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Synthesis, characterization and antibacterial activity of some new triphenyltin(IV) sulfanylcarboxylates: Crystal structure of $[(SnPh_3)_2(p\text{-mpspa})]$, $[(SnPh_3)_2(cpa)]$ and $[(SnPh_3)_2(tspa)(DMSO)]$

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Abstract

Five new triphenyltin(IV) sulfanylcarboxylates of the general formula $[(SnPh_3)_2L]$ (L = pspa, tspa, fspa, p-mpspa or cpa, where p = 3-(2-phenyl)-, t = 3-(2-thienyl)-, f = 3-(2-furyl)-, p-mp = 3-(4-methoxyphenyl)-, spa = 2-sulfanylpropenoato and cpa = 2-cyclopentilyden-2-sulfanylacetate) have been synthesized by reacting triphenyltin(IV) hydroxide with the corresponding acid in ethanol/acetone. The complexes have been characterized by elemental analysis and mass spectrometry and by vibrational and NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopies. In the case of $[(SnPh_3)_2(p\text{-mpspa})]$ and $[(SnPh_3)_2(cpa)]$, X-ray structural studies showed that in both compounds each Sn atom is coordinated to three phenyl C atoms and to one S or O atom of the bridge ligand L. All five complexes are active against strains of *Staphylococcus aureus*, but are inactive against *Escherichia coli* and *Pseudomonas aeruginosa*. From a solution of $[(SnPh_3)_2(tspa)]$ in DMSO-d_6 the new complex $[(SnPh_3)_2(tspa)(DMSO)]$ was isolated. The single-crystal X-ray diffractometric study of this complex is also reported, showing that both Sn atoms are bridged by the tspa ligand, whereas the molecule of DMSO is coordinated to one of the tin atoms via the oxygen atom.

Keywords: Organotin(IV); Triphenyltin(IV); Sulfanylcarboxylato; Crystal structure; Antibacterial activity

1. Introduction

The chemistry of the organotin(IV) derivatives is being subject of study with growing interest [1], not only because of the environmental consequences of the widespread use of these compounds [2], but also as due to the increasingly importance of their medical assays for bactericide and antitumour purposes [3]. In this respect, various triorganotins have been reported recently [4] to be effective against mosquito larvae and adult mosquitoes responsible for malaria and yellow fever, and also some phenyltin derivatives display cardiovascular activity [5]. In general, the structure–activity relationship in this kind of compounds is still subject of controversy, but it seems been established that, for instance, in the case of triorganotin carboxylates, those containing *trans*-O_2SnC_3 moieties exhibit a greater biocidal activity than those containing *cis*-O_2SnC_3 [6].

In previous work [7], we have reported the synthesis and characterization of some organotin compounds, as well as their biological activity. In continuing with this type of studies, we describe in this paper the synthesis, structural study and bacteriostatic activity of a new series of triphenyltin(IV) complexes of the 3-(aryl)-2-sulfanylpropenoic acids depicted in Scheme 1. The R groups of these acids were chosen partly because of their possibility of modulate

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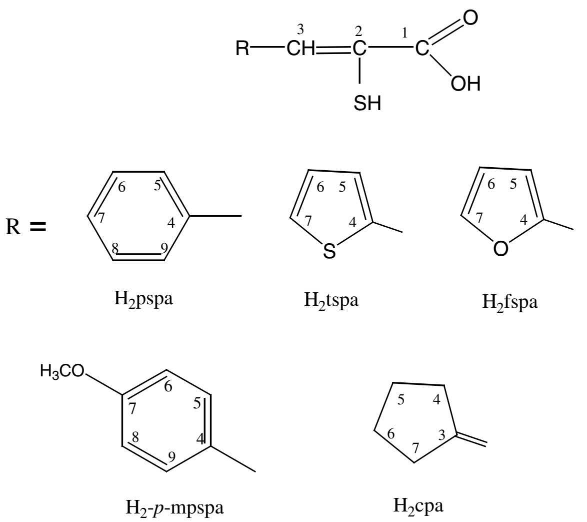


Scheme 1.

intermolecular interactions, and partly because of their likely influence on the hydrophilicity and lipophilicity of the complexes prepared, which are of great importance for pharmaceutical activity.

2. Experimental

2.1. Methods and materials

Triphenyltin(IV) hydroxide and rhodanine (Aldrich-Chemie) were used as supplied. Elemental analyses were performed with a Carlo Erba 1108 apparatus. The IR spectra were recorded on a Bruker IFS 66v FT-IR spectrometer, and the Raman spectra were recorded on the same spectrometer using an FRA-106 accessory. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker AMX300 spectrometer operating at 300.14 and 75.48 MHz, respectively, and referred to $SiMe_4$. ^{119}Sn NMR spectra in the same solvent were recorded on a Bruker AMX500 apparatus operating at 186.50 MHz, and referred to $SnMe_4$, all of them at room temperature. Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 data system and operating under EI (70 eV, 250 °C) and FAB conditions (Xe, 8 eV) using as liquid matrix 3-nitrobenzyl alcohol. Crystallographic data were recorded at room temperature on a Bruker CCD Smart apparatus using Mo Kα radiation ($\lambda = 0.71073$ Å). An absorption correction was made by means of the SADABS program [8], and the structure solution was carried out using the SHELX-97 program [9]. The DMSO molecule in **2.DMSO** had a disordered sulphur atom. This was modelled successfully using two alternative sites with the same occupancy factors (50%). Least-squares full-matrix refinements on F^2 were performed using the program SHELXL97 [9], and the illustrations were obtained with the PLATON package [10]. The crystal data, experimental details and refinement results are summarized in Table 1. CCDC reference numbers 279011 (**2.DMSO**), 279012 (**4**) and 279013 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Antibacterial activity was initially assayed by Müller-Hinton agar diffusion methods. Discs of paper 5 mm in diameter were loaded with 20 μl of a 2 mg/ml solution of the substance to be tested in 9:1 ethanol–water; control discs were loaded with solvent alone. The discs were placed on dishes of Müller-Hinton agar inoculated with *Escherichia coli* (CECT 101), *Pseudomonas aeruginosa* (CECT 110) or *Staphylococcus aureus* (CECT 240) and incubated for 24 h at 37 °C. The bacterial growth inhibition zones were recovered. All the assays were carried out in duplicate. The ligands were also assayed as negative control. For those products which showed activity, minimum inhibitory concentration (MIC), defined as the lowest concentration of active compound which inhibits the growth of the tested organism under optimal concentration, was determined using serial dilutions in Müller-Hinton broth as described in the literature [11]. A portion of 0.1 ml of nutrient broth containing 10^8 cells ml^{-1} of the sensitive bacterial culture was added to solutions of the compounds at concentrations from 80 to 0 μg ml^{-1}. Results were observed after 18 h of incubation at 35 °C. Serial dilutions of 90% ethanol were assayed as experimental control. Minimal bactericidal concentration (MBC), defined as the lowest concentration of compound that totally kills the tested bacterium, was also assayed by spreading with a swab on Müller-Hinton agar plates with subcultures of tubes that showed inhibitory action. The plates were incubated for 24 h at 35 °C.

2.2. Synthesis of the compounds

3-Aryl-2-sulfanylpropenoic acids were prepared by condensation of the appropriated aldehyde with rhodanine [12], subsequent hydrolysis in NaOH 1 M and ulterior acidification with aqueous HCl 1 M [13]. For the preparation of 2-cyclopentilyden-2-sulfanylacetic acid, in the condensation reaction a ketone (cyclopentanone) was used instead [14].

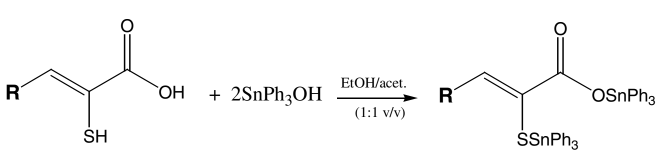
The complexes were synthesized by reacting the corresponding acid in ethanol/acetone (1:1 v/v) with triphenyltin(IV) hydroxide in the same solvent, in a donor/acceptor 1:2 mole ratio, as indicated in Scheme 2.

2.2.1. $[(SnPh_3)_2(pspa)]$ (*1*)

To a solution of 0.100 g (0.55 mmol) of 3-(2-phenyl)-2-sulfanylpropenoic acid in 10 ml of ethanol/acetone (1:1 v/v), 0.407 g (1.11 mmol) of triphenyltin(IV) hydroxide dissolved in 10 ml of the same solvent were added. After refluxing for 5 h the solution was concentrated to about 1/2 the original volume in a Dean-Stark apparatus. The resulting precipitate was filtered off and dried in vacuo. Colourless. Yield: 32%. Mp: 300 °C. Anal. Calc. for $C_{45}H_{36}O_2SSn_2$: C, 61.54; H, 4.13; S, 3.64. Found: C,

Table 1
Crystal and structure refinement data for complexes **2.DMSO**, **4** and **5**

	$[(SnPh_3)_2(tspa)(DMSO)]$	$[(SnPh_3)_2(p\text{-mpspa})]$	$[(SnPh_3)_2(cpa)]$
Empirical formula	$C_{45}H_{40}O_3S_3Sn_2$	$C_{46}H_{38}O_3SSn_2$	$C_{43}H_{38}O_2SSn_2$
Formula weight	962.33	908.20	856.17
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$
Unit cell dimensions			
a (Å)	11.1262(7)	10.448(2)	17.8683(13)
b (Å)	12.1475(8)	10.968(2)	18.6039(14)
c (Å)	18.5999(13)	18.864(4)	11.4215(9)
α (°)	95.2370(10)	105.791(5)	
β (°)	97.8690(10)	97.519(5)	90.305(2)
γ (°)	117.2200(10)	102.734(5)	
Volume (Å^3)	2180.4(3)	1986.5(8)	3796.7(5)
Z	2	2	4
Calculated density (Mg m^{-3})	1.466	1.518	1.498
Absorption coefficient (mm^{-1})	1.326	1.349	1.405
$F(000)$	964	908	1712
Crystal size (mm)	$0.30 \times 0.25 \times 0.22$	$0.12 \times 0.17 \times 0.25$	$0.04 \times 0.16 \times 0.22$
(θ) Range for data collection(°)	1.91–28.02	1.97–28.19	1.58–28.04
Index ranges	$-13 \leqslant h \leqslant 14$	$-13 \leqslant h \leqslant 13$	$-19 \leqslant h \leqslant 23$
	$-15 \leqslant k \leqslant 9$	$-14 \leqslant k \leqslant 13$	$-24 \leqslant k \leqslant 23$
	$-24 \leqslant l \leqslant 24$	$-24 \leqslant l \leqslant 18$	$-15 \leqslant l \leqslant 13$
Reflections collected	12804	11009	20653
Independent reflections	8948 [$R_{int} = 0.0261$]	7734 [$R_{int} = 0.0871$]	8470 [$R_{int} = 0.0803$]
Completeness to $\theta = 28.19°$	84.8%	79.2%	
Absorption correction	None	Multi-scan	Semi-empiric
Maximum and minimum transmission	1.000/0.811	1.000/0.602	1.000/0.841
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8948/0/439	7734/0/458	8470/0/433
Goodness-of-fit on F^2	0.903	0.791	0.564
Final R indices [$I > 2(\sigma)(I)$]	$R_1 = 0.0616$	$R_1 = 0.0814$	$R_1 = 0.0417$
	$wR_2 = 0.1660$	$wR_2 = 0.1841$	$wR_2 = 0.0900$
R indices (all data)	$R_1 = 0.1184$	$R_1 = 0.2160$	$R_1 = 0.1644$
	$wR_2 = 0.1865$	$wR_2 = 0.2234$	$wR_2 = 0.1451$
Largest difference peak and hole (e Å^{-3})	1.680 and −1.143	2.400 and −1.274	0.474 and −0.331



Scheme 2.

61.23; H, 3.84; S, 3.55%. The main signals in the EI spectrum are at m/z (ion, intensity): 351 $[SnPh_3]^+$ (94); 274 $[SnPh_2]^+$ (37); 197 $[SnPh]^+$ (100); 120 $[Sn]^+$ (93%). Besides these signals the EI spectrum shows signals for H_2pspa and its fragments and the FAB spectrum shows the same metallated signals and another one at 801 $[M\text{-}Ph]^+$ (2%). IR (Raman) (cm^{-1}): 1595s, $\nu_{asym}(CO_2)$; 1330s (1331w), $\nu_{sym}(CO_2)$; 280w, ν_{asym}(Sn–C); 235w (235w), ν_{sym}(Sn–C); 390m, ν(Sn–S); 446m, ν(Sn–O). $[\nu_{asym}(CO_2) - \nu_{sym}(CO_2)] = 265$. ^{1}H NMR (CDCl$_3$): δ (ppm) = 8.04 (s, 1H, C(3)H); 8.09 (d, 2H, C(5)H); 7.41 (t, 2H, C(6)H); 7.29 (t, 1H, C(7)H); 7.47–7.00 (m, 12H, Ph$_o$); 7.36–7.32 (m, 18H, Ph$_{m,p}$). ^{13}C NMR (CDCl$_3$): δ (ppm) = 134.1 C(2), 131.2 C(3), 136.9 C(4), 125.0 C(5), 125.6 C(6), 123.3 C(7), 131.2 C$_o$, 122.9 C$_m$, 123.7 C$_p$. ^{119}Sn NMR (CDCl$_3$): δ (ppm) = −94.6 (s); −121.3 (s).

2.2.2. *[(SnPh$_3$)$_2$(tspa)] (**2**)*

To a solution containing 0.100 g (0.54 mmol) of 3-(2-thienyl)-2-sulfanylpropenoic acid in 10 ml of ethanol/acetone (1:1 v/v), 0.395 g (1.08 mmol) of triphenyltin hydroxide in 10 ml of the same solvent were added. The resulting orange solution was refluxed for 5 h in a Dean-Stark apparatus. After stirring for a further 12 h term a solid was formed; this was filtered off and dried in vacuo. Colour: yellow. Yield: 30%. Mp: 300 °C. Anal. Calc. for $C_{43}H_{34}O_2S_2Sn_2$: C, 58.41; H, 3.88; S, 7.25. Found: C, 57.03; H, 3.81; S, 7.01%. The main signals in the EI spectrum are at m/z (ion, intensity): 351 $[SnPh_3]^+$ (100); 274 $[SnPh_2]^+$ (22); 197 $[SnPh]^+$ (96); 120 $[Sn]^+$ (76). Apart from these signals, the EI spectrum shows signals for H_2tspa and its fragments and the FAB spectrum shows the same metallated signals and another one at 655 $[M\text{-}3Ph]^+$ (27%). IR (Raman) (cm^{-1}): 1590s, $\nu_{asym}(CO_2)$; 1333s (1333s), $\nu_{sym}(CO_2)$; 272s, ν_{asym}(Sn–C); 234m, ν_{sym}(Sn–C); 343m (341w), ν(Sn–S); 445s (447w), ν(Sn–O). $[\nu_{asym}(CO_2) - \nu_{sym}(CO_2)] = 257$. ^{1}H

NMR ($CDCl_3$): δ (ppm) = 8.27 (s, 1H, C(3)H); 7.59 (d, 1H, C(5)H); 7.11 (d, 1H, C(6)H); 7.74 (s, 1H, C(7)H); 7.50 (m, 12H, Ph_o); 7.36 (m, 18H, $Ph_{m,p}$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 173.1 C(1), 126.1 C(2), 122.9 C(3), 140.4 C(4), 132.4 C(5), 127.8 C(6), 128.8 C(7), 141.4 C_i, 136.4 C_o [$^2J(^{119}Sn–^{13}C)$, 42.6 Hz], 128.6 C_m [$^3J(^{119}Sn–^{13}C)$, 63.8 Hz], 130.1 C_p. ^{119}Sn NMR ($CDCl_3$): δ (ppm) = −98.4 (s); −109.8 (s).

From a DMSO-d_6 solution of a fraction of this product suitable crystals for X-ray diffraction were obtained. The structural study by single-crystal X-ray diffraction showed this solid to be the new and unexpected complex **2.DMSO** where a DMSO molecule is attached to one Sn atom via the oxygen atom.

2.2.3. *[(SnPh$_3$)$_2$(fspa)] (**3**)*

To the brown solution obtained by adding 0.100 g (0.59 mmol) of 3-(2-furyl)-2-sulfanylpropenoic acid to 10 ml of a mixture ethanol/acetone (1:1 v/v), 0.432 g (1.18 mmol) of triphenyltin hydroxide in 10 ml of the same solvent were added. By refluxing for 4 h in a Dean-Stark apparatus, the azeotropic mixture was eliminated, after which the solution was stirred for 12 h. The resulting solid was filtered off and vacuum dried. Colour: brown. Yield: 32%. Mp: 178 °C. Anal. Calc. for $C_{43}H_{34}O_3SSn_2$: C, 59.49; H, 3.95; S, 3.69. Found: C, 58.22; H, 3.86; S, 3.66%. The main signals in the EI spectrum are at m/z (ion, intensity): 351 $[SnPh_3]^+$ (93); 274 $[SnPh_2]^+$ (29); 197 $[SnPh]^+$ (96); 120 $[Sn]^+$ (91). Besides these signals the EI spectrum shows signals for H_2fspa and its fragments and the FAB spectrum shows the same metallated signals. IR (Raman) (cm^{-1}): 1590s, $\nu_{asym}(CO_2)$; 1335s (1337m), $\nu_{sym}(CO_2)$; 273m, ν_{asym}(Sn–C); 236m (236w), ν_{sym}(Sn–C); 353m (352w), ν(Sn–S); 450m (473w), ν(Sn–O). [$\nu_{asym}(CO_2) - \nu_{sym}(CO_2)$] = 255. ^1H NMR ($CDCl_3$): δ (ppm) = 8.05 (d, 1H, C(3)H); 7.58 (d, 1H, C(5)H); 7.33 (d, 1H, C(6)H); 7.61 (d, 1H, C(7)H); 7.51 (m, 12H, Ph_o); 7.39 (m, 18H, $Ph_{m,p}$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 172.7 C(1), 126.6 C(2), 123.6 C(3), 142.0 C(4), 129.3 C(5), 127.8 C(6), 128.7 C(7), 143.1 C_i, 136.3 C_o [$^2J(^{119}Sn–^{13}C)$, 43.0 Hz], 128.4 C_m [$^3J(^{119}Sn–^{13}C)$, 58.6 Hz], 130.1 C_p. ^{119}Sn NMR ($CDCl_3$): δ (ppm) = −93.1 (s); −122.1 (s).

2.2.4. *[(SnPh$_3$)$_2$(p-mpspa)] (**4**)*

From 0.100 g (0.48 mmol) of 3-(4-methoxyphenyl)-2-sulfanylpropenoic acid solved in 10 ml of ethanol/acetone (1:1 v/v) and 0.349 g (0.96 mmol) of triphenyltin hydroxide in 10 ml of the same solvent a yellowish solution was formed. After 12 h stirring the solution was refluxed for 5 h in a Dean-Stark apparatus and reduced in volume to ca. 10 ml. The formed solid was filtered off, and the filtrate was air-evaporated, yielding crystals suitable for X-ray analysis. Colour: yellow. Yield: 34%. Mp: 184 °C. Anal. Calc. for $C_{46}H_{38}O_3SSn_2$: C, 60.83; H, 4.22; S, 3.53. Found: C, 60.35; H, 3.83; S, 3.42%. The main signals in the EI spectrum are at m/z (ion, intensity): 351 $[SnPh_3]^+$ (100); 274 $[SnPh_2]^+$ (12); 197 $[SnPh]^+$ (16). Besides these signals the EI spectrum shows signals for H_2-p-mpspa and its fragments and the FAB spectrum shows the same metallated signals and another one at 120 $[Sn]^+$ (11%). IR (Raman) (cm^{-1}): 1586s, $\nu_{asym}(CO_2)$; 1327s (1328s), $\nu_{sym}(CO_2)$; 274m, ν_{asym}(Sn–C); 236m (238w), ν_{sym}(Sn–C); 356w, ν(Sn–S); 453s, ν(Sn–O). [$\nu_{asym}(CO_2) - \nu_{sym}(CO_2)$] = 259. ^1H NMR ($CDCl_3$): δ (ppm) = 8.05 (d, 1H, C(3)H); 8.07 (d, 1H, C(5)H); 7.21 (d, 2H, C(6)H); 3.80 (s, 3H, OCH_3); 7.48 (m, 12H, Ph_o); 7.33 (m, 18H, $Ph_{m,p}$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 173.9 C(1), 137.3 C(2), 142.2 C(3), 132.7 C(4), 130.2 C(5), 113.6 C(6), 159.9 C(7), 55.3 OCH_3, 136.7 C_i, 136.4 C_o [$^2J(^{119}Sn–^{13}C)$, 45.1 Hz], 128.2 C_m, 128.7 C_p. ^{119}Sn NMR ($CDCl_3$): δ (ppm) = −96.9 (s); −121.6 (s).

2.2.5. *(SnPh$_3$)$_2$(cpa)] (**5**)*

To 0.050 g (0.32 mmol) of 2-cyclopentilyden-2-sulfanylacetic acid solved in 10 ml of ethanol/acetone (1:1 v/v), 0.232 g (0.64 mmol) of triphenyltin hydroxide in 10 ml of the same solvent were added. After 12 h stirring, the yellow suspension was refluxed for a further 5 h and concentrated by means of a Dean-Stark apparatus to 1/2 the original volume. The formed solid was filtered off and vacuum dried. From the mother liquor crystals suitable for X-ray analysis were separated. Colourless. Yield: 36%. Mp: 211 °C. Anal. Calc. for $C_{43}H_{38}O_2SSn_2$: C, 60.32; H, 4.47; S, 3.74. Found: C, 59.85; H, 4.77; S, 3.31%. The main signals in the EI spectrum are at m/z (ion, intensity): 351 $[SnPh_3]^+$ (100); 274 $[SnPh_2]^+$ (11); 197 $[SnPh]^+$ (47); 120 $[Sn]^+$ (19). Besides these signals the EI spectrum shows signals for H_2(fspa) and its fragments and the FAB spectrum shows the same metallated signals and another one at 781 $[M-Ph]^+$ (62%). IR (Raman) (cm^{-1}): 1594s, $\nu_{asym}(CO_2)$; 1346s, $\nu_{sym}(CO_2)$; 272s, ν_{asym}(Sn–C); 237m (239w), ν_{sym}(Sn–C); 360m, ν(Sn–S); 446s, ν(Sn–O). [$\nu_{asym}(CO_2) - \nu_{sym}(CO_2)$] = 248. ^1H NMR ($CDCl_3$): δ (ppm) = 2.65 (m, 4H, C(4)2H); 1.60 (m, 4H, C(5)2H); 1.60 (m, 4H, C(6)2H); 2.65 (m, 4H, C(7)2H); 7.48 (m, 12H, Ph_o); 7.34 (m, 18H, $Ph_{m,p}$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 166.6 C(1), 129.9 C(2), 138.2 C(3), 38.4 C(4), 27.7 C(5), 25.7 C(6), 36.4 C(7), 141.1 C_i, 136.8 C_o [$^2J(^{119}Sn–^{13}C)$, 48.0 Hz], 128.8 C_m [$^3J(^{119}Sn–^{13}C)$, 58.7 Hz], 128.4 C_p. ^{119}Sn NMR ($CDCl_3$): δ (ppm) = −99.1 (s); −109.7 (s).

3. Results and discussion

3.1. *X-ray studies*

3.1.1. *Structure of **2.DMSO***

Fig. 1 shows an ORTEP representation of the molecular structure for this complex, and selected bond distances and angles are listed in Table 2.

The asymmetric unit contains two metal centres, each one of them surrounded by 5 atoms in a distorted trigonal-bipyramidal environment, where the tspa ligand acts as a bridge between the two metal atoms: as an O-donor ligand with respect to Sn(2) and as an S,O-donor chelating

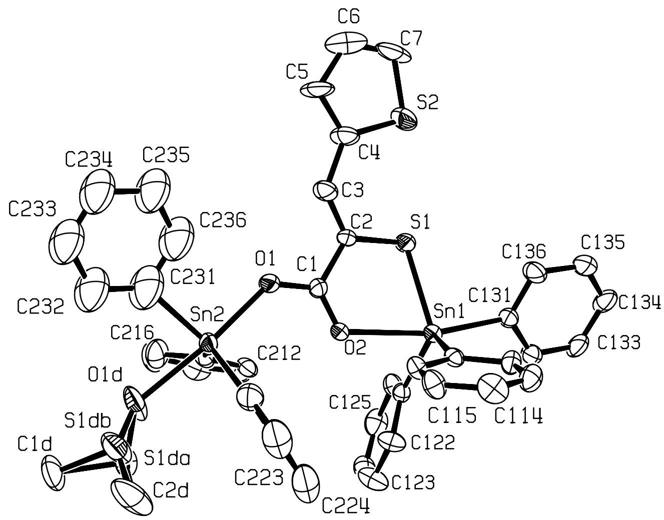


Fig. 1. Molecular structure of complex **2.DMSO**. Ellipsoids at 30% probability.

Table 2
Selected bond lengths (Å) and angles (°) for **2.DMSO**

Bond		Angle	
Sn(1)–C(121)	2.131(8)	C(121)–Sn(1)–C(111)	115.2(3)
Sn(1)–C(111)	2.146(7)	C(121)–Sn(1)–C(131)	104.0(3)
Sn(1)–C(131)	2.187(8)	C(111)–Sn(1)–C(131)	102.4(3)
Sn(1)–S(1)	2.439(2)	C(121)–Sn(1)–S(1)	121.5(2)
Sn(1)–O(2)	2.453(5)	C(111)–Sn(1)–S(1)	115.2(2)
Sn(2)–C(211)	2.105(10)	C(131)–Sn(1)–S(1)	92.3(2)
Sn(2)–C(221)	2.122(8)	C(121)–Sn(1)–O(2)	79.9(2)
Sn(2)–O(1)	2.137(5)	C(111)–Sn(1)–O(2)	87.1(2)
Sn(2)–C(231)	2.177(6)	C(131)–Sn(1)–O(2)	166.5(2)
Sn(2)–O(1D)	2.321(7)	S(1)–Sn(1)–O(2)	74.91(13)
O(2)–C(1)	1.237(8)	C(211)–Sn(2)–C(221)	119.5(4)
O(1)–C(1)	1.283(8)	C(211)–Sn(2)–O(1)	95.2(3)
Sn(2)–O(2)	3.382(5)	C(221)–Sn(2)–O(1)	98.5(3)
		C(211)–Sn(2)–C(231)	115.3(3)
		C(221)–Sn(2)–C(231)	121.9(3)
		O(1)–Sn(2)–C(231)	94.1(2)
		C(211)–Sn(2)–O(1D)	87.2(4)
		C(221)–Sn(2)–O(1D)	84.8(3)
		O(1)–Sn(2)–O(1D)	174.2(3)
		C(231)–Sn(2)–O(1D)	80.1(4)

ligand in its attachment to Sn(1). So that, the coordination polyhedron around Sn(2) is formed by 2 oxygen atoms (from DMSO and tspa, respectively) located on the apical positions of the bipyramid, and 3 phenyl carbon atoms in the equatorial sites. A considerable distortion arises from the presence of the bridge ligand, as indicated by the O(1)–Sn(2)–O(1D) angle value [174.2(3)° instead of the expected 180°]. In the same way, the bond angles in the equatorial plane take values slightly different from 120° [115.3(3), 121.9(3), 119.5(4)°], whereas the angles between the apical positions and the equatorial plane have values such as 80.1(4) or 98.5(3)°.

The polyhedron around Sn(1) is even more distorted, as expected from the presence of the tspa chelating ligand, the sulfanyl S(1) atom of which is located in the equatorial plane, occupying the carboxylic O(2) atom one of the apical positions in the bipyramid. So that, the C(131)–Sn(1)–O(2) [166.5(2)°] and the S(1)–Sn(1)–O(2) [74.91(13)°] angles have values quite different from the theoretically expected 180° and 90°, respectively.

Regarding the two Sn–O bond lengths between the bridge ligand and both metal centres, their values are 2.453(5) Å for Sn(1)–O(2), and 2.137(5) Å for Sn(2)–O(1), whereas the sum of the covalent radii is 2.13 Å [15]. As expected, the oxygen atom more weakly bound to Sn is closer to C than the other one [1.237(8) vs. 1.283(8) Å]. The Sn–C bond lengths, on the other hand, are unremarkable, being all of them in the range found for other compounds of this type and close to the sum of the covalent radii (2.17 Å). Finally, the oxygen atom [O(2)] attached to Sn(1) is located at 3.382(5) Å from Sn(2); although the sum of the van der Waals radii is 3.70 Å, that value is out of the range reported as corresponding to an Sn–O bond [2.263(6)–3.071(2) Å] [16]. Nevertheless, the existence of a weak interaction between both atoms (which would be responsible of the previously discussed slight distortion of the Sn bipyramidal environment) cannot be discarded.

3.1.2. Structure of $[(SnPh_3)_2(p\text{-mpspa})]$ (**4**)

Fig. 2 shows an ORTEP representation of this complex, and Table 3 lists some selected bond lengths and angles. The asymmetric unit contains two $SnPh_3$ moieties bridged by the p-mpspa ligand. Each Sn atom is surrounded by three phenyl C atoms and one atom of the bridge ligand: the oxygen atom O(1) is bound to Sn(2), and the sulphur atom (S) to Sn(1). Moreover, the O(2) atom is separated by 2.914(9) Å from Sn(2) and 2.556(9) Å from Sn(1). Although neither of these interactions may be considered to represent a strong bonding interaction, these distances are short enough [16] to make this oxygen atom stereochemically active around the two Sn atoms, and so that responsible for the resulting geometry in both cases, which compares with a trigonal bipyramid rather than a tetrahedron. In fact, the coordination sphere around Sn(2) may be thought to be formed by the O(2) atom of the ligand in one

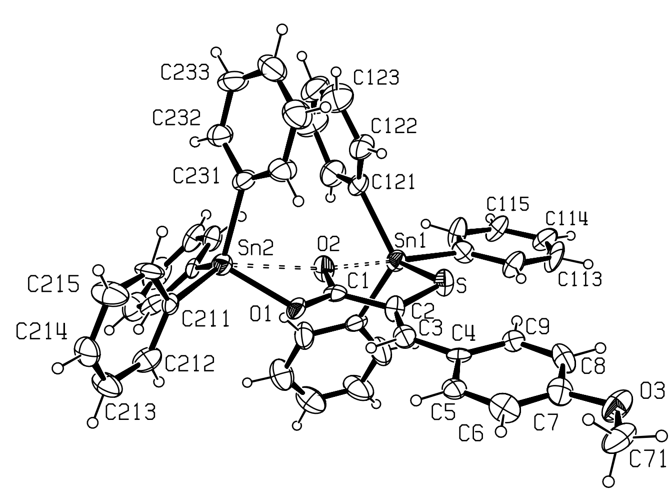


Fig. 2. Molecular structure of complex **4**. Ellipsoids at 30% probability.

Table 3
Selected bond lengths (Å) and angles (°) for complex **4**

Bond		Angle	
Sn(2)–C(211)	2.110(9)	C(221)–Sn(2)–O(2)	77.8(4)
Sn(2)–O(1)	2.064(8)	C(231)–Sn(2)–O(2)	85.4(5)
Sn(2)–C(221)	2.082(15)	C(211)–Sn(2)–C(231)	111.8(5)
Sn(2)–C(231)	2.120(15)	O(1)–Sn(2)–C(231)	102.4(5)
Sn(2)–O(2)	2.914(9)	C(221)–Sn(2)–C(231)	111.8(6)
O(1)–C(1)	1.289(14)	C(211)–Sn(2)–O(2)	146.6(3)
O(2)–C(1)	1.240(14)	O(1)–Sn(2)–O(2)	48.9(3)
Sn(1)–C(131)	2.133(15)	C(211)–Sn(2)–O(1)	99.0(4)
Sn(1)–C(111)	2.139(15)	C(211)–Sn(2)–C(221)	115.0(5)
Sn(1)–C(121)	2.164(14)	O(1)–Sn(2)–C(221)	115.5(4)
Sn(1)–S	2.441(4)	C(131)–Sn(1)–C(121)	116.0(5)
Sn(1)–O(2)	2.556(9)	C(131)–Sn(1)–C(111)	103.1(6)
		C(131)–Sn(1)–O(2)	85.4(5)
		C(131)–Sn(1)–S	116.4(4)
		C(111)–Sn(1)–O(2)	169.0(4)
		C(121)–Sn(1)–O(2)	77.9(4)
		S–Sn(1)–O(2)	72.8(2)
		C(111)–Sn(1)–S	96.9(4)
		C(111)–Sn(1)–C(121)	104.0(5)

apical position of a bipyramid, and one phenyl C atom [C(2 1 1)] in the other, the equatorial positions being occupied by the other two phenyl C atoms and the O(1) atom of the p-mpspa ligand. The bite of the ligand makes the O–Sn–O angle much narrower than 90° [48.9(3)°]. The other metal atom, Sn(1), is surrounded in a similar but more regular way by three phenyl C atoms, the sulphur atom of the ligand and the bridge atom O(2). This last atom occupies one of the apical positions, whereas one of the C atoms [C(1 1 1)] is located at the second one. When compared the structure of this compound with that of the DMSO complex commented above, the Sn–S bond lengths are almost identical in both species, and they are in the range found in other similar systems [17]; by contrast, the Sn–O distance is in this case much shorter than there. This difference may be explained taking into account that in the DMSO complex this ligand provides to the Sn atom with electronic charge enough to make less necessary the proximity of the metal to the other O atom. Besides, in the former complex this O atom occupies an apical position of the pseudo-bipyramid, whereas in the latter it is located on an equatorial site. For the description of the bonding in the five-coordinate Sn compounds, a three-centre orbital model is usually adopted [18]. According to this model, (and assuming that the contribution of tin 5d orbitals to the bonding is very low), the three equatorial bonds are formed by sp^2 hybrid orbitals, whilst the remaining 5p orbital participates in a weaker bond with the substituents on the apical positions using a three-centre molecular orbital of the linear type.

3.1.3. Structure of $[(SnPh_3)_2(cpa)]$ (**5**)

The structure of this complex and the numbering scheme is showed in Fig. 3, whereas selected bond lengths and angles are listed in Table 4.

The asymmetric unit is formed by two metal centres, each one of them surrounded by three phenyl C atoms

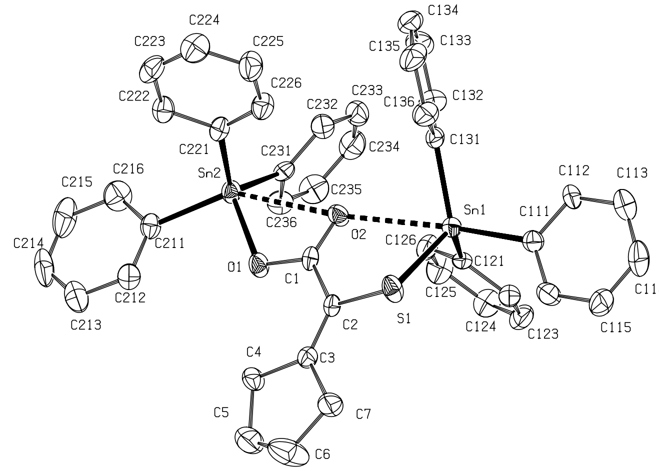


Fig. 3. Molecular structure of complex **5**. Ellipsoids at 30% probability.

and one atom of the cpa bridge ligand, the S atom in the case of Sn(1) and the O atom in the case of Sn(2). As in the p-mpspa complex commented above, the non-coordinating O(2) atom of the cpa ligand plays an important role in the resulting geometry around the two Sn atoms, since the Sn(1)–O(2) and Sn(2)–O(2) distances are 2.743(5) and 2.824(5) Å, respectively. Therefore, we may consider the existence of a trigonal-bipyramidal environment around each Sn atom. The bridge ligand constrains the angles around Sn(1) to narrow; for instance, 166.9(2)° for C(1 1 1)–Sn(1)–O(2) (instead of 180°) or 112.6(18)–117.1(3)° in the equatorial plane (instead of 120°). Again, the environment around Sn(2) is less regular, and we can find values for the bond angles such as 50.50(16)° [O(1)–Sn(2)–O(2)], instead of 90°. On the other hand, the bond lengths, in each metal centre, between the Sn atom and the O atom located in the apical position are quite different to each other [2.743(5) and 2.824(5) Å, respectively], but in

Table 4
Selected bond lengths (Å) and angles (°) for complex **5**

Bond		Angle	
Sn(1)–C(111)	2.166(8)	C(121)–Sn(1)–C(131)	117.1(3)
Sn(1)–O(2)	2.743(5)	C(121)–Sn(1)–C(111)	106.0(3)
Sn(1)–C(121)	2.123(8)	C(131)–Sn(1)–C(111)	105.5(3)
Sn(1)–C(131)	2.128(7)	C(121)–Sn(1)–S(1)	112.63(18)
Sn(1)–S(1)	2.432(2)	C(131)–Sn(1)–S(1)	115.1(2)
Sn(2)–O(1)	2.056(5)	C(111)–Sn(1)–S(1)	97.79(19)
Sn(2)–C(221)	2.110(8)	C(121)–Sn(1)–O(2)	84.6(2)
Sn(2)–C(231)	2.119(8)	C(131)–Sn(1)–O(2)	75.4(2)
Sn(2)–C(211)	2.126(7)	C(111)–Sn(1)–O(2)	166.9(2)
Sn(2)–O(2)	2.824(5)	S(1)–Sn(1)–O(2)	70.54(11)
		O(1)–Sn(2)–C(221)	106.4(3)
		O(1)–Sn(2)–C(231)	112.0(2)
		C(221)–Sn(2)–C(231)	118.5(3)
		O(1)–Sn(2)–C(211)	95.5(3)
		C(221)–Sn(2)–C(211)	110.2(3)
		C(231)–Sn(2)–C(211)	111.8(3)
		O(1)–Sn(2)–O(2)	50.50(16)
		C(221)–Sn(2)–O(2)	86.9(2)
		C(231)–Sn(2)–O(2)	82.7(2)
		C(211)–Sn(2)–O(2)	145.8(2)

both cases they are longer than the sum of their covalent radii. In the cpa ligand, as expected, the shorter C–O bond corresponds to the non-coordinating oxygen atom, whereas the Sn–C bond distances are unremarkable.

3.2. Spectroscopic studies

The vibrational patterns of the complexes have been analyzed in the light of the X-ray diffraction structural results. Thus, while the spectra of the ligands H_2pspa, H_2tspa, H_2fspa, H_2-p-mpsa and H_2cpa show the bands characteristic of the SH and OH groups at about 2560–2580 and 1395–1440 cm^{-1}, respectively, the lack of these bands in the complexes spectra confirms the di-deprotonation of the ligand upon coordination. This coordination to Sn via the S and O atoms is also revealed by the presence of (Sn–S) and (Sn–O) stretching bands at about 360 and 450 cm^{-1}, respectively. On the other hand, the v_{asym}(COO) and v_{sym}(COO) vibrations of the carboxylato group give rise to bands at about 1590 and 1335 cm^{-1}, respectively, with calculated values for $\Delta v(=v_{asym} - v_{sym})$ in the range 248–265 cm^{-1}, as expected from the monodentate or asymmetric bidentate behaviour of the carboxylate ligand [19,20].

The ^{1}H NMR spectra of the complexes show, apart from the absence of the C(1)OH and C(2)SH signals due to the di-deprotonation of the ligand, the signals of the phenyl groups attached to Sn in the range 7.30–7.90 ppm, as usually occurs in this type of triphenyltin(IV) compounds. Regarding the ^{13}C NMR spectra, the C(1) signal is shifted downfield, with respect to the ligand spectra, at about 174 ppm, indicating the monodentate behaviour of the carboxylato group. This signal, nevertheless, was not found in the case of [$(SnPh_3)_2$(pspa)], which spectrum is of poor quality due to the low solubility of this complex in $CDCl_3$. Besides, the coordination to Sn via the S atom causes a shielding of C(3), while the other signals of the ligand remain practically unchanged upon coordination. Finally, the ^{119}Sn NMR spectra show, in all cases, two signals (indicating the existence of two different coordination environments around the Sn atoms) in the usual range for four-coordinate Sn complexes [21], denoting the cleavage in solution of the weak Sn–O bond commented above. One of these signals, attributable to the Ph_3SnS moiety, occurs at −90 to −100 ppm, while the other, due to the Ph_3SnO polyhedron, appears between −110 and −120 ppm.

3.3. Antibacterial activity

No antibacterial activity was exhibited by the ligands or solvent. The complexes were tested against standard strains of *Escherichia coli* (CECT 101), *Pseudomonas aeruginosa* (CECT 110) and *Staphylococcus aureus* (CECT 240), and all five compounds showed to be active against the Gram-positive bacterium *S. aureus*, but inactive against the Gram-negative bacteria *E. coli* and *P. aeruginosa*. This result is in accordance with that previously reported for other triphenyltin(IV) carboxylato complexes [7,22].

Table 5
Antibacterial activity against *Staphylococcus aureus* of the complexes: diameters of the bacterial growth inhibition zones, MIC and MBC values

	Diameter (mm)	MIC (μg ml^{-1})	MBC (μg ml^{-1})
[$(SnPh_3)_2$(pspa)]	1.7	0.9	5.0
[$(SnPh_3)_2$(tspa)]	2.1	2.5	15.0
[$(SnPh_3)_2$(fspa)]	2.0	2.5	15.0
[$(SnPh_3)_2$(p-mpspa)]	1.8	5.0	22.0
[$(SnPh_3)_2$(cpa)]	1.7	5.0	60.0

In the case of the only sensitive strain, *S. aureus*, the MIC and MBC values were also determined for the different complexes. Table 5 shows the diameter, in mm, of the bacterial growth inhibition zone for each complex assayed together with the MIC and MBC values in μg ml^{-1}. The MIC results, in the range 0.9–5.0 μg ml^{-1}, are much lower as compared, for instance, to antibiotic ampicillin (MIC 12.5 μg ml^{-1}), and similar to the values reported for antibiotic norfloxacin (MIC 3.0 μg ml^{-1}) against the same bacterium [5].

The MBC values confirmed the results obtained on Müller-Hinton broth.

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References

[1] L. Pellerito, L. Nagy, Coord. Chem. Rev. 224 (2002) 111, and references therein.
[2] P. Quevauviller, R. Ritsema, R. Morabit, W.M.R. Dirkx, Appl. Organomet. Chem. 8 (1994) 541.
[3] J. Crowe, Appl. Organomet. Chem. 1 (1987) 143.
[4] (a) G. Eng, C. Whitmyer, B. Sina, N. Ogwuru, Main Group Met. Chem. 22 (1999) 311;
(b) N. Ogwuru, Q. Duong, X. Song, G. Eng, Main Group Met. Chem. 24 (2001) 775;
(c) G. Eng, X. Song, Q. Duong, D. Strickman, J. Glass, L. May, Appl. Organomet. Chem. 17 (2003) 218.
[5] M. Nath, S. Pokharia, G. Eng, X. Song, A. Kumar, Eur. J. Med. Chem. 40 (2005) 289.
[6] (a) K.C. Molloy, T.G. Purcell, M.F. Mahon, E. Minshall, Appl. Organomet. Chem. 1 (1987) 507;
(b) K.C. Molloy, in: F.R. Hartley (Ed.), The Chemistry of Metal–Carbon Bonds, Wiley, New York, 1985, p. 465;
(c) S.J. Blunden, P.J. Smith, B. Sugavanam, Pestic. Sci. 15 (1984) 253.
[7] J.S. Casas, A. Castiñeiras, M.D. Couce, M.L. Jorge, U. Russo, A. Sánchez, R. Seoane, J. Sordo, J.M. Varela, Appl. Organomet. Chem. 14 (2000) 421.
[8] G.M. Sheldrick, SADABS, An Empirical Absorption Correction Program for Area Detector Data, University of Göttingen, Germany, 1996.
[9] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.
[10] A.L. Spek, PLATON v. 3.04.02, University of Utrecht, The Netherlands, 2002. http://www.cryst.chem.uu.nl/platon/.

[11] E.W. Koneman, S.D. Allen, V.R. Dowell Jr., H.M. Sommers, Color Atlas and Textbook of Diagnostic Micribiology, J.B. Lippincott Co., USA, 1979, p. 321.
[12] C. Gränacher, Helv. Chim. Acta 5 (1922) 610.
[13] E. Campaigne, R.E. Cline, J. Am. Chem. Soc. 21 (1956) 32.
[14] F.C. Brown, K. Bradsher, S.G. McCallum, M. Potter, J. Org. Chem. 15 (1950) 174.
[15] E.J. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry. Principles of Structure and Reactivity, fourth ed., Harper Collins College Publishers, New York, 1993, p. 292.
[16] A.R. Forrester, S.J. Garden, R.A. Howie, J.L. Wardell, J. Chem. Soc. Dalton Trans. (1992) 2615.
[17] B.D. James, R.J. Magee, W.C. Patalinghug, B.W. Skelton, A.H. White, J. Organomet. Chem. 467 (1994) 51.
[18] R. Okawara, M. Wada, in: F.G.A. Stone, R. West (Eds.), Advances in Organometallic Chemistry, vol. 5, Academic Press, New York, London, 1967.
[19] M. Danish, A. Badshah, M. Mazhar, Ali Saqib, N. Islam, M. Iqbal Chaudary, Iran. J. Chem. Eng. 13 (1994) 1.
[20] A.K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed., Part B, John Wiley, New York, 1997, p. 60.
[21] J. Holeček, M. Nádvorník, K. Handlíř, A. Lyčka, J. Organomet. Chem. 241 (1983) 177.
[22] M. Nath, R. Yadav, Bull. Chem. Soc. Jpn. 70 (1997) 1331.