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Synthesis, characterization and biological activities of some new organotin(IV) derivatives: Crystal structure of $[(Sn\ Ph_3)\ (OOCC_6H_4OH)]$ and $[(SnMe_3)_2\ (OOC)_2C_6Cl_4\ (DMSO)_2]$

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ABSTRACT

Some new organotin(IV) carboxylates **1**–**3** of 2-hydroxybenzoic acid (L_A) and **4**–**6** of 2,3,4,5-tetrachloro-6-(methoxycarbonyl) benzoic acid (L_B) have been synthesized, respectively, by the esterification of triorganotin oxide/hydroxide with the corresponding acids in an appropriate mole ratios. Multinuclear NMR (^1H, ^{13}C and ^{119}Sn), IR and X-ray crystallographic studies were carried out to elucidate their structures both in solution and in solid state. The X-ray crystallographic data for **3** was recollected at low temperature. The compound **4** was dissolved in DMSO and a new compound **4** · 2DMSO $[(SnMe_3)_2(OOC)_2C_6Cl_4(DMSO)_2]$ was crystallized out. The structure shows that two Sn moieties are attached to the ligand (L_B) through two carboxylic groups. The two molecules of DMSO are coordinated to each of the Sn atoms via oxygen atom to terminate the conventional polymeric chain of trimethyl carboxylates to a discrete molecule, having trigonal bipyramidal geometry around the Sn atoms. Some of the synthesized compounds exhibited significant antifungal activities and have a potential to be used as drugs.

1. Introduction

The chemistry of substituted aromatic carboxylic acids such as acetylsalicylic acid and phenyl acetic acids have been a subject of study in life sciences, particularly for their in vitro antitumor, anti-inflammatory and antipyretic properties [1–3]. The syntheses of metal complexes with such type of active ligands are a research area of increased interest for inorganic, pharmaceutical and medicinal chemistry as an approach to the development of new drugs [4]. This is because the judicious choice of ligands can modulate the properties of complexes. The on co-protective roles of food derived polyphenol antioxidants have been well documented but their mechanism have yet to be known [5]. Triorganotin salicylate and substituted phenol derivatives have been actively studied group of organotin compounds for their possible bactericidal [6,7], fungicidal [8,9], and antifouling [10] activities. The main phenolic acids found in food are mostly derivatives of 4-hydroxybenzoic acid and 4-hydroxycinnamic acid and the possible role of phenolic acids in cancer protective and antigenocity has also been investigated [11,12]. The widely used fungicide 2,4,5,6-tetrachloroisophthalonitrile (chlorthalonil) has both agricultural and household uses, however, its prolonged exposure may cause skin rashes [13,14]. So there is a need to develop such fungicides which do not pose serious threats to the environment as well as to the human beings. Chloroderivative such as 2,2′-methylene-bis (3,4,6-trichlorophenol) (hexachlorophene) served as a useful anti-infective and anti-bacterial agent in cosmetics and agriculture, particularly for citrus mite control [15]. In continuation to our previous work [16,17], herein we report the syntheses, characterization and biological studies of tin(IV) derivatives with 2-hydroxybenzoic acid and 2,3,4,5-tetrachloro-6-(methoxycarbonyl) benzoic acid to widen their scope in biological applications (Scheme 1).

2. Experimental

2.1. General

Triorganotin(IV) hydroxides/oxides were purchased from Aldrich/Alfa Aesar while the salicylic acid and 3,4,5,6-tetrachlorophthalicanhyride were procured from Peoples Republic of China and used as received. The 3,4,5,6-tetrachlorophthalicanhyride was converted into a hemi- ester by a reported procedure [18] (Scheme 1). All chemical reactions were carried out in common organic solvents which were dried before use in accordance to standard methods [19].

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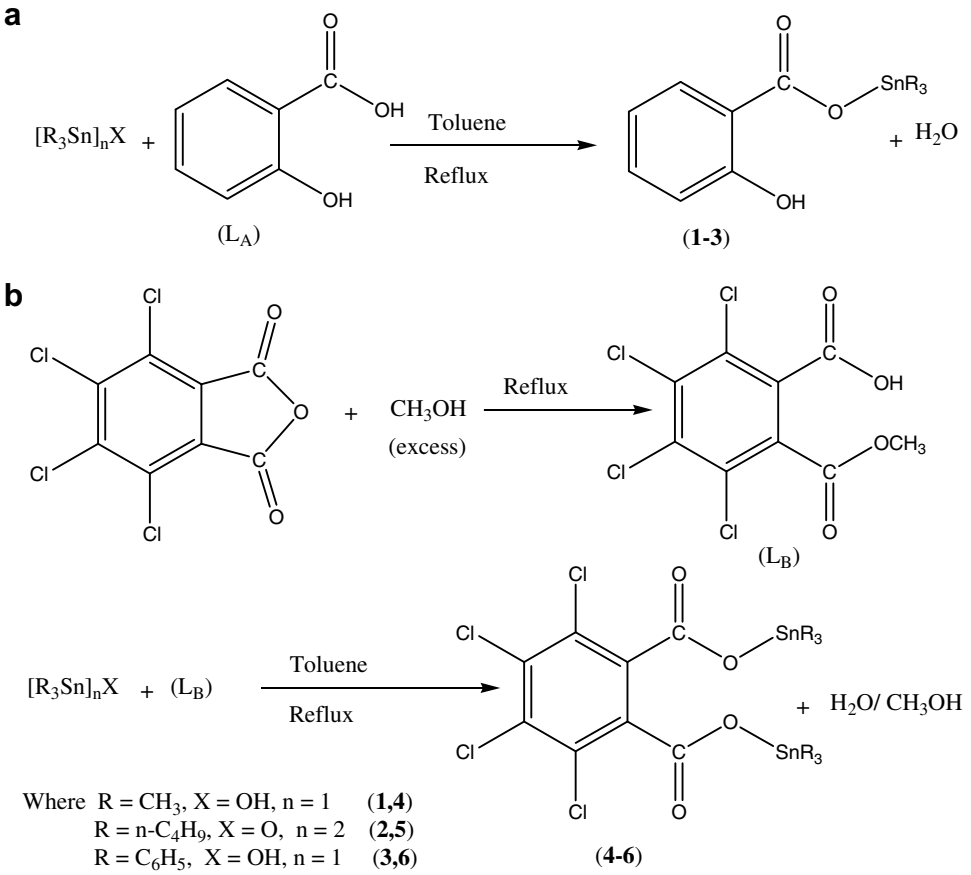

Scheme 1.

Elemental analyses were carried out by Leco CHNS-932 analyzer (USA). Melting points were determined with a Gallenkemp (UK) apparatus and are uncorrected. Infrared spectra were recorded on Bio-Rad Excalibur FT-IR Model FTS 3000 MX as KBr discs 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra in solution(s) were recorded at ambient temperature on a Bruker 300 spectrometer operating at 300 and 75.45 MHz, respectively, using TMS as an internal reference. ^{119}Sn NMR spectra were obtained on a Bruker 300 spectrometer with Me_4Sn as an external reference.

2.2. X-ray crystallography

Crystals of **3** and **4** · 2DMSO were grown by slow evaporation of chloroform/DMSO solutions at room temperature. The colorless crystals were mounted in random orientation on a glass fiber on a Stoe IPDS-II two circle diffractometer [20] equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was performed using the MULABS option in PLATON [21]. The structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 with SHELXL-97 [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a difference map but refined using a riding model. Table 1 summarizes the crystal data and refinement details. For molecular graphics XP from the SHELXTL suite [23] was used.

2.3. Biological studies

The compounds **1**–**6** were preliminary screened against various strains of bacteria and fungi by agar well diffusion and agar tube dilution protocol methods, respectively [24,25].

2.4. Synthesis & characterization of compounds **1**–**6**

The methodology of [26,27] was followed for the synthesis of target compounds **1**–**6** as mentioned in Scheme 1. Appropriate stoichiometric ratios of the respective organotin hydroxides/oxides and ligands L_A or L_B were suspended in dry toluene (50 ml) and refluxed for 6–8 h under inert atmosphere. Water formed during the reaction was removed by Dean–Stark apparatus. The contents were allowed to stand for sometime at room temperature and the solvent was then evaporated on rotary evaporator and the solid mass, thus obtained, was recrystallized in chloroform/*n*-hexane (3:1) for **1**–**3** and DMSO for **4**–**6**.

2.4.1. Synthesis of 2-hydroxybenzoatotrimethyltin(IV) (**1**) [26]

Quantities used were 0.138 g (1 mmol) L_A and 0.18 g (1 mmol) trimethyltin hydroxide in toluene. Yield: 86%. M.p.: 145.7 °C. Anal. Calc. for $C_{10}H_{14}O_3Sn$ (300.90): C, 39.92; H, 4.69. Found: C, 40.01; H, 4.74. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ^{2}J [^{119}Sn–^{1}H] in Hz): 0.59 [59.0] (s, 9H, H_3C–Sn); 6.9–7.9 (m, 4H, H_4C_6–); 5.4 (s, 1H, HO-Ph). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ, ^{n}J [^{119}Sn–^{13}C] in Hz): −2.8 [392.8] (H_3C–Sn); 115.6, 115.8, 122.3, 131.6, 135.2, 161.7(H_4C_6OH); 172 (COO). ^{119}Sn NMR ($CDCl_3$, δ): 140.6. IR (KBr disc, cm^{-1}): ν_{asym}(COO) 1581, ν_{sym}-(COO) 1348, $\Delta\nu$ = 233; ν(Sn–C) 586; ν(Sn–O) 498.

2.4.2. Synthesis of 2-hydroxybenzoatotributyltin(IV) (**2**) [8]

Quantities used were 0.28 g (2 mmol) L_A and 0.60 g (1 mmol) Bis(tributyltin)oxide in toluene. Yield: 74%. M.p.: 68.9 °C. Anal. Calc. for $C_{19}H_{32}O_3Sn$ (427.12): C, 53.43; H, 7.5. Found: C, 53.54; H, 7.48%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.9 (t, 9H, H_3C–), 1.2–1.6 (m, 18H, $(H_2C)_3$–Sn); 6.8–7.9 (H_4C_6–); 5.4 (HO-Ph). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ, ^{n}J [^{119}Sn–^{13}C] in Hz): 17.5[344], 27.6[24],

Table 1
Crystallographic data for compounds **4** · 2DMSO and **3**

	4 · 2DMSO	**3**
Empirical formula	$C_{18}H_{30}C_{l4}O_6S_2Sn_2$	$C_{25}H_{20}O_3Sn$
Formula weight	785.72	487.10
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.4556(6)	13.2865(7)
b (Å)	17.7707(12)	12.0286(7)
c (Å)	18.8485(12)	14.5970(9)
α (°)	73.964(5)	90
β (°)	79.412(5)	116.694(4)
γ (°)	78.549(5)	90
Volume (Å^3)	2955.3(3)	2084.2(2)
Z	4	4
Density (Mg/m^3) (calculated)	1.766	1.552
Absorption coefficient (mm^{-1})	2.222	1.249
F(000)	1544	976
Crystal size (mm^3)	0.28 × 0.25 × 0.18	0.23 × 0.11 × 0.10
Theta range	3.52–25.58°	3.50–25.57°
Index ranges	$-11 \leqslant h \leqslant 11$ $-21 \leqslant k \leqslant 21$ $-20 \leqslant l \leqslant 22$	$-16 \leqslant h \leqslant 16$ $-14 \leqslant k \leqslant 14$ $-17 \leqslant l \leqslant 17$
Reflections collected	31 504	26 465
Independent reflections [R_{int}]	11 037 [0.0513]	3893 [0.0941]
Completeness to theta = 25.00°	99.6%	99.7%
Absorption correction	Empirical from equivalents	Empirical from equivalents
Maximum and minimum transmission	0.6905 and 0.5750	0.8853 and 0.7621
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	11 037/0/597	3893/0/267
Goodness-of-fit on F^2	1.017	0.953
Final R indices [$I > 2\sigma$ (I)]	R_1 = 0.0411, wR_2 = 0.1033	R_1 = 0.0326, wR_2 = 0.0625
R indices (all data)	R_1 = 0.0509, wR_2 = 0.1074	R_1 = 0.0517, wR_2 = 0.0663
Largest difference peak and hole (e Å^{-3})	2.667 and −2.596	0.488 and −0.799

26.6[62], 13.5 (C_4H_9–Sn); 115.6, 115.8, 122.3, 131.8, 135.6, 162.4 (C_6H_4OH); 172 (COO).^{119}Sn NMR ($CDCl_3$, δ): 114.7. IR (KBr disc, cm^{-1}): ν_{asym}(COO) 1558, ν_{sym}(COO) 1334, $\Delta\nu$ = 224; ν(Sn–C) 567; ν(Sn–O) 486.

*2.4.3. Synthesis of 2-hydroxybenzoatotriphenyltin(IV) (**3**) [8]*

Quantities used were 0.14 g (1 mmol) L_A and 0.37 g (1 mmol) triphenyltin hydroxide in toluene. Yield: 81%. M.p.: 121.3 °C. Anal. Calc. for $C_{25}H_{20}O_3Sn$ (486.25): C, 61.75; H, 4.14. Found: C, 61.84; H, 4.37%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.9–7.9 (m, 4H, C_6H_4–), 5.4 (s, 1H, HO-Ph), 7.2–7.3 (m, 15H, $(C_6H_5)_3$–Sn). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ, ^nJ [^{119}Sn–^{13}C] in Hz): 115.6, 116.1, 121.5, 131.8, 134.9, 161.7 (C_6H_4OH); 138.0[646], 136.9[48], 130.2, 128.7(C_6H_5–Sn); 172.6 (COO). ^{119}Sn NMR ($CDCl_3$, δ): −108.6. IR (KBr disc, cm^{-1}); ν_{asym}(COO) 1575, ν_{sym}(COO) 1344, $\Delta\nu$ = 231, ν(Sn–C) 551; ν(Sn–O) 445.

*2.4.4. Synthesis of 3,4,5,6-tetrachlorophenyl-1,2-dicarboxylatobis[trimethyltin(IV)] (**4**)*

Quantities used were 0.32 g (1 mmol) L_B and 0.36 g (1 mmol) trimethyltin hydroxide in toluene. Yield: 78%. M.p.: 159 °C. Anal. Calc. for $C_{14}H_{18}$ O_4Cl_4 Sn_2 (510.78): C, 32.92; H, 3.54. Found: C, 32.45; H, 4.01%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 0.56 (s, 18H, H_3C–Sn). ^{13}C NMR (75.45 MHz, DMSO-d_6, δ, ^nJ [^{119}Sn–^{13}C] in Hz): -2.3 (H_3C–Sn); 131.6, 132.7, 139.6(C_6Cl_4); 169.7(COO). ^{119}Sn NMR (DMSO-d_6, δ): −123.8. IR (KBr disc, cm^{-1}): ν_{asym}(COO) 1599, $\nu\nu_{sym}$(COO) 1412, $\delta\nu$ = 187, ν_{asym}(COO) 1538, ν_{sym}(COO) 1318, $\Delta\nu$ = 220; ν(Sn–C) 519, 559; ν(Sn–O) 440; ν(Ar–Cl) 1130.

*2.4.5. Synthesis of 3,4,5,6-Tetrachlorophenyl-1,2-dicarboxylatobis[tributyltin(IV)] (**5**) [10]*

Quantities used were 0.32 g (1 mmol) L_B and 0.60 g (1 mmol) Bis(tributyltin)oxide in toluene. Yield: 80%. M.p.: 82.5 °C. Anal. Calc. for $C_{32}H_{54}O_4Cl_4Sn$ (621.414): C, 61.85; H, 8.75. Found: C, 61.32; H, 8.91%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 0.9 (t, 9H, H_3C–Sn); 1.3–1.7 (m, 18H, $(H_2C)_3$–Sn). ^{13}C NMR (75.45 MHz, DMSO-d_6, δ, ^nJ [^{119}Sn–^{13}C] in Hz):17.3[520], 27.4, 25.7, 13.7 (C_4H_9–Sn); 131.5, 131.8, 139.5 (C_6Cl_4); 171 (COO). ^{119}Sn NMR (DMSO-d_6, δ): −68.4. IR (KBr disc, cm^{-1}); ν_{asym}(COO) 1555, ν_{sym}(COO) 1342, $\Delta\nu$ = 213, ν(Sn–C) 556, ν(Sn–O) 460, ν(Ar–Cl) 1128.

*2.4.6. Synthesis of 3,4,5,6-tetrachlorophenyl-1,2-dicarboxylatobis[triphenyltin(IV)] (**6**)*

Quantities used were 0.32 g (1 mmol) L_B and 0.74 g (2 mmol) triphenyltin hydroxide in toluene. Yield. 80%; M.p.: 131.6 °C. Anal. Calc. for $C_{44}H_{30}O_4SnCl_4$ (883.176): C, 59.83; H, 3.42. Found: C, 59.46; H, 3.59%. ^{1}H NMR (300 MHz, DMSO-d_6, δ); 7.3–7.8 (m, 30H, H_5C_6–Sn). ^{13}C NMR (75.45 MHz, DMSO-d_6, δ, ^nJ [^{119}Sn–^{13}C] in Hz): 131.7, 132.4, 139.8 (C_6Cl_4); 128.7[794], 129.4, 131.8, 137.5 (C_6H_5–Sn); 169.8 (COO). ^{119}Sn NMR (DMSO-d_6, δ): −174. IR (KBr disc, cm^{-1}): ν_{asym}(COO) 1549, $\nu\nu_{sym}$(COO) 1334, $\Delta\nu$ = 215; ν(Sn–C) 536; ν(Sn–O) 484; ν(Ar–Cl) 1131.

3. Results and discussion

Some new organotin(IV) derivatives of substituted phenyl carboxylic acids were prepared by the reaction of the ligands L_A or L_B with the selected triorganotin(IV) hydroxide/oxide in appropriate mole ratio in dry toluene, using the Dean–Stark apparatus (Scheme 1). The compounds **1**–**6** are quite stable in moist-air and are also soluble in common organic solvents.

3.1. Spectroscopic data

The compounds **1**–**6** were characterized by multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR, IR spectroscopy and single crystal X-ray analysis in combination with melting point and elemental analyses. The spectroscopic data have been mentioned in the synthesis Section 2.2. The ^{1}H NMR spectra were recorded for the compounds **1**–**3** in $CDCl_3$ and in DMSO-d_6 for **4**–**6**. The characteristic chemical shifts were identified by their intensity and multiplicity patterns. The total numbers of protons, calculated from the integration curve, are in agreement with the expected molecular composition of the compounds. The proton chemical shifts assignment of the carbon attached to Sn exhibits a singlet at 0.59 ppm for compounds **1** and **4** and at nearly 1.6 ppm as multiplets in case of compounds **2** and **5**. The aromatic protons of the ligand and the phenyltin moieties for **3** and **6** resonate as multiplets in the expected range 6.84–7.93 ppm [28]. The proton chemical shift assignment of the trimethyltin moiety is straight forward from the multiplicity pattern and the ^2J [^{119}Sn–^{1}H] coupling constant values. The C–Sn–C angles, calculated by applying Lockhart's equation [29] Table 3, also support the tetrahedral environment around the Sn atom for **1**. However, coupling constant, ^nJ [^{119}Sn–^{1}H] for *n*-butyl and phenyltin derivatives could not be calculated due to their complex multiplet pattern.

The ^{13}C NMR data explicitly resolved the resonances of all the distinct carbon atoms present in the compounds. The aromatic carbon resonances of the triphenyltin moieties are easily assigned on the basis of both aromatic ^nJ [^{13}C–^{119}Sn] coupling constant(s) and signal intensities. The aromatic carbon resonances were assigned by comparison of experimental chemical shift with those calculated from incremental method [30]. The phenyl groups give signals in the expected ranges as earlier reports manifested [31].

The ^{1}J [^{13}C–^{119}Sn] coupling constant can be used to assess the coordination number of the Sn atom in organotin compounds. The coupling constants were calculated and found to be in the order of 392.8 Hz for trimethyltin **1**, 344 Hz for tributyltin **2** and 646 Hz for triphenyltin **3** compounds which are the characteristic values for tetrahedral compounds as given in Table 3 [32,33]. Another characteristic feature for triphenyltin derivatives is the observance of ^{13}C chemical shift of the *ipso*-carbon at about 138 ppm which is attributed to a four coordinated tin atom [32]. The chemical shifts of the carboxylic carbon in these organotin are observed in range 169–172 ppm in comparison to 181–182 ppm in the ligands, confirming the coordination of the ligand through carboxylic oxygen to the organotin(IV) moiety. The calculated value of the ^{1}J [^{13}C–^{119}Sn] coupling constant for **5** and **6** are 520 and 794 Hz, respectively which described the penta coordinated environment about the Sn atom in these compounds.

The ^{119}Sn NMR data (in $CDCl_3$) for **1**–**3** show a single resonance at 140.6 ppm for trimethyltin compound **1**, 114.7 ppm for tributyltin compound **2** and −108.6 ppm for triphenyltin compound **3**. These values are in conformity to four coordination around the Sn atom as reported earlier [31,32]. However, the δ ^{119}Sn NMR in DMSO-d_6 shows the coordination of the solvent through the oxygen atom to the Sn atom, and the values are −123.8 ppm for trimethyltin derivative, −68.4 ppm for tributyltin and −174 ppm for triphenyltin derivatives which confirms penta coordinated tin geometry for compounds **4**–**6**. This feature has been confirmed by single crystal XRD studies when one of the compounds **4** was crystallized in DMSO.

The characteristic IR bands of the compounds **1**–**6** have been identified by comparing the data with the literature values [27,28]. The vibrational absorptions of interest include: ν(Sn–C), 550–586 cm^{-1}; ν(Sn–O), 440–486 cm^{-1} and $\nu(COO)_{asym}$, 1538–1581 cm^{-1}; $\nu(COO)_{sym}$, 1318–1348 cm^{-1}. The mode of coordination of the carboxylate ligand to tin(IV) has been attributed to the parameter $\delta\nu[\nu_{asym}(COO)–\nu_{sym}(COO)]$. The magnitude of $\delta\nu$ values for these compounds lie in range 213–233 which described the monodentate nature of the carboxylate group in these compounds. The solid state structures for **2** and **4** were further confirmed by X-ray crystallographic studies.

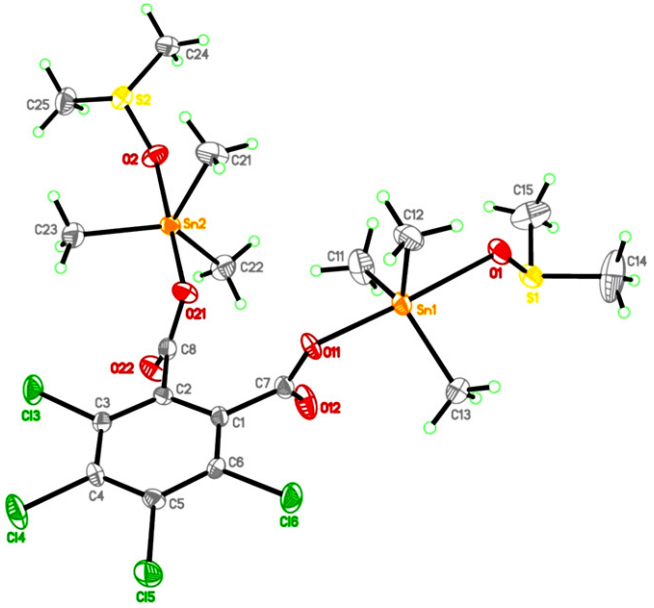

Fig. 1. ORTEP diagram of **4** · 2DMSO. Ellipsoids drawn at 30% probability.

3.2. Crystal structures

3.2.1. Structure of **4** · 2DMSO

Fig. 1 shows an ORTEP representation of the molecular structure for this complex, and the selected bond distances and angles are listed in Table 2. There are two independent molecules in the asymmetric unit, each having a slightly different geometry. For the sake of simplicity and clarity, the geometry of one molecule is discussed here. Each molecule contains two metal centers, each of them surrounded by five atoms in a distorted trigonal bipyramidal environment, where the ligand acts as a bridge between the two metal atoms: as an O-donor ligand with respect to Sn(1) and Sn(2). So that, the coordinating polyhedron around Sn(1) and Sn(2) is formed by 2 oxygen atoms (one from DMSO and the other one from the ligand) located on the apical positions of the bipyramid and the three methyl carbon atoms in the equatorial sites [34]. A considerable distortion arises from the presence of the bridged ligand, as indicated by the O(1)–Sn(1)–O(11) and O(2)–Sn(2)–O(2) angle values [176.58(12)° and 178.22(13)° instead of the ex-

Table 2
Selected geometric parameters (Å, °) for **4** · 2DMSO

Bonds		Angles	
Sn(1)–C(11)	2.123(6)	C(21)–Sn(2)–C(23)	118.5(3)
Sn(1)–C(13)	2.132(6)	C(22)–Sn(2)–O(21)	98.42(18)
Sn(1)–C(12)	2.142(6)	C(21)–Sn(2)–O(21)	89.18(19)
Sn(1)–O(11)	2.182(3)	C(23)–Sn(2)–O(21)	93.08(19)
Sn(1)–O(1)	2.470(3)	C(22)–Sn(2)–O(2)	83.19(18)
Sn(2)–C(22)	2.128(5)	C(21)–Sn(2)–O(2)	89.4(2)
Sn(2)–C(21)	2.134(6)	C(23)–Sn(2)–O(2)	86.69(19)
Sn(2)–C(23)	2.137(5)	O(21)–Sn(2)–O(2)	178.22(13)
Sn(2)–O(21)	2.208(3)	C(7)–O(11)–Sn(1)	115.4(3)
Sn(2)–O(2)	2.381(4)	C(8)–O(21)–Sn(2)	116.3(3)
Sn(1A)–C(11A)	2.125(6)	S(1)–O(1)–Sn(1)	121.92(19)
Sn(1A)–C(13A)	2.137(7)	S(2)–O(2)–Sn(2)	122.0(2)
Sn(1A)–C(12A)	2.141(6)	C(11A)–Sn(1A)–C(13A)	114.4(3)
Sn(1A)–O(71A)	2.215(4)	C(11A)–Sn(1A)–C(12A)	130.0(3)
Sn(1A)–O(1A)	2.451(6)	C(13A)–Sn(1A)–C(12A)	114.5(3)
Sn(2A)–C(22A)	2.117(6)	C(11A)–Sn(1A)–O(71A)	94.2(2)
Sn(2A)–C(21A)	2.127(6)	C(13A)–Sn(1A)–O(71A)	92.1(3)
Sn(2A)–C(23A)	2.133(6)	C(12A)–Sn(1A)–O(71A)	94.0(2)
Sn(2A)–O(81A)	2.193(3)	C(11A)–Sn(1A)–O(1A)	84.0(2)
Sn(2A)–O(2A)	2.404(3)	C(13A)–Sn(1A)–O(1A)	91.2(3)
Angles		C(12A)–Sn(1A)–O(1A)	85.0(3)
C(11)–Sn(1)–C(13)	125.5(3)	O(71A)–Sn(1A)–O(1A)	176.67(16)
C(11)–Sn(1)–C(12)	117.1(3)	C(22A)–Sn(2A)–C(21A)	122.9(3)
C(13)–Sn(1)–C(12)	115.7(2)	C(22A)–Sn(2A)–C(23A)	116.9(3)
C(11)–Sn(1)–O(11)	96.23(19)	C(21A)–Sn(2A)–C(23A)	118.9(3)
C(13)–Sn(1)–O(11)	95.79(18)	C(22A)–Sn(2A)–O(81A)	96.9(2)
C(12)–Sn(1)–O(11)	90.38(17)	C(21A)–Sn(2A)–O(81A)	94.93(19)
C(11)–Sn(1)–O(1)	84.36(19)	C(23A)–Sn(2A)–O(81A)	89.54(18)
C(13)–Sn(1)–O(1)	86.57(18)	C(22A)–Sn(2A)–O(2A)	85.1(2)
C(12)–Sn(1)–O(1)	86.36(17)	C(21A)–Sn(2A)–O(2A)	85.64(19)
O(11)–Sn(1)–O(1)	176.58(12)	C(23A)–Sn(2A)–O(2A)	87.67(18)
C(22)–Sn(2)–C(21)	118.0(3)	O(81A)–Sn(2A)–O(2A)	177.07(13)
C(22)–Sn(2)–C(23)	122.3(2)	S(1A)–O(1A)–Sn(1A)	127.4(3)

Table 3
(C–Sn–C) angles (°) based on NMR parameters of some selected compounds

Number	Compound	^{1}J [^{119}Sn, ^{13}C] (Hz)	^{2}J [^{119}Sn, ^{1}H] (Hz)	θ (°)	
				^{1}J	^{2}J
1	**1**	392.8	59	111	
2	**2**	344	–	112	
3	**3**	646	–	116	
4	**5**	520	–	127	
5	**6**	794	–	125	

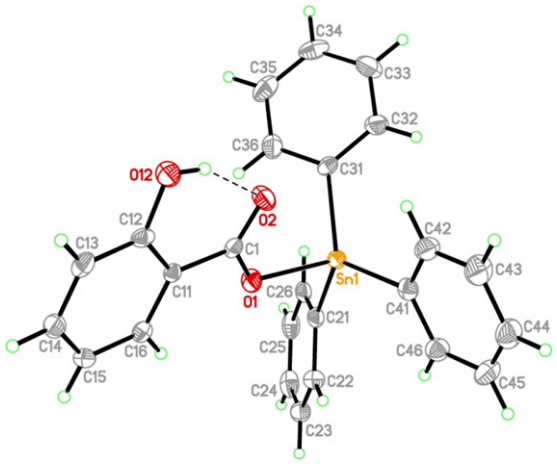

Fig. 2. ORTEP diagram of **3** [35]. Ellipsoids drawn at 30% probability.

pected 180°]. In the same way, bond angles in the equatorial plane take values slightly different from 120° [C–Sn(1)–C; 115.7(2)°, 117.1(3)°, 125.5(3)°, C–Sn(2)–C; 118.0(3)°, 118.5(3)°, 122.3(2)°], whereas the angles between the apical positions and the equatorial plane have the values such as 84.36(19)° or 96.23(19)° for C–Sn(1)–O and 83.19(18)° or 98.42(18)° for C–Sn(2)–O.

*3.2.2. Structure of [($SnPh_3$)($OOCC_6H_4OH$)] (**3**)*

Fig. 2 shows an ORTEP representation of this complex [35], redetermined at low temperature with greater number of reflections collected/used and high degree of completeness of θ, submitted to the Cambridge Structural Database as a Private communication [36]. Some crystallographic data of **3** are presented here solely for comparison purposes. The asymmetric unit contains a single $SnPh_3$ moiety connected to a 2-hydroxybenzoate ligand through Sn(1)–O(1) bond. Sn(1) atom is surrounded by three phenyl C atoms and one ligand O atom resulting a distorted tetrahedron. The sum of the angles subtended at Sn(1) atom by the three phenyl C(C21, C31, C41) and the ligand O(O1) atom is 437.22°, which is close to the ideal value (436.20°) for a regular tetrahedron. The dihedral angle constituted by the salicylate plane [O(1), C(1), C(11), O(2)] with $SnPh_3$ plane[C(21), C(31), C(41), Sn(1)] is 82.5°. The hydroxyl H(12) atom makes an intramolecular H-bond with the carbonyl oxygen O(2). The co-planarity of the O(12), C(12), C(11), C(1), O(2) moiety with phenyl ring [C(11), C(12), C(13), C(14), C(15), C(16)] salicylate group is associated with the intramolecular hydrogen bond [O(12)–H(12)···O(2)], as indicated by the torsional angles O(2)–C(1)–C(11)–C(12), 3.515° and C(1)–C(11)–C(12)–O(12), 6.1(5)°.

4. Biological studies

4.1. Antibacterial activity

The compounds **1**–**6** were tested by agar well diffusion method and the results are presented in Table 4. The activity of these compounds against six different types of bacteria namely *Bacillus subtilis, Escherichia coli, Pseudomonas aeroginosa*, *Staphylococcus auerus, Salmonella typhi* and *Shigella flexneri* were studied using Imipenum as a reference drug. The bactericidal activity of **2** and **3** are fairly good except *E. coli* and *P. aeroginosa* as earlier reports demonstrated [6,7], the same is true for **1**. The antibacterial studies of the compounds show relatively better activity against various bacteria than the free ligands but low activity in comparison to the reference drug.

4.2. Antifungal activity

The agar tube dilution protocol method was employed to test the antifungal activities of the synthesized compounds against six types of fungi, namely *Trichophyton longifusus, Candida albicans, Aspergillus flavus, Candida glabrata, Fusarium solani* and *Mycobacterium canis*. The triorganotin derivatives of L_B **4**–**6** Table 5 demonstrated good antifungal activities against the enlisted fungal species in comparison to the derivatives of L_A **1**–**3**. The fungicidal activities of the compounds **1**–**3** were investigated and found that compound **2** and **3** have comparable activities as reported earlier [6,8]. The antifungal activities of compounds **4**–**6** were assessed and found some encouraging results. The compound **5** have already been studied mostly against marine fouling organisms and has been using in antifouling paints [10]. However present studies described that the chloro-substituted organotins have broad activity spectrum against the enlisted species of fungi. The compound **6** was found to be more active in the series having 80–90% inhibition of *C. albicans, C. glabrata* and *F. solani,* which is comparable to the standard drug. The compounds **2** and **5** show moderate activity against the *M. canis.* A limited structure activity relationship revealed that the nature and position of substituent in the benzene ring is critical for displaying the antifungal activity, as the compounds containing chloro-substituted phenyl ring are found to be more active than the compounds having hydroxyl substituted phenyl ring. The order of activities of the synthesized compounds were

Table 4
Anti-bacterial activity data[a,b] of organotin(IV) derivatives **1**–**6**

Name of bacterium	Zone of inhibition (mm)								Ref. drug[c]
	Ligands		**1**	**2**	**3**	**4**	**5**	**6**	
	L_A	L_B							
Bacillus subtilis	13	11	20	17	19	11	14	10	31
Escherichia coli	–	10	18	13	18	13	15	17	30
Pseudomonas aeroginosa	–	13	20	20	19	17	20	25	46
Staphylococcus auerus	–	12	18	22	27	21	19	29	40
Salmonella typhi	18	15	21	23	21	23	25	24	33
Shigella flexneri	–	13	23	21	22	25	17	21	41

(–) No activity.
[a] In vitro.
[b] Concentration = 2 mg/ml of DMSO, colony forming unit (CFU) ml = 104–106, size of well = 6 mm (diameter).
[c] Standard drug = Imipenum.

Table 5
Anti-fungal activity data[a,b,c] of organotin(IV) derivatives **1**–**6**

Name of fungi	Percent inhibition								Standard drug [*]MIC ($\mu g\ ml^{-1}$)
	Ligands		**1**	**2**	**3**	**4**	**5**	**6**	
	L_A	**L_B**							
Trichophyton longifusus	30	46	40	42	45	62	67	70	70
Candida albicans	40	54	45	44	65	60	67	90	110
Aspergillus flavus	36	48	45	40	42	58	69	72	30
Candida glabrata	35	57	45	49	58	73	78	85	111
Fusarium solani	42	51	41	48	63	71	74	87	74
Mycobacterium canis	42	53	45	55	57	56	54	67	98

[a] In vitro.
[b] Concentration of sample = 100 μg/ml of DMSO.
[c] Standard drug = Miconazole and Amphotericin B (for *A. flavis*), percent inhibition = 100.
[*] MIC, minimum inhibitory concentration.

found to be as follows; triphenyltin derivatives > tributyltin derivatives > trimethyltin derivatives.

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Appendix A. Supplementary material

CCDC 607279 and 681174 contains the supplementary crystallographic data for **3** and **4** · 2DMSO. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.jorganchem.2008.06.027.

References

[1] (a) L. Pellerito, L. Nagy, Coord. Chem. Rev. 224 (2002) 111;
(b) A. Meriem, R. Willem, M. Biesemans, B. Mahieu, D. devos, P. Lelieveld, M. Gielen, Appl. Organomet. Chem. 5 (1991) 195.
[2] A. Bianco, N. Ucella, Food Res. Int. 33 (2000) 475.
[3] K. Yoon, C. Jeong-Yong, K. Ju-Hee, Curr. Microbiol. 48 (2004) 312.
[4] R. Cini, R. Comments, Inorg. Chem. 22 (2000) 151. and references therein;
(a) C. Rice-Evan, N. Miller, G. Paganga, Free Radic. Biol. Med. 20 (1996) 933;
(b) K.V. Marileno, Breast Cancer Res. 6 (2004) R63.
[5] K. Herrmann, Crit. Rev. Food Sci. Nutr. 28 (1989) 315.
[6] A.J. Nok, M.N. Shuaibu, J.J. Bonire, A. Daho, Z. Wushishi, S. Ado, J. Enzyme Inhibit. 15 (2000) 411.
[7] A.J. Nok, H.I. Nock, J.J. Bonire, Appl. Organomet. Chem. 17 (2003) 17.
[8] T.N. Srivastava, B. Srivastava, M.C. Bhatia, Acta Ciencia Indica 3 (1977) 306.
[9] A.J. Crowe, R. Hill, P.J. Smith, T.R.G. Cox, Wood Preserv. 1 (1996) 156.
[10] (a) A. Fargasova, J. Kizlink, Ecotoxicol. Environ. Safe. 34 (1996) 156;
(b) A. Fargasova, Ecotoxicol. Environ. Safe. 41 (1998) 222.
[11] M.N. Clifford, J. Sci. Food Agric. 80 (2000) 1033.
[12] C. Cox, J. Pest. Reforms 17 (1997) 4.
[13] D.P. Bruynzeel, W.G. Van Ketal, Contact Dermat. 14 (1986) 67.
[14] R.B. Johnson, Florida Entomol. 49 (1966) 195.
[15] H. Penagos, Contact Dermat. 35 (1986) 214.
[16] (a) M.A. Saeed, D.C. Craig, A. Badshah, S. Ali, M.K. Rauf, Acta Crystallogr. E61 (2005) m2595;
(b) M. Parvez, S. Anwar, A. Badshah, B. Ahmad, A. Majeed, M. Ashfaq, Acta Crystallogr. C56 (2000) 159.
[17] Imtiaz-ud-Din, M. Mazhar, K.C. Molloy, K.M. Khan, J. Organomet. Chem. 691 (2006) 1643.
[18] G. Sabitha, R. Srividya, J.S. Yadav, Tetrahedron 55 (1999) 4015.
[19] D.D. Parrin, W.L.F. Armarega, Purification of Laboratory Chemicals, third ed., Butterworth Heinemann, Oxford, 1997.
[20] Stoe & Cie. X-AREA. Stoe & Cie, Darmstadt, Germany, 2001.
[21] A. L Spek, J. Appl. Crystallogr. 36 (2003) 7.
[22] G.M. Sheldrick, SHELXS-97 and SHELXL-97. University of Göttingen, Germany, 1997.
[23] G.M. Sheldrick, SHELXTL-Plus. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1991.
[24] J.D. Paxton, Meth. Plant Biochem. 6 (1991) 33.
[25] Atta-ur-Rehman, M.I. Choudhary, W.J. Thomson, Bioassay Techniques for Drug Development, Harward Academic Publishers, Amsterdam, 2001.
[26] P.J. Smith, R.O. Day, V. Chandrasekhar, J.M. Holmes, R.R. Holmes, Inorg. Chem. 25 (1986) 2495.
[27] Imtiaz-ud-Din, M. Mazhar, K.C. Molloy, Main Group Met. Chem. 29 (2006) 11.
[28] Imtiaz-ud-Din, M. Mazhar, S. Ali, K.M. Khan, Nat. Prod. Res. 21 (2007) 749.
[29] T.P. Lockhart, W.F. Manders, E.M. Holt, J. Am. Chem. Soc. 108 (1986) 6611.
[30] H.O. Kolinowski, S. Berger, S. Brown, ^{13}C NMR Spektroscopie, Thieme-Verlag, Stuttgart, Germany, 1984.
[31] M. Gielen, A. El-Khloufi, M. Biesemans, F. Kayser, R. Willem, Appl. Organomet. Chem. 7 (1993) 20.
[32] R. Willem, A. Bouhdid, M. Biesemans, J.C. Martins, D. Vos, E.R.T. Tiekink, M. Gielen, J. Organomet. Chem. 514 (1996) 203.
[33] J. Holecek, M. Nadvornik, K. Handlir, J. Organomet. Chem. 241 (1983) 177.
[34] P. Alvarez-Boo, J.S. Casas, M.D. Couce, R. Farto, V.F. Moreira, E. Freijanes, J. Sordo, E. Vazquiel-Lopez, J. Organomet. Chem. 691 (2006) 45.
[35] J.F. Vollano, R.O. Day, D.N. Rau, V. Chandrasekhar, R.R. Holmes, Inorg. Chem. 25 (1986) 2495.
[36] M.K. Rauf, A. Badshah, M. Bolte, M.A. Saeed, Imtiaz-ud-Din, B. Mirza, Private Communication to the Cambridge Structural Database, Deposition Number CCDC 607279, 2008.