Turk J Chem
34 (2010) , 109 – 118.

doi:10.3906/kim-0805-39

Some bioactive organotin(IV) derivatives with 3,4-dichlorophenylacetic acid: synthesis, spectroscopic properties, and X-ray structure of $[Sn_4(C_4H_9)_8(OOCCH_2C_6H_3Cl_2)_4O_2]$

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Received 22.05.2008

Some bioactive organotin(IV) derivatives of 3,4-dichlorophenylacetic acid (HL) were synthesized by reacting the ligand acid with various di- or tri-organotin compounds (in suitable mole ratios) in the presence of triethylamine. The structural investigation was carried out via multinuclear (^{1}H, ^{13}C, and ^{119}Sn) NMR, IR spectroscopy, and X-ray crystallography. The crystal structure of **4** comprises a central Sn_2O_2 core with O atoms bonded to 2 dibutylbis(3,4-dichlorophenylacetato)tin(IV) units. All the Sn atoms of **4** are essentially 5-coordinated in distorted trigonal-bipyramidal geometry. Some of the compounds exhibited significant antibacterial and antifungal activity.

Key Words: Organotin(IV), spectroscopy, distannoxane, X-ray structure, antibacterial, antifungal.

Introduction

Organotin compounds are a group of organometallics that have been intensely studied for many years due to their widespread industrial and biological applications.[1,2] Organotin carboxylates exhibit considerable structural diversity, such as monomers, dimers, tetramers, and polymers.[3] Organotin(IV) compounds are eco-toxicants

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whose action depends on their structure.[4] Various studies[5] have shown that a judicious choice of ligand, coordinated to the organotin(IV) fragment, can modulate the activity of these complexes. Commonly used fungicides are mostly chloro-derivatives, such as chlorthalonil, which is sold under the trade name Daconil, and are typically used on peanuts, potatoes, roses, and turf.[6] To further explore the structural possibilities and the effect of ligands on the biological activity of organotin compounds, a series of organotin derivatives of 3,4-dichlorophenylacetic acid were synthesized (Scheme 1).

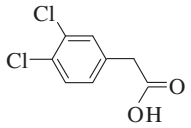

Figure 1. Structure of 3,4-dichlorophenylacetic acid (HL).

$$R_nSnCl_{4-n} + Cl_2C_6H_3CH_2COOH \xrightarrow[\text{toluene/reflux}]{Et_3N} R_nSn[O_2CCH_2C_6H_3Cl_2]_{4-n} + Et_3NHCl$$
(HL) (**1-3,5**)

where n = 2, R = CH_3 (**2**),
n = 3, R = CH_3 (**1**), *n*- C_4H_9 (**3**), C_6H_5 (**5**)

$$4(n\text{-}C_4H_9)_2SnO + 4Cl_2C_6H_3CH_2COOH \xrightarrow[\text{reflux}]{\text{toluene}} [(C_4H_9)_2Sn(O_2CCH_2C_6H_3Cl_2)_2O]_2 + H_2O$$
(HL) (**4**)

Scheme 1. Chemical reaction and equation.

The dimeric distannoxane (**4**) was synthesized by the condensation reaction of the ligand (HL) with dibutyltin(IV) oxide in equimolar ratio, based on their reported catalytic activity in many reactions.[7]

Experimental

Materials and instrumentation

Diorganotin and triorganotin halides were purchased from Aldrich (Germany), while 3,4-dichlorophenylacetic acid (Figure 1) was procured from the People's Republic of China and used as received. All chemical reactions were carried out in common organic solvents, which were dried before use in accordance with standard methods.[8]

Elemental analyses were carried out in-house using a Leco CHNS-932 analyzer (USA). Melting points were determined with a Gallenkamp (UK) apparatus and are uncorrected. Infrared spectra were recorded on a Bio-Rad Excalibur FT-IR Model FTS 3000 MX as KBr discs. ^{1}H- and ^{13}C-NMR spectra in solution ($CDCl_3$) 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.

X-ray crystallography

A methodology from the literature[9] was followed to obtain a crystal suitable for X-ray analysis. Crystallographic and experimental details are given in Table 1. For compound **4** the data set was collected at 294 K on a Nonnius

CAD-4 diffractometer using M_oK_α radiation; LP and absorption corrections (semi-empirical from equivalents) were applied. Refinement of F^2 was accomplished by full-matrix-least squares (RAELS), using anisotropic thermal parameters for non-H atoms. H atoms were included in positions calculated for each cycle, and were assigned thermal parameters equal to their bonded atoms. A number of n-butyl C atoms, particularly terminal ones, were difficult to locate and refine, and were clearly affected by high thermal motion and disorder. Each of these was defined as being disordered over sites of equal occupancy using isotropic thermal parameters where appropriate. The distannoxane structure of **4** is given in Figures 2 and 3, and selected geometric data are presented in Table 2. Software used included SIR 92,[10] RAELS 96,[11] ORTEP-3, and POV-3.6[12]

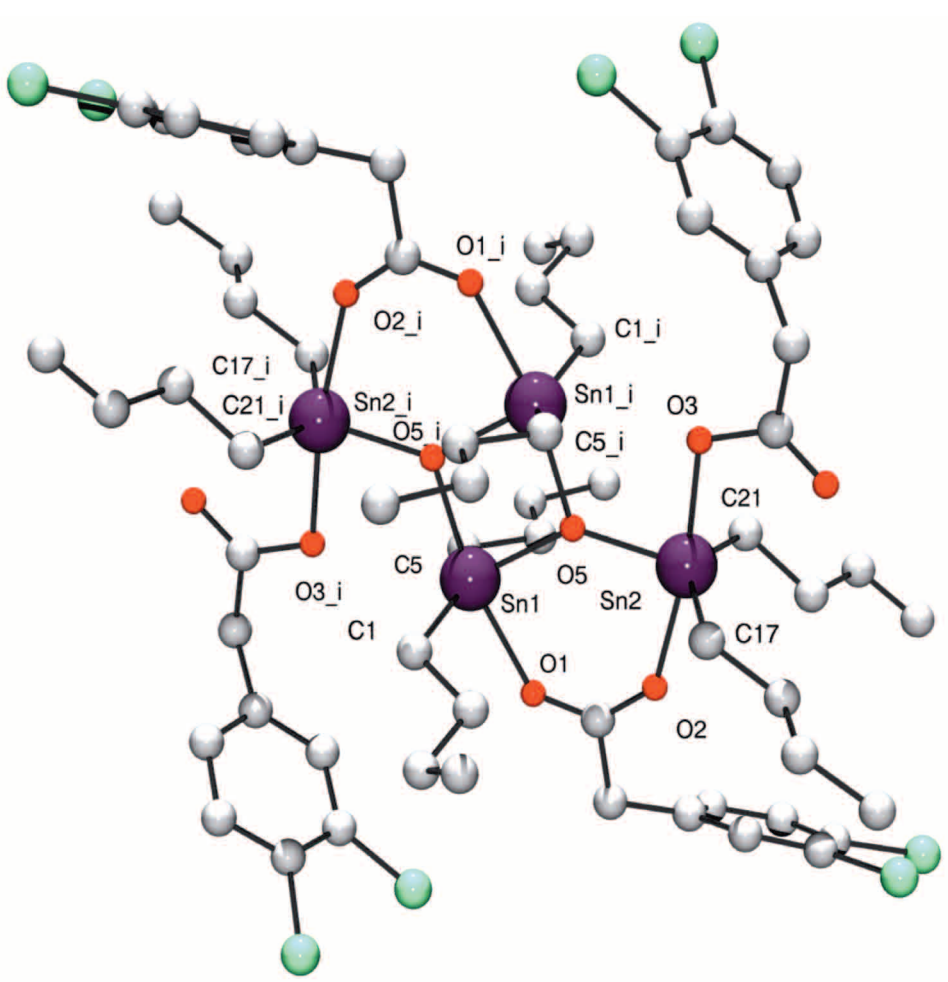

Figure 2. The ORTEP(Pluto)-POV molecular structure of **4** drawn at the 30% probability level. H atoms have been omitted. For clarity, only one component of the disordered n-butyl groups is shown.

Biological studies

Compounds **1-5** were bio-assayed to determine their possible antibacterial and antifungal activity via agar well diffusion and agar tube dilution methods, respectively.[13–14] The antibacterial activity of these compounds

against 4 different types of bacteria, namely *Escherichia coli, Bacillus subtilis*, *Staphylococcus auerus*, and *Micrococcus luteus*, were evaluated using roxithromycin as a reference drug. Compounds **1-5** were also screened for their antifungal activity against 3 types of fungi, *Aspergillus niger, Aspergillus flavus*, and *Mucor* spp.

Table 1. Crystallographic data for **4**.

Empirical formula	$C_{64}H_{92}Cl_8O_{10}Sn_4$
Formula weight	1779.8
Crystal system	Monoclinic
Space group	C2/c
a(Å)	16.753(5)
b(Å)	19.625(3)
c(Å)	24.902(6)
$\beta(^o)$	104.25(1)
V(Å^3)	7932(2)
Z (Calculated density) (mg m^{-3})	4, 1.49
$\mu(M_o \quad - K_\alpha)$, mm^{-1}	1.571
$\theta_{max}(^\circ)$	25
Reflections collected	7159
Independent reflections	6982 [R_{int} = 0.055]
Reflections observed ($> 2\delta$)	3559
Goodness-of-fit on F^2	1.55
Final R_1, wR_2 indices [$I > 2\delta(I)$]	0.066, 0.086
$\Delta\delta_{max}$(eÅ^{-3})	1.33
$\Delta\delta_{min}$(eÅ^{-3})	-2.27

Synthesis

General procedure for the synthesis and characterization of organotin(IV) complexes (1-5)

3,4-Dichlorophenylacetic acid (HL) was suspended in dry toluene and treated with triethylamine in a 1:1 molar ratio at refluxing temperature for 3-4 h. To a stirred solution of triethylamine and ligand acid (HL), diorganotin(IV) dichloride or triorganotin(IV) chloride was added in appropriate mole ratios and then the reaction mixture was refluxed for 6-8 h to yield the product. The precipitate of Et_3NHCl was filtered off. The filtrate was evaporated on a rotary evaporator and the solid mass was recrystallized in a chloroform/*n*-hexane (3:1) mixture.

3,4-Dichlorophenylacetatotrimethyltin(IV) (1)

Quantities used were 1.0 g (4.4 mmol) of (HL) and 0.90 g (4.4 mmol) of trimethyltin(IV) chloride in toluene. Yield = 86%; mp = 117-118 °C. Anal. Calc. for $C_{11}H_{14}Cl_2O_2Sn$ (MW = 367.84): C, 35.92; H, 3.84. Found: C, 35.48; H, 3.17%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ^2J [^{119}Sn-^{1}H] in Hz); 0.36 (s, 9H, H_3C-Sn [58]), 3.37

(s, 2H, H_2C-Ar), 6.92-7.18 (m, 3H, $H_3C_6Cl_2$). ^{13}C-NMR (75.45 MHz, $CDCl_3$, δ, ^nJ [^{119}Sn-^{13}C] in Hz); -4.8 [394] (H_3C-Sn), 135.7, 130.8, 132.2, 131.3, 130.3, 128.8 (C_6H_3 Cl_2), 40.9 (H_2C-Ar), 175.8 (COO). ^{119}Sn-NMR ($CDCl_3$, δ); 130. IR (KBr disc, cm^{-1}); ν_{asym}(COO) 1560, ν_{sym}(COO) 1386, $\Delta\nu$ = 174, ν(Sn–C) 586, ν(Sn–O) 498, ν(Ar–Cl) 1128.

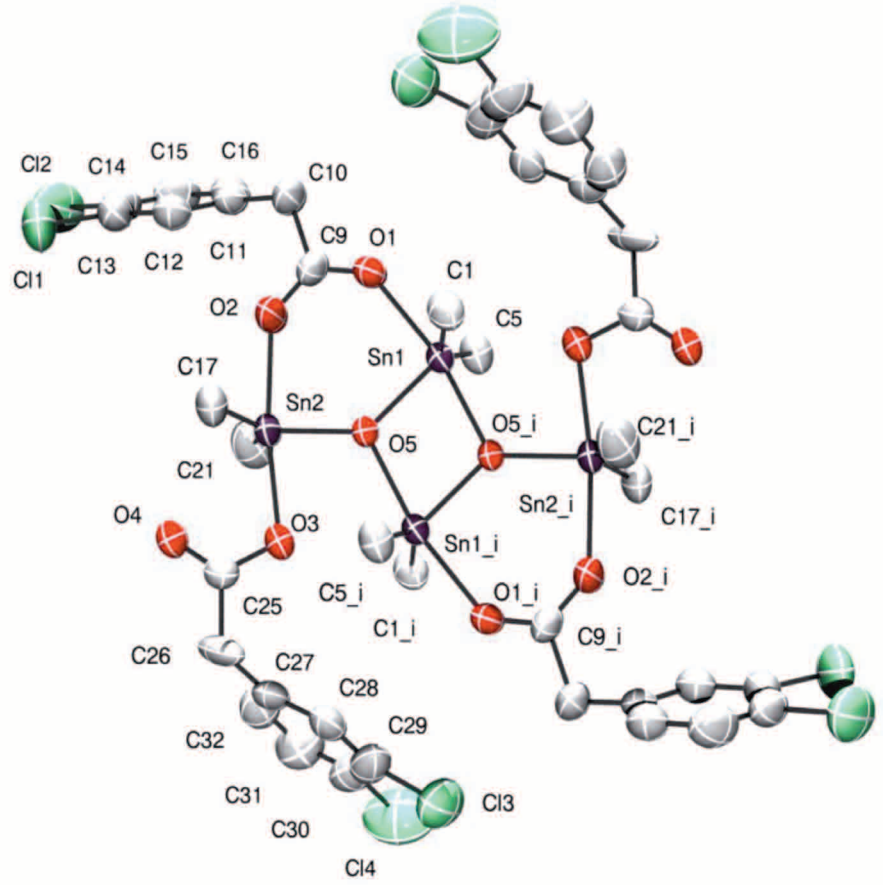

Figure 3. The ORTEP-POV molecular structure of **4** drawn at the 30% probability level. For clarity, only the connecting C atoms of the n-butyl groups are shown.

Bis(3,4-dichlorophenylacetato)dimethyltin(IV)(**2**)

Quantities used were 1.0 g (4.40 mmol) of (HL) and 0.483 g (2.20 mmol) of dimethyltin(IV) chloride in toluene. Yield = 74%; mp = 118-120 °C. Anal. Calc. for $C_{18}H_{16}O_4Cl_4Sn$ (MW = 556.84): C, 38.83; H, 2.90. Found: C, 38.17; H, 2.82%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ^2J [^{119}Sn-^{1}H] in Hz); 1.01 (s, 6H, H_3C-Sn [76]), 3.66 (s, 4H, H_2C-Ar), 7.15-7.42 (m, 6H, $C_6H_3Cl_2$). ^{13}C-NMR (75.45 MHz, $CDCl_3$, δ ^nJ [^{119}Sn-^{13}C] in Hz); -4.7 [651] (H_3C-Sn), 134.1, 131.3, 132.6, 131.4, 130.5, 128.7 ($C_6H_3Cl_2$), 40.9 (H_2C-Ar), 178.4 (COO). ^{119}Sn-NMR ($CDCl_3$, δ); -140. IR (KBr disc, cm^{-1}); ν_{asym}(COO) 1558, ν_{sym}(COO) 1354, $\Delta\nu$ = 204, ν(Sn–C) 567, ν(Sn–O) 486, ν(Ar–Cl) 1127.

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

Sn(1)–O(1)	2.257 (9)	Sn(2)–O(2)	2.235 (11)
Sn(1)–O(5)	2.054 (6)	Sn(2)–O(3)	2.167 (8)
Sn(1)–O(5)	2.165 (6)	Sn(2)–O(5)	2.012 (5)
Sn(1)–C(1)	2.112 (13)	Sn(2)–C(17)	2.181 (14)
Sn(1)–C(5)	2.089 (11)	Sn(2)–C(21)	2.139 (15)
O(1)–Sn(1)–C(1)	89.3 (5)	O(2)–Sn(2)–O(3)	171.6 (3)
O(1)–Sn(1)–C(5)	86.1 (5)	O(2)–Sn(2)–C(17)	85.9 (6)
O(1)–Sn(1)–O(5)	92.0 (3)	O(2)–Sn(2)–C(21)	88.8 (6)
O(1)–Sn(1)–C^{i}(5)	168.3 (3)	O(2)–Sn(2)–O(5)	90.9 (3)
C(1)–Sn(1)–C(5)	143.8 (5)	O(3)–Sn(2)–C(17)	96.2 (5)
C(1)–Sn(1)–O(5)	107.8 (4)	O(3)–Sn(2)–C(21)	94.7 (5)
C(1)–Sn(1)–O^{i}(5)	95.3 (4)	O(3)–Sn(2)–O(5)	80.8 (3)
C(5)–Sn(1)–O(5)	108.3 (4)	C(17)–Sn(2)–C(21)	139.9 (5)
C(5)–Sn(1)–O^{i}(5)	96.3 (4)	C(17)–Sn(2)–O(5)	108.8 (4)
O(5)–Sn(1)–O^{i}(5)	76.4 (2)	C(21)–Sn(2)–O(5)	110.9 (4)

$^{(i)}x,y,z$

***3,4-Dichlorophenylacetatotributyltin(IV)* (3)**

Quantities used were 1.0 g (4.4 mmol) of (HL) and 1.20 g (4.4 mmol) of tributyltin chloride in toluene. Yield = 81%; mp = 49-51 °C. Anal. Calc. for $C_{20}H_{32}O_2Cl_2Sn$ (MW = 494.08): C, 48.62; H, 6.53. Found: C, 48.71; H, 6.58%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ^{n}J [^{1}H-^{1}H] in Hz); 0.91 (t, 9H, H_3C-Sn [7]), 1.29-1.57 (m, 18H, $(H_2C)_3$-Sn), 3.58 (s, 2H, H_2C-Ar), 7.14-7.41 (m, 3H, $C_6H_3Cl_2$). ^{13}C-NMR (75.45 MHz, $CDCl_3$, δ, ^{n}J [^{119}Sn-^{13}C] in Hz); 27.4[350], 136.1, 132.2, 130.6, 131.3, 130.2, 128.8 ($C_6H_3Cl_2$), 41.3 (H_2C-Ar), 178.7 (COO). ^{119}Sn-NMR ($CDCl_3$, δ); 116. IR (KBr disc, cm^{-1}); ν_{asym}(COO) 1575, ν_{sym}(COO) 1382, $\Delta\nu$ = 193, ν(Sn–C) 551, ν(Sn–O) 445, ν(Ar–Cl) 1128.

***Tetrabutylbis(3,4-dichlorophenylacetato)distannoxane dimer* (4)**

Quantities used were 2.0 g (4.4 mmol) of (HL) and 1.34 g (4.4 mmol) of dibutyltin(IV)oxide in toluene. Yield = 76%; mp = 57-58 °C. Anal. Calc. for $C_{64}H_{92}O_{10}Cl_8Sn_4$ (MW = 1779.87): C, 43.19; H, 5.21. Found: C, 43.21; H, 5.20%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ^{n}J [^{1}H-^{1}H] in Hz); 0.86-99 (t, 6H, [7.1]), 1.31-1.85 (m, 12H, $(CH_2)_3$-Sn), 3.58 (s, 2H, CH_2COOH), 7.14-7.48 (m, 3H, $Cl_2C_6H_3$). ^{13}C-NMR (75.45 MHz, $CDCl_3$, δ, ^{n}J [^{119}Sn-^{13}C] in Hz); 27.2 [696], 25.6 [586.0], 27.4 [36.5], 26.6 [31.2], 26.5 [100], 26.3 [67.0], 13.5, 13.6 (6.7) (Sn-CH_2-CH_2-CH_2-CH_3), 128.8, 130.2, 130.6, 131.3, 132.2, 136.1 ($C_6H_3Cl_2$), 41.8 (CH_2-Ar), 176.8 (COO). ^{119}Sn-NMR ($CDCl_3$, δ); -206, -213. IR (KBr disc, cm^{-1}); ν_{asym}(COO) 1599, ν_{sym}(COO) 1412, $\Delta\nu$ = 187, ν_{asym}(COO) 1724, ν_{sym}(COO) 1420, $\Delta\nu$ = 254, ν(Sn–C) 519, 559, ν(Sn–O) 440, ν(Ar–Cl) 1130.

***3,4-Dichlorophenylacetatotriphenyltin(IV)*(5)**

Quantities used were 1.0 g (4.40 mmol) of (HL) and 1.69 g (4.40 mmol) of triphenyltin(IV) chloride in toluene. Yield = 80%; mp = 130 °C. Anal. Calc. for $C_{26}H_{20}O_2Cl_2Sn$ (MW = 554.05): C, 56.36; H, 3.64. Found: C, 56.58; H, 3.67%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ; 7.04-7.10 (m, 15H, C_6H_5Sn), 3.30 (s, 2H, H_2C-Ar), 7.28-7.61 (m, 6H, $Cl_2C_6H_3$). ^{13}C-NMR (75.45 MHz, $CDCl_3$, δ, ^nJ [^{119}Sn-^{13}C] in Hz); 135.7, 132.5, 134.7, 133.5 [648.8] (C_6H_5Sn), 128.7, 142.9, 135.6, 127.8, 136.06, 132.1 ($C_6H_3Cl_2$), 41.8 (H_2C-Ar), 177.5 (COO). ^{119}Sn-NMR ($CDCl_3$, δ); -112. IR (KBr disc, cm^{-1}); ν_{asym}(COO) 1555, ν_{sym}(COO) 1382, $\Delta\nu$ = 173, ν(Sn–C) 556, ν(Sn–O) 460, ν(Ar–Cl) 1128.

Results and discussion

Compounds **1-5** were synthesized by reacting the acid (HL) and the di- or tri-organotin(IV) chlorides in toluene in the presence of triethylamine. The colorless compounds thus obtained were quite stable in moist air. They were characterized by multinuclear (^{1}H, ^{13}C, and ^{119}Sn) NMR, IR spectroscopy, and single crystal X-ray crystallography, in combination with melting point and elemental analyses.

Spectroscopic data

Spectroscopic data were mentioned in the synthesis section. The ^{1}H-NMR spectra were recorded for the free ligand and the synthesized compounds in non-coordinating solvent ($CDCl_3$), and the characteristic chemical shifts were identified by their intensity and multiplicity patterns. The total number of protons, calculated from the integration curve, is in agreement with the expected molecular composition of the compounds. The methylene protons of the acetate moiety appeared at about 3.60 ppm, whereas aromatic protons of the ligand and the phenyltin moieties resonate as multiplets in the range of 7.04-7.61 ppm.[15] The proton chemical shift assignment of the triorganotin moiety is straightforward from the multiplicity pattern and the ^2J [^{119}Sn-^{1}H] coupling constants that conform to the tetrahedral environment around the Sn atom. The dimethyltin derivative coupling constant, ^2J[^{119}Sn-^{1}H], was calculated to be about 76.5 Hz;[16] however, the coupling constant, ^nJ [^{119}Sn-^{1}H], for *n*-butyl and phenyltin derivatives could not be calculated due to the complexity of the multiplet pattern.

^{13}C-NMR data (in $CDCl_3$) 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 the aromatic ^nJ[^{13}C-^{119}Sn] coupling constant and signal intensities. It has already been reported that the ^1J[^{13}C-^{119}Sn] coupling constant can be used to assess the coordination number of the tin atom in organotin compounds.[17,18] The coupling constants were determined to be in the order of 392.8 Hz for trimethyltin, 344 Hz for tributyltin, and 646 Hz for triphenyltin compounds, which are the characteristic values for tetrahedral compounds; that is, the solid state polymeric structure of each of these compounds breaks down into its monomeric 4-coordinated tetrahedral structure in solution. Another characteristic feature of the triphenyltin derivatives is the observance of a ^{13}C chemical shift of the *ipso*-carbon at about 138 ppm, which is attributed to a tetrahedral tin atom.[17] The coupling constant values for diorganotin compounds described a distorted octahedral environment around the Sn atom.[19] The chemical shift of the carboxylic carbon in these organotins

is observed in the range of 175-177 ppm, in comparison to 180.7 ppm in the ligand, describing coordination of the ligand through carboxylic oxygen to the organotin(IV) moiety.

^{119}Sn-NMR data (in $CDCl_3$) show a single resonance at 130 ppm for the trimethyltin compound (**1**), 116 ppm for the tributyltin compound (**3**), and -112 ppm for the triphenyltin compound (**5**). These values are in conformity to 4 coordination around the Sn atom, as reported earlier.[17,19] Diorganotin(IV) compounds also exhibit a single tin chemical shift around -140 ppm for **2**, which is the characteristic value for a skew trapezoidal bipyramidal geometry around the Sn atom.

^{1}H- and ^{13}C-NMR spectral data for compound **4** exhibited 2 sets of signals due to 2 different environments around the alkyl groups attached to the endo- and exocyclic Sn atoms. Compound **4** also shows two ^{119}Sn NMR signals at -206 and -213 ppm due to the 2 non-equivalent tin sites in the molecule.[19]

The characteristic IR bands of compounds **1-5** were identified by comparing our data with previously reported values.[15,16] The vibrational absorption of interest includes ν(Sn–C), 550-586 cm^{-1}; ν(Sn–O), 440-486 cm^{-1}; $\nu(\mathrm{COO})_{asym}$, 1549-1599 cm^{-1}; and $\nu(\mathrm{COO})_{sym}$, 1372-1394 cm^{-1}. The mode of coordination of the carboxylate ligand to tin(IV) was attributed to the parameter, $\Delta\nu[\nu_{asym}(\mathrm{COO}) - \nu_{sym}(\mathrm{COO})]$. The magnitude of $\Delta\nu$ values for **1**, **3**, and **5** lie in the range of 173-193, which describes the monodentate nature of the carboxylate group in these compounds, whereas for compound **2** the value 204 is indicative of the bidentate nature of the carboxylate group in solid state. Data for distannoxane **4** explicitly show 2 tin atoms with different modes of coordination. The presence of an absorption band around 450 cm^{-1} clearly demonstrates the existence of a Sn–O–C unit in these compounds.

X-ray diffraction analysis

The crystal structure of **1** has previously been reported[21] and describes the polymeric chains involving both O atoms of the carboxylate group in the solid state. The X-ray structure of **4** is delineated in Figures 2 and 3, and selected bond lengths and bond angles are given in Table 2. The structure is composed of a centrosymmetric dimer of an oxoditin(IV) complex comprising 2 dibutylbis[3,4-dichlorophenylacetato]tin(IV) units with monodentate and bridging bidentate carboxylate ligands. The central Sn_2O_2 core is fused with 2 six-membered rings Sn(1)/O(1)/C(9)/O(2)/Sn(2)/O(5) incorporating O and C atoms of the ligand that show different modes of coordination with Sn. The endocyclic Sn atoms of the Sn_2O_2 core are 5-coordinated in a C_2SnO_3 distorted trigonal-bipyramidal environment in which Sn is coordinated to 2 α-C atoms of the n-butyl groups at axial positions, and 2 bridging O-atoms and 1 O-atom of the ligand form the basal plane. The endocyclic Sn–O distances in the Sn_2O_2 core are 2.165(6) and 2.054(6) Å, and in exocyclic 6-membered rings Sn(1)/O(1)/C(9)/O(2)/Sn(2)/O(5) they are 2.235(11) and 2.257(9) Å, which is in accordance with the reported structures.[22,23] Thus, both the Sn atoms assume distorted trigonal-bipyramidal geometry with Sn-C distances lying in the range of 2.089(11)-2.181(14) Å, while Sn-O distances are in the range of 2.054(6)-2.257(9) Å.

Biological studies

Antibacterial activity

Compounds **1-5** were tested against 4 bacterial strains using the agar well diffusion method and the results are presented in Table 3. Compound **4** exhibited highly significant activity against all the tested bacteria, while

compounds **3** and **5** exhibited good activity against both *Escherichia coli* and *Micrococcus luteus*; however, compound **2** exhibited good activity only against *Micrococcus luteus*. These results indicate that compound **4** could be a potent antibacterial agent.

Table 3. Antibacterial activity data[a,b] for compounds **1-5**.

Name of Bacteria	Zone of Inhibition (mm)						
	Ligand (HL)	**1**	**2**	**3**	**4**	**5**	Standard Drug*
Escherichia coli	8	10	10	14	26	18	28
Bacillus subtilis	13	13	13	16	22	14	38
Staphylococcus aureus	10	12	11	10	24	12	38
Micrococcus luteus	12	12	18	16	26	16	28

*Standard drug = roxithromycin

[a](In vitro) concentration = 100 μ g mL^{-1}.

[b]Size of well = 4 mm (diameter).

Antifungal activity

The agar tube dilution method was employed to test the antifungal activity of the synthesized compounds (Table 4). The overall results show that these compounds exhibited moderate activity. Compound **3** was active against *Aspergillus niger* and compounds **2** and **4** were active against *Aspergillus flavus*; however, these compounds were the least active against the *Mucar* spp.

Table 4. Antifungal activity data[a,b,c] for compounds **1-5**.

Name of fungus	Percentage Inhibition					
	Ligand (HL)	**1**	**2**	**3**	**4**	**5**
Aspergillus niger	12	14	9	49	26	17
Aspergillus flavus	15	19	45	18	45	34
Mucor spp.	2	0	26	6	2	28

*Standard drug = miconazole (100% inhibition).

[a]Incubation period = 5-7 days.

[b]Incubation temperature = 25 °C.

[c]Concentration = 100 μ g mL^{-1} of medium.

Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper were deposited at the Cambridge Crystallographic Data Centre, as supplementary publication no. CCDC-610168 for **4**. Copies of the available materials can be obtained, free of charge, upon application to the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)-1223-336033, or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment

M. Khawar Rauf is grateful to the HEC, Pakistan, for financial support of a PhD program (scholarship No. ILC-0363104).

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