Vibrational spectra

Vibrational spectra of the complexes suggest that the tspa complex shares structural similarities of the pspa and pyspa derivatives. The carboxylato bands lie at similar wavenumbers in all three compounds,

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Table 3 Selected bond lengths (Å) and angles (°) in [Q][$SnPh_3$(pspa)]

Tin environment				
Sn(1)–C(31)	2.136(2)	Sn(1)–O(11)	2.383(2)	
Sn(1)–C(21)	2.141(2)	Sn(1)–S(1)	2.4371(7)	
Sn(1)–C(41)	2.179(2)			
C(31)-Sn(1)-C(21)	119.49(9)	C(41)-Sn(1)-O(11)	169.96(7)	
C(31)-Sn(1)-C(41)	102.20(9)	C(31)-Sn(1)-S(1)	116.07(7)	
C(21)-Sn(1)-C(41)	100.97(9)	C(21)-Sn(1)-S(1)	116.97(7)	
C(31)-Sn(1)-O(11)	82.57(7)	C(41)-Sn(1)-S(1)	94.12(6)	
C(21)-Sn(1)-O(11)	83.97(8)	O(11)-Sn(1)-S(1)	75.84(4)	
pspa ligand				
S(1)–C(12)	1.757(2)	C(14)–C(19)	1.388(4)	
O(11)–C(11)	1.256(3)	C(15)–C(16)	1.388(4)	
O(12)–C(11)	1.246(3)	C(16)–C(17)	1.362(5)	
C(11)–C(12)	1.519(3)	C(17)–C(18)	1.364(6)	
C(12)–C(13)	1.343(3)	C(18)–C(19)	1.380(5)	
C(13)–C(14)	1.457(3)			
C(14)–C(15)	1.375(4)			
O(12)-C(11)-O(11)	122.3(2)	C(19)-C(14)-C(13)	117.9(3)	
O(12)-C(11)-C(12)	119.7(2)	C(14)-C(15)-C(16)	121.6(3)	
O(11)-C(11)-C(12)	117.97(19)	C(17)-C(16)-C(15)	120.5(3)	
C(13)-C(12)-C(11)	118.5(2)	C(16)-C(17)-C(18)	119.1(3)	
C(13)-C(12)-S(1)	123.75(19)	C(17)-C(18)-C(19)	120.3(4)	
C(11)-C(12)-S(1)	117.78(16)	C(12)-C(13)-C(14)	133.2(2)	
C(15)-C(14)-C(19)	116.5(3)	C(18)-C(19)-C(14)	121.8(4)	
C(15)-C(14)-C(13)	125.6(2)			
Hydrogen bonds				
D—H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(1)—H(10)···O(12)	0.82(3)	2.16(3)	2.953(3)	163(3)
N(1)—H(20)···O(12)[a]	0.91(3)	1.90(3)	2z.788(3)	165(3)

[a] Symmetry operation: $-x+1,\ -y+1,\ -z+2$.

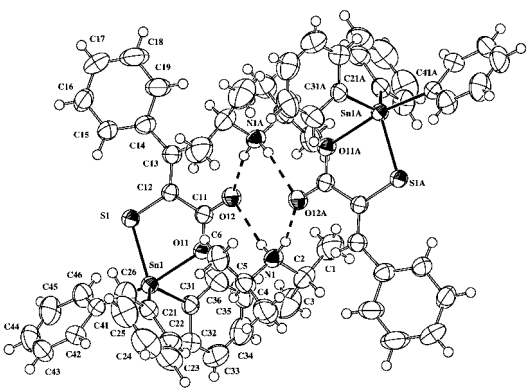

Figure 2 The crystal structure of $[Q]_2[SnPh_3(pspa)]_2$ dimers, showing the hydrogen bonds creating the dimers.

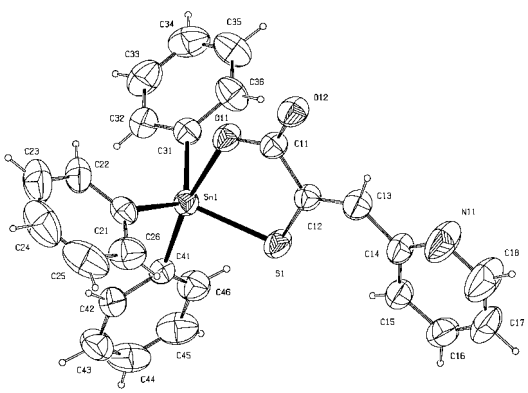

Figure 3 The crystal structure of the $SnPh_3$(pyspa) anion, showing the numbering scheme.

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Table 4 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [Q][$SnPh_3$(pyspa)][a]

	x	*y*	*z*	*U*(eq)
Sn(1)	6749(1)	8759(1)	7018(1)	40(1)
S(1)	8238(1)	8586(1)	8429(1)	56(1)
O(11)	6258(2)	7017(2)	8053(2)	48(1)
O(12)	6457(2)	5759(2)	9446(2)	58(1)
N(11)	9617(4)	6698(3)	11591(3)	96(1)
C(11)	6780(3)	6651(3)	8890(2)	42(1)
C(12)	7850(3)	7324(3)	9228(2)	41(1)
C(13)	8411(4)	6919(3)	10109(3)	51(1)
C(14)	9424(3)	7329(3)	10671(2)	51(1)
C(15)	10129(4)	8262(3)	10345(3)	53(1)
C(16)	11072(4)	8536(4)	10947(3)	61(1)
C(17)	11283(4)	7891(4)	11860(3)	73(1)
C(18)	10532(6)	7004(5)	12150(4)	111(2)
C(21)	4713(3)	9291(3)	7357(2)	45(1)
C(22)	3707(4)	9068(3)	6776(3)	59(1)
C(23)	2392(5)	9434(5)	6991(5)	87(2)
C(24)	2085(6)	10037(5)	7782(6)	99(2)
C(25)	3041(7)	10283(4)	8350(5)	94(2)
C(26)	4375(5)	9911(4)	8148(3)	69(1)
C(31)	7292(3)	7629(3)	5914(2)	42(1)
C(32)	7028(4)	7989(4)	4905(3)	56(1)
C(33)	7420(5)	7298(4)	4165(3)	74(1)
C(34)	8078(5)	6242(4)	4431(4)	77(1)
C(35)	8353(5)	5870(4)	5419(4)	75(1)
C(36)	7971(4)	6552(3)	6154(3)	61(1)
C(41)	7441(3)	10390(3)	6269(2)	41(1)
C(42)	6558(4)	11371(3)	6038(3)	50(1)
C(43)	6995(5)	12395(3)	5533(3)	68(1)
C(44)	8298(5)	12465(4)	5250(3)	75(1)
C(45)	9186(5)	11518(4)	5479(3)	73(1)
C(46)	8760(4)	10495(4)	5979(3)	59(1)
N(1)	3995(3)	5303(3)	8563(2)	47(1)
C(1)	4997(7)	3452(6)	8171(5)	97(2)
C(2)	4140(4)	4517(3)	7765(3)	61(1)
C(3)	4607(8)	5156(7)	6760(4)	104(2)
C(4)	1716(6)	6187(5)	8128(7)	101(2)
C(5)	3096(4)	6410(3)	8357(3)	58(1)
C(6)	3130(6)	7026(4)	9264(4)	74(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

with $\Delta\nu$ ($= \nu_{as}COO - \nu_{sym}COO$) values of 213 cm^{-1} for **1**, 189 cm^{-1} for **2** and 192 cm^{-1} for **3**. These values are small in comparison with those found in other complexes in which a ligand coordinates via just one of the oxygen atoms of a carboxylato group;[24] this is attributed to the N–H–O hydrogen bond, which significantly lengthens the C–O bond of the non-coordinated oxygen. As regards the remaining bands, ν(Sn–S) is close to the positions found for diorganotin derivatives of these ligands,[22] and ν(Sn–C) (a ligand vibration probably contributes to the ν_{sym} band) is located at positions typical of a non-planar SnC_3 framework.[7]

Mössbauer spectra

As expected from their chemical formulae, the Mössbauer spectra of the reported compounds show only a single, slightly asymmetric, quadrupole split doublet. Since the linewidths are narrow enough to rule out overlapping, this implies that there is just a single tin site in each complex. The isomer shift data for the complexes, which are very similar to each other, are typical of SnR_3 derivatives (expected range 0.86–1.72 mm s^{-1}),[25] but throw little light on the geometry around the tin atom except to suggest that all three compounds have the same coordination mode. The quadrupole splitting values of the three compounds are also very close to each other and are surprisingly low, falling in the lowest part of the range for tetrahedral complexes and far below the usual range for *fac*-SnR_3 tbp structures (1.82–2.55 mm s^{-1}). However, it should be borne in mind that in the tbp compound with the lowest previously reported value, (*p*-tolyl)$_3$Sn[ON(Ph)-CO(Ph)] (1.82 mm s^{-1}),[26] the tin atom is bound to two oxygen atoms instead of one oxygen and one sulphur, so the values found in this study may be attributed to the known very negative pqs values of sulphur. By contrast, [$SnPh_3$(2-SPyO)] (ΔE_Q = 1.86 mm s^{-1})[27] has the same bonding atoms but a different structure, being one of the few square pyramidal organotin compounds. The positions of its oxygen atoms (one in the square base of the pyramid and the other in the apical position) imply that the difference between its quadrupole splitting value and those of the complexes characterized in this study may be attributed to the totally different distribution of charge among the tin hybrid orbitals.

In the framework of the point charge formalism, the crystallographic data for **2** and **3**, together with published pqs values of the phenyls (−0.89 mm s^{-1} for the apical group, −0.98 mm s^{-1} for the equatorial ones) and the coordinated carboxylate oxygen (−0.10 mm s^{-1}; this group is not considered as bridging, even though the second oxygen atom is hydrogen-bonded to the counterion), allow optimization of the value for the sulphur atom at −0.30 mm s^{-1}, not too far from the values reported in the literature.[28] For both [Q][$SnPh_3$(pspa)] and [Q][$SnPh_3$(pyspa)], this affords an ΔE_Q value of 1.50 mm s^{-1}, very close to the experimental measurement.

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Table 5 Selected bond lengths (Å) and angles (°) in [Q][$SnPh_3$(pyspa)]

Tin environment				
Sn(1)–C(21)	2.139(3)	Sn(1)–O(11)	2.366(2)	
Sn(1)–S(1)	2.4422(9)	Sn(1)–C(41)	2.183(3)	
Sn(1)–C(31)	2.141(3)			
C(21)-Sn(1)-C(31)	121.24(12)	C(41)-Sn(1)-O(11)	169.96(9)	
C(21)-Sn(1)-C(41)	100.81(11)	C(21)-Sn(1)-S(1)	115.65(9)	
C(31)-Sn(1)-C(41)	102.38(11)	C(31)-Sn(1)-S(1)	115.68(9)	
C(21)-Sn(1)-O(11)	83.47(9)	C(41)-Sn(1)-S(1)	93.82(8)	
C(31)-Sn(1)-O(11)	82.74(10)	O(11)-Sn(1)-S(1)	76.15(6)	
pspa ligand				
S(1)–C(12)	1.753(3)	C(13)–C(14)	1.461(5)	
O(11)–C(11)	1.254(3)	C(14)–C(15)	1.370(5)	
O(12)–C(11)	1.248(3)	C(15)–C(16)	1.371(5)	
N(11)–C(18)	1.327(6)	C(16)–C(17)	1.345(6)	
N(11)–C(14)	1.343(4)	C(17)–C(18)	1.347(6)	
C(11)–C(12)	1.527(4)			
C(12)–C(13)	1.329(4)			
C(18)-N(11)-C(14)	117.2(4)	N(11)-C(14)-C(15)	120.6(3)	
O(12)-C(11)-O(11)	122.2(3)	N(11)-C(14)-C(13)	113.2(3)	
O(12)-C(11)-C(12)	119.4(3)	C(15)-C(14)-C(13)	126.1(3)	
O(11)-C(11)-C(12)	118.4(3)	C(14)-C(15)-C(16)	119.9(4)	
C(13)-C(12)-C(11)	118.0(3)	C(17)-C(16)-C(15)	119.4(4)	
C(13)-C(12)-S(1)	124.7(3)	C(16)-C(17)-C(18)	117.8(4)	
C(11)-C(12)-S(1)	117.4(2)	N(11)-C(18)-C(17)	125.0(4)	
C(12)-C(13)-C(14)	133.1(3)			
(*c*) Hydrogen bonds				
D—H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(1)—H(10)···O(12)	0.85(3)	2.16(4)	2.942(4)	153(3)
N(1)—H(20)···O(12)[a]	0.99(4)	1.81(4)	2.782(4)	166(3)

[a] Symmetry operation: $-x+1, -y+1, -z+2$.

Solution studies

The molar conductivities of the three complexes in CH_3CN and DMF are low for 1:1 electrolytes in these solvents. This is attributable[29] to the low ionic mobility of the ions.

NMR data for the complexes are listed in Tables 6 and 7, together with data for the ligands taken from our earlier study.[22] Note that H_2pyspa is a thione in which the pyridine nitrogen is protonated. In the ^{1}H NMR spectra of the complexes (Table 6) the septuplet at *ca* 3.3 ppm, the doublet at *ca* 1.2 ppm and the very broad singlet integrating to two protons at 8.0–8.1 ppm are attributed to the di-isopropylammonium cation. The signals for the $SnPh_3$ moiety are multiplets appearing at unremarkable positions: H^o at 7.53 ppm [flanked by two satellites 56 Hz apart due to $^3J(^1H–Sn)$] and H^m and H^p at 7.27 ppm. The absence of signals for C(1)OH and SH [and of the N(9)H signal in the case of [Q][$SnPh_3$(pyspa)] indicates di-deprotonation of the ligand. The shifts of the C(3)H and pyridine ring signals in the spectra of [Q][$SnPh_3$(pyspa)] relative to their positions in the spectrum of the free ligand may be attributed, as in the case of [$SnPh_2$(pyspa)],[22] to the deprotonation of the pyridine N and the alteration of the charge distribution upon coordination. In the case of the pspa complex the C(3)H signal undergoes no shift, and in [Q][$SnPh_3$(tspa)], as in [$SnPh_2$(tspa)],[22] C(3)H is more shielded than in H_2tspa. The ring proton signals of the pspa and tspa complexes exhibit qualitatively the same behaviour as in the corresponding diphenylstannates.[22]

The ^{13}C NMR data (Table 7) reflect the change from the thione H_2pyspa to the thiol-type CCS fragment of [Q][$SnPh_3$(pyspa)] in the marked shielding of C(2) and the deshielding of C(3), as in the case of [$SnPh_2$(pyspa)].[22] This thione-to-thiol evolution, together with the deprotonation of the

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Table 6 ^{1}H NMR data for H_2pyspa, H_2pspa, H_2tspa and their compounds[a,b]

	H_2pyspa	[Q][$SnPh_3$(pyspa)]	H_2pspa	[Q][$SnPh_3$(pspa)]	H_2tspa	[Q][$SnPh_3$(tspa)]
N(9)H	17.85,brs(1)	—	—	—	—	—
C(1)OH	12,85,vbrs(1)	—	13.00,vbrs	—	12.82,brs(1)	—
C(2)SH	—	—	5.22,vbrs	—	—	—
C(3)H	7.32,s(1)	7.79,s(1)	7.73,s(1)	7.70,s(1)	8.13,s(1)	7.93,s(1)
C(5)H	7.70,d(1)	8.38,d(1)	7.68,d(2),H^o	7.94,d(2),H^o	7.57,d(1)	7.32
C(6)H	8.15,td(1)	7.79,td(1)	7.47,t,H^m	7.36,t(2),H^m	7.08,pt(1)	7.08,dd(1)
C(7)H	7.51,t(1)	7.16,dd(1)	7.39,m H^p	7.22,t(1)H^p	7.77,d(1)	7.52
C(8)H	8.53,t(1)	8.56,d(1)	—	—	—	—
Ph_3Sn	—	7.53,m(6) H^o [56.4] 7.28,m(9)H^m,H^p		7.53,m(6),H^o [55.9] 7.27,m(9),H^m,H^p	—	7.53,m, H^o [55.9] 7.28,m,H^m,H^p
CH[Q]		3.32,sp[c]		3.28,sp(2)		3.29,sp[c]
CH_3[Q]		1.17,d(12)		1.16,d(12)		1.15,d(12)
NH_2[Q]		8.09,brs(2)		8.09,vbrs		8.00,vbrs

[a] δ in ppm. Coupling constants (in square brackets) in Hz;s, singlet; brs, broad singlet; vbrs, very broad singlet; d, doublet; dd, doublet of doublets; td, triplet of doublets; t, triplet; pt, pseudo-triplet; sp, septuplet; m, multiplet.
[b] For numbering, see Scheme 1.
[c] Overlapping with water peak.

pyridine ring, is responsible for the ring carbon atoms being only slightly shielded or deshielded with respect to those of the $SnPh_2$ compound. In the complexes of the thiols H_2pspa and H_2tspa, coordination through C(2)S is reflected by the deshielding of C(2) and the shielding of C(3). The coordination behaviour of the carboxy group is shown by the chemical shifts of C(1),[30] which in the complexes studied in this work are very close to the 170.74 ppm reported for a monodentate carboxylato group.[30,31] This and the results discussed above together imply that in DMSO-d_6 the complexes

Table 7 ^{13}C and ^{119}Sn NMR data for H_2pyspa, H_2pspa, H_2tspa and their compounds[a,b]

	H_2pyspa	[Q][$SnPh_3$(pyspa)]	H_2pspa	[Q][$SnPh_3$(pspa)]	H_2tspa	[Q][$SnPh_3$(tspa)]
C(1)	167.6	167.4	167.1	167.8	166.2	167.6
C(2)	167.8	139.3	129.5	135.4	123.1	126.2
C(3)	113.1	129.1	145.6	128.1	140.4	126.5
C(4)	151.7	156.4	134.4	137.5	137.3	142.2
C(5)	126.2	123.2	131.3 C^o	129.1 C^o	137.7	133.2
C(6)	142.1	135.8	129.4 C^m	128.0 C^m	127.2	122.1
C(7)	121.0	121.1	130.8 C^p	126.6 C^p	134.2	128.5
C(8)	135.7	149.2	—	—	—	—
C(Ph)		147.7 iC 136.3 C^o [42.7] 127.8 C^p 127.7 C^m		147.8 iC 136.3 C^o [42.5] 127.7 C^p 127.6 C^m [56.7]		147.8 iC 136.2 C^o [42.8] 127.7 C^p 127.6 C^m
CH[Q]		46.3		46.2		46.1
CH_3[Q]		18.8		18.7		18.9
^{119}Sn		−216.8(230)[d] −182.8[c](390)		−218.0 (250)[d] −178.5[c](380)		−217.2 (250)[d] −176.0[c](340)

[a] In brackets, ^{13}C–^{119}Sn coupling constants in Hz.
[b] For numbering, see Scheme 1.
[c] In $CDCl_3$.
[d] $W_{1/2}$.

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retain the same coordination mode as in the solid state, with the ligand bound to the tin atom via the sulphur atom and one of the oxygen atoms of the carboxylato group. In the organometallic moiety, the most significant difference with respect to the corresponding $SnPh_2$ complexes is the deshielding of C(i) by *ca* 7 ppm. The peaks located at high field, *ca* 46 and 18 ppm, are respectively assigned to the methine and methyl carbons of the di-isopropylammonium cation.

Table 7 also includes ^{119}Sn chemical shifts in $CDCl_3$ and DMSO-d_6. In both solvents, the narrowness of the peaks indicates that solvent–ligand exchange phenomena are absent or of very low intensity. In $CDCl_3$, the chemical shifts of all three compounds lie close to the upper limit of the range accepted for five-coordinated compounds (-180 to -260 ppm)[32] and far below the range for tetrahedral geometry (-40 to -120 ppm).[3,32] In DMSO-d_6, the chemical shifts are very similar to those reported previously for five-coordinated Ph_3Sn compounds.[33] These data reinforce[32–34] the ^{13}C NMR data in implying the retention of the solid-state coordination scheme in $CDCl_3$ solutions, and suggest that the same is true in DMSO.

Antibacterial activity

No antibacterial activity was exhibited by the ligands, di-isopropylammonium hydrochloride or solvent. All three complexes were active against *S. aureus* and *E. coli* but not against a standard strain of *Ps. aeruginosa*. Solutions of the complexes that were kept at 4 °C for 30 days exhibited the same activity as fresh solutions. The MICs of **1, 2** and **3** against *S. aureus* were 10, 5 and 2.5 $\mu g\,ml^{-1}$ respectively, and their MICs against *E. coli* were respectively 40, >80 and 40 $\mu g\,ml^{-1}$; these values are similar to those reported for other tin compounds.[35]

The possession of greater activity against Gram-positive than Gram-negative bacteria, which has also been reported for other phenyltin compounds,[36,37] seems likely to be due to these compounds having difficulty in penetrating the outer membrane of Gram-negative bacteria. This hypothesis is supported by the finding that when **1, 2** and **3** were tested against two clinical strains of *Ps. aeruginosa*, they were all weakly active against one, with MICs of about 80 $\mu g\,ml^{-1}$, but exhibited no activity against the other, a strain that is resistant to meropenem due to alteration of its membrane transport system.[38]

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