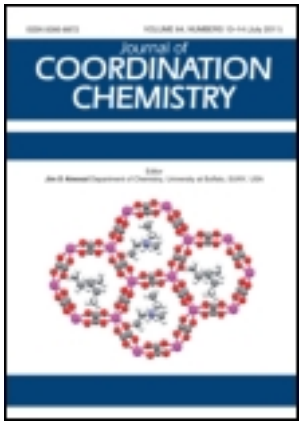


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Syntheses, structural characteristics, and antimicrobial activities of new organotin(IV) 3-(4-bromophenyl)-2-ethylacrylates

Niaz Muhammad [a b], Zia-Ur-Rehman [a], Shaukat Shujah [a], Afzal Shah [a], Saqib Ali [a], Auke Meetsma [c] & Zahid Hussain [d]

[a] Department of Chemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan

[b] Department of Chemistry, Abdul Wali Khan University, Mardan, Pakistan

[c] Crystal Structure Center, Chemical Physics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, NL-9747 AG GRONINGEN, The Netherlands

[d] Institute of Industrial Biotechnology, G.C. University, Lahore, Pakistan

Accepted author version posted online: 03 Aug 2012.Published online: 17 Sep 2012.

To cite this article: Niaz Muhammad, Zia-Ur-Rehman, Shaukat Shujah, Afzal Shah, Saqib Ali, Auke Meetsma & Zahid Hussain (2012) Syntheses, structural characteristics, and antimicrobial activities of new organotin(IV) 3-(4-bromophenyl)-2-ethylacrylates, Journal of Coordination Chemistry, 65:21, 3766-3775, DOI: 10.1080/00958972.2012.718076

To link to this article: http://dx.doi.org/10.1080/00958972.2012.718076

Journal of Coordination Chemistry
Vol. 65, No. 21, 10 November 2012, 3766–3775

Syntheses, structural characteristics, and antimicrobial activities of new organotin(IV) 3-(4-bromophenyl)-2-ethylacrylates

NIAZ MUHAMMAD†‡, ZIA-UR-REHMAN†, SHAUKAT SHUJAH†, AFZAL SHAH†, SAQIB ALI*†, AUKE MEETSMA§ and ZAHID HUSSAIN¶

†Department of Chemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan
‡Department of Chemistry, Abdul Wali Khan University, Mardan, Pakistan
§Crystal Structure Center, Chemical Physics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, NL-9747 AG GRONINGEN, The Netherlands
¶Institute of Industrial Biotechnology, G.C. University, Lahore, Pakistan

(*Received 17 May 2012; in final form 17 July 2012*)

New organotin(IV) carboxylates, [*n*-Bu_2SnL_2] (**1**), [Et_2SnL_2] (**2**), [Me_2SnL_2] (**3**), [*n*-Oct_2SnL_2] (**4**), [*n*-Bu_3SnL]$_n$ (**5**), [Me_3SnL]$_n$ (**6**), and [Ph_3SnL]$_n$ (**7**), where L = 3-(4-bromophenyl)-2-ethylacrylate, were synthesized and characterized by elemental analysis, FT-IR, and multinuclear NMR (^{1}H, ^{13}C, and ^{119}Sn). Spectroscopic studies confirm coordination of L to the organotin moiety *via* COO group. Single-crystal X-ray analysis reveals bridging mode of coordination in **6**. Packing diagram established a supramolecular cage-like structure for **6** due to Sn–O interactions (3.287 Å). Subsequent antimicrobial activities proved them to be active biologically.

Keywords: Organotin(IV) carboxylate; Crystal structure; Antimicrobial

1. Introduction

Drug resistance in microbial strains is a serious public health concern [1–6] and demands urgent development of new and more efficient antibacterial and antifungal agents. Organotin(IV) complexes with carboxylate ligands have been the subject of interest due to their numerous biological activities [7–15]. Antifungal and antibacterial properties of a range of organotin(IV) carboxylates have been evaluated, with improved properties of organotin(IV) carboxylates over parent ligands [7, 12, 13]. This enhanced activity may be attributed to a variety in coordination number, geometries, thermodynamic, and kinetic stability of organotin(IV) carboxylates. Although data are available, work is in progress for development of more effective compounds in terms of biological activity, stability, and compromised solubility in both aqueous and lipid layers. From structural and biological diversity of organotin carboxylates and in connection with our interest in coordination chemistry of organotin compounds with different carboxylic acids [7, 16], herein we report the synthesis, characterization,

*Corresponding author. Email: drsa54@yahoo.com

ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.718076

antibacterial, and antifungal activities of organotin(IV) 3-(4-bromophenyl)-2-ethylacrylates.

2. Experimental

Organotin(IV) precursors, 4-bromobenzaldehyde and ethylmelonic acid were purchased from Aldrich and used without purification. Solvents were dried according to reported procedures [17]. Melting points were recorded on an electrothermal melting point apparatus, model MP-D mitamura Riken Kogyo (Japan). Microanalyses were done using a Leco CHNS 932 apparatus. IR spectra were recorded with KBr pellets from 4000 to 400 cm^{-1} using a Bio-Rad Excalibur FT-IR, model FTS 300 MX spectrometer (USA). ^{1}H and ^{13}C-NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker Avance Digital 300 MHz NMR spectrometer (Switzerland) and a Varian Unity 500-MHz instrument [^{119}Sn; $SnMe_4$ (ext) ref].

2.1. *Synthesis*

2.1.1. 3-(4-bromophenyl)-2-ethylacrylic acid (HL). Synthesis and single-crystal analysis of 3-(4-bromophenyl)-2-ethylacrylic acid (HL) were reported [18], while other spectroscopic data are given below. Yield: 65%;. m.p. 138.5–139.5°C. Anal. Calcd for $C_{11}H_{11}BrO_2$ (%): C, 51.76; H, 4.31. Found: C, 51.76; H, 4.33. IR (cm^{-1}): 3328–2529 ν(OH), 1663 $\nu(OCO)_{asym}$, 1409 $\nu(OCO)_{sym}$, 254 $\Delta\nu$. ^{1}H-NMR ($CDCl_3$ ppm): 11.68 (s, H_1, 1H); 7.73 (s, H_3, 1H); 7.29 (d $H_{5,5'}$, 2H); 7.56 (d, $H_{6,6'}$, 2H); 2.58 (q, H_8, 2H); 1.23 (t, H_9, 3H). ^{13}C-NMR ($CDCl_3$ ppm), 173.8 (C-1), 134.3 (C-2), 139.5 (C-3), 134.6, 131.8, 130.9, 123.0 (Ar–C), 20.6 (C-8), 13.7 (C-9).

2.1.2. Na-salt of 3-(4-bromophenyl)-2-ethylacrylate (NaL). The sodium salt of ligand, NaL, was prepared by dropwise addition of an equimolar amount of sodium hydrogen carbonate dissolved in distilled water to a methanolic solution of HL. The solution was stirred for 2 h at room temperature and evaporated under reduced pressure to give a white solid.

2.1.3. Di-n-butyltin(IV) bis[3-(4-bromophenyl)-2-ethylacrylate] (1). NaL (1.38 g, 5 mmol) was refluxed for 10 h with dibutyltin(IV) dichloride (0.76 g, 2.5 mmol) in dry toluene contained in a 250 mL two neck round bottom flask. A turbid solution obtained was left overnight at room temperature. The precipitated sodium chloride was filtered off and the filtrate was rotary evaporated. The resultant solid was recrystallized from chloroform and *n*-hexane (4 : 1). Yield: 71%; m.p. gel. Anal. Calcd for $C_{30}H_{38}Br_2O_4Sn$ (%): C, 48.52; H, 5.12. Found: C, 48.56; H, 5.13. IR (cm^{-1}): 1560 $\nu(OCO)_{asym}$, 1411 $\nu(OCO)_{sym}$, 149 $\Delta\nu$, 575 ν(Sn–C), 452 ν(Sn–O). ^{1}H-NMR ($CDCl_3$ ppm): 7.72 (s, H_3, 2H); 7.29 (d, $H_{5,5'}$, 4H); 7.55 (d, $H_{6,6'}$, 4H); 2.57 (q, H_8, 4H); 1.21 (t, H_9, 6H); 1.77–1.72 (m, $H_{\alpha,\beta}$, 8H); 1.48–1.41 (m, H_γ, 4H); 0.94 (t, H_δ, 6H). ^{13}C-NMR ($CDCl_3$ ppm), 177.0 (C-1), 134.6 (C-2), 138.6 (C-3), 135.2, 131.7, 130.8, 122.7 (Ar–C), 21.0 (C-8), 13.7 (C-9), 25.3 (C-α), 26.8 (C-β), 26.4 C-γ, 13.6 (C-δ).^{119}Sn-NMR ($CDCl_3$, ppm): −161.3.

2.1.4. Diethyltin(IV) bis[3-(4-bromophenyl)-2-ethylacrylate] (2). Compound **2** was prepared and recrystallized in the same way as **1** using NaL (1.38 g, 5 mmol) and diethyltin(IV) dichloride (0.62 g, 2.5 mmol). Yield: 89%; m.p. 90–92°C. Anal. Calcd for $C_{26}H_{30}Br_2O_4Sn$ (%): C, 45.48; H, 4.37. Found: C, 45.43; H, 4.40. IR (cm^{-1}): 1559 $\nu(OCO)_{asym}$, 1407 $\nu(OCO)_{sym}$, 152 $\Delta\nu$, 573 ν(Sn–C), 437 ν(Sn–O). ^{1}H-NMR ($CDCl_3$ ppm): 7.74 (s, H_3, 2H); 7.30 (d, $H_{5,5'}$, 4H); 7.54 (d, $H_{6,6'}$, 4H); 2.57 (q, H_8, 4H); 1.21 (t, H_9, 6H); 1.76 (q, H_α, 4H); 1.38 (t, H_β, 6H). ^{13}C-NMR ($CDCl_3$ ppm), 177.9 (C-1), 134.7 (C-2), 138.6 (C-3), 135.2, 131.7, 130.8, 122.6 (Ar–C), 21.1 (C-8), 13.8 (C-9), 17.6 (C-α), 9.0 (C-β). ^{119}Sn-NMR ($CDCl_3$, ppm): −165.8.

2.1.5. Dimethyltin(IV) bis[3-(4-bromophenyl)-2-ethylacrylate] (3). Compound **3** was prepared and recrystallized in the same way as **1** using NaL (1.38 g, 5 mmol) and dimethyltin(IV) dichloride (0.55 g, 2.5 mmol). Yield: 67%; m.p. 101–103°C. Anal. Calcd for $C_{24}H_{26}Br_2O_4Sn$ (%): C, 43.77; H, 3.95. Found: C, 43.80; H, 4.10. IR (cm^{-1}): 1553 $\nu(OCO)_{asym}$, 1400 $\nu(OCO)_{sym}$, 153 $\Delta\nu$, 579 ν(Sn–C), 438 ν(Sn–O). ^{1}H-NMR ($CDCl_3$ ppm), ^2J[(^{119}Sn, ^{1}H), Hz]: 7.73 (s, H_3, 2H); 7.27 (d, $H_{5,5'}$, 4H); 7.54 (d, $H_{6,6'}$, 4H); 2.56 (q, H_8, 4H); 1.20 (t, H_9, 6H); 1.10 {(s, H_α, 3H) [82]}. ^{13}C-NMR ($CDCl_3$ ppm): 177.7 (C-1), 134.6 (C-2), 138.9 (C-3), 135.1, 131.8, 130.8, 122.7 (Ar–C), 21.1 (C-8), 13.7 (C-9), 4.7 (C-α). ^{119}Sn-NMR ($CDCl_3$, ppm): −133.4.

2.1.6. Di-n-octyltin(IV) bis[3-(4-bromophenyl)-2-ethylacrylate] (4). HL (1.28 g, 5 mmol) and dioctyltin(IV)oxide (0.90 g, 2.5 mmol) were suspended in dry toluene (100 mL) in a single-neck round-bottom flask (250 mL) equipped with a Dean-Stark apparatus. The mixture was refluxed for 10 h and water formed during the condensation was removed at regular intervals. A clear solution thus obtained was cooled to room temperature and solvent was removed under reduced pressure. The solid obtained was recrystallized from chloroform and *n*-hexane (4 : 1). Yield: 78%; m.p. gel. Anal. Calcd for $C_{38}H_{54}Br_2O_4Sn$ (%): C, 53.40; H, 6.32. Found: C, 53.37; H, 6.29. IR (cm^{-1}): 1560 $\nu(OCO)_{asym}$, 1410 $\nu(OCO)_{sym}$, 150 $\Delta\nu$, 576 ν(Sn–C), 447 ν(Sn–O). ^{1}H-NMR ($CDCl_3$ ppm): 7.72 (s, H_3, 2H); 7.29 (d, $H_{5,5'}$, 4H); 7.54 (d, $H_{6,6'}$, 4H); 2.57 (q, H_8, 4H); 1.20 (t, H_9, 6H); 1.41–1.18 (bs, $H_{\alpha,\beta}$, 8H); 1.41–1.18 (bs, $H_{\gamma-\gamma'}$, 20H); 0.87 (t, H_δ, 6H). ^{13}C-NMR ($CDCl_3$ ppm), 177.8 (C-1), 134.7 (C-2), 138.4 (C-3), 135.4, 131.7, 130.8, 122.6 (Ar–C), 21.1 (C-8), 13.8 (C-9), 25.6 (C-α), 24.6 (C-β), 33.3 (C-γ), 32.0 (C-δ), 29.2 (C-α'), 29.0 (C-β'), 22.7 (C-γ'), 14.1 (C-δ'). ^{119}Sn-NMR ($CDCl_3$, ppm): −161.3.

2.1.7. Tri-n-butyltin(IV) 3-(4-bromophenyl)-2-ethylacrylate (5). Compound **5** was prepared in the same way as **1** using equimolar molar amounts of NaL (1.38 g, 5 mmol) and tributyltin(IV) chloride (1.62 g, 5 mmol). The product was recrystallized from chloroform and *n*-hexane (4 : 1). Yield: 82%; m.p. gel. Anal. Calcd for $C_{23}H_{37}BrO_2Sn$ (%): C, 50.64; H, 6.79. Found: C, 50.58; H, 6.84. IR (cm^{-1}): 1593 $\nu(OCO)_{asym}$, 1390 $\nu(OCO)_{sym}$, 203 $\Delta\nu$, 567 ν(Sn–C), 444 ν(Sn–O) (%): ^{1}H-NMR ($CDCl_3$ ppm): 7.55 (s, H_3, 1H); 7.25 (d, $H_{5,5'}$, 2H); 7.51 (d, $H_{6,6'}$, 2H); 2.52 (q, H_8, 2H); 1.16 (t, H_9, 3H); 1.76–1.61 (m, H_α, 6H); 1.44–1.27 (m, $H_{\beta,\gamma}$, 12H); 0.94 (t, H_δ, 9H). ^{13}C-NMR ($CDCl_3$ ppm), ^nJ[($^{119/117}$Sn, ^{13}C), Hz]: 173.2 (C-1), 135.4 (C-2), 137.4 (C-3), 136.0, 131.5, 130.7, 122.0 (Ar–C), 21.4 (C-8), 13.7 (C-9), 16.6 {(C-α), [359/342]}, 27.9 {(C-β), [21]}, 27.1 {(C-γ), [65]}, 13.6 (C-δ). ^{119}Sn-NMR ($CDCl_3$, ppm): 107.9.

2.1.8. Trimethyltin(IV) 3-(4-bromophenyl)-2-ethylacrylate (6). Compound **6** was prepared in the same way as **1** using equimolar molar amounts of NaL (1.38 g, 5 mmol) and trimethyltin(IV) chloride (1.00 g, 5 mmol). Yield: 79%; m.p. 128–130°C. Anal. Calcd for $C_{14}H_{19}BrO_2Sn$ (%): C, 40.10; H, 4.53. Found: C, 40.15; H, 4.55. IR (cm^{-1}): 1587 $\nu(OCO)_{asym}$, 1398 $\nu(OCO)_{sym}$, 189 $\Delta\nu$ 545 ν(Sn–C); 463 ν(Sn–O). ^{1}H-NMR ($CDCl_3$ ppm), $^2J[(^{119/117}Sn, ^1H)$, Hz]: 7.58 (s, H_3, 1H); 7.25 (d, $H_{5,5'}$, 2H); 7.52 (d, $H_{6,6'}$, 2H); 2.52 (q, H_8, 2H); 1.17 (t, H_9, 3H); 0.62 {(s, H_α, 3H), [58/56]}. ^{13}C-NMR ($CDCl_3$ ppm), $^1J[(^{119/117}Sn, ^{13}C)$, Hz]: 173.2 (C-1), 135.2 (C-2), 138.9 (C-3), 136.5, 131.6, 130.7, 122.1 (Ar–C), 21.3 (C-8), 13.8 (C-9), −2.3 {(C-α), [398/380]}. ^{119}Sn-NMR ($CDCl_3$, ppm): 132.3.

2.1.9. Triphenyltin(IV) 3-(4-bromophenyl)-2-ethylacrylate (7). Compound **7** was prepared in the same way as **1** using equimolar molar amounts of NaL (1.38 g, 5 mmol) and triphenyltin(IV) chloride (1.93 g, 5 mmol). Yield: 75%; m.p. 320°C (dec.). Anal. Calcd for $C_{29}H_{25}BrO_2Sn$ (%): C, 57.52; H, 4.13. Found: C, 57.47; H, 4.13. IR (cm^{-1}): 1577 $\nu(OCO)_{asym}$, 1398 $\nu(OCO)_{sym}$, 179 $\Delta\nu$, 443 ν(Sn–O). ^{1}H-NMR ($CDCl_3$ ppm): 7.58 (s, H_3, 1H); 7.26 (d $H_{5,5'}$, 2H); 7.52 (d, $H_{6,6'}$, 2H); 2.51 (q, H_8, 2H); 1.16 (t, H_9, 3H); 7.80–7.68 (m, $H_{\beta,\gamma,\delta}$, 15H). ^{13}C-NMR ($CDCl_3$ ppm), $^nJ[(^{119}Sn, ^{13}C)$, Hz]: 174.3 (C-1), 135.3 (C-2), 137.4 (C-3), 136.5, 131.5, 130.7, 122.0 (Ar–C), 21.3 (C-8), 13.8 (C-9), 137.7 {(C-α), [642]}, 136.8 {(C-β), [48]}, 129.2 {(C-γ), [63]}, 130.2 {(C-δ), [12]}. ^{119}Sn-NMR ($CDCl_3$, ppm): −119.1.

2.2. *X-ray crystallographic studies*

A crystal fragment, cut to fit in the homogeneous part of the X-ray beam, was mounted on top of a glass fiber and aligned on a Bruker SMART APEX CCD diffractometer (Platform with full three-circle goniometer). The crystal was cooled to 100(1) K using the Bruker KRYOFLEX low-temperature device. Intensity measurements were performed using graphite monochromated Mo-Kα radiation from a sealed ceramic diffraction tube (SIEMENS). Data integration and global cell refinement were performed with SAINT [19]. The program suite SAINTPLUS was used for space group determination (XPREP) [19]. The structure was solved by the Patterson method; extension of the model was accomplished by direct methods and applied to difference structure factors using DIRDIF [20]. Refinement calculations and graphics were performed with SHELXL, PLUTO, and PLATON package.

3. Results and discussion

3.1. *Syntheses of 1–7*

Reaction of $R_3SnCl/R_2SnCl_2/n$-Oct_2Sn with NaL/HL in 1 : 1/1 : 2/1 : 2 molar ratios, respectively, led to formation of complexes according to equations (1)–(3) in scheme 1. The resulting complexes were obtained in good yield (67–89%). All the complexes were white solids/gel, stable in air, and soluble in $CHCl_3$ and DMSO. The numbering scheme of ligand and alkyl/aryl groups attached to Sn is shown in scheme 1.

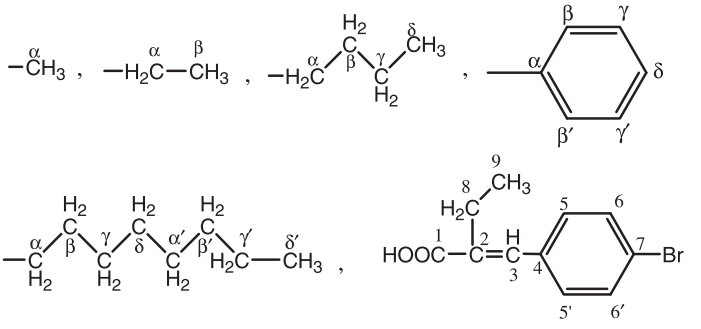
$$R_2SnCl_2 + 2NaL \rightarrow R_2SnL_2 + 2NaCl \quad (1)$$

R = *n*-Butyl (**1**), Ethyl (**2**), Methyl (**3**)

$$n\text{-}Oct_2SnO + 2HL \rightarrow n\text{-}Oct_2SnL_2 + H_2O \quad (2)$$

$$R_3SnCl + NaL \rightarrow R_3SnL + NaCl \quad (3)$$

R = *n*-Butyl (**5**), Methyl (**6**), Phenyl (**7**)



Scheme 1. Synthesis of organotin(IV) derivatives, **1**–**7**, and numbering scheme of ligand and organic groups attached to Sn atom.

3.2. *IR spectra*

In IR spectra of **1**–**7**, the absence of a band at 3328–2529 cm^{-1} due to –OH stretch in the free ligand acid signifies metal–ligand bond formation *via* this site. This is further supported by the absorption at 463–437 cm^{-1}, characteristic of an Sn–O bond [21, 22]. The bonding mode of the ligand was confirmed by $\Delta\nu$, $\{\nu_{asym}(COO) - \nu_{sym}(COO)\}$ [23]. The $\Delta\nu$ values signified that ligand coordination is a chelated bidentate (**1**–**4**) and bridging bidentate (**5**–**7**). The conclusions drawn from the IR data are consistent with the X-ray structure for **6**.

3.3. *NMR spectra*

Assignment of proton resonances were made by peak multiplicities, intensity pattern, and comparison of integration values of protons with the expected composition. In spectra of **1**–**7**, ^1H resonances of protons attached to the α-alkyl of the ligand appear as quartets (for CH_2) and triplet (for CH_3), whereas olefinic protons of the ligand resonate as a sharp singlet, of *E*-configuration at 7.74–7.55 ppm [24–26]. The aromatic part of the ligand gave two doublets due to two non-equivalent sets of protons. Protons of alkyl/aryl groups attached to Sn presented signals as expected [27, 28]. Coordination around Sn was deduced from [^2J (^{119}Sn, ^1H)] coupling constants. For **3** and **6**, the values were 82 and 58 Hz, respectively, consistent with CSnC angles of 133.42° and 111.00°, thus confirming five- and four-coordinate Sn, respectively, in solution [29]. In spectra of all complexes, the presence of the exact number of carbon resonances for ligand and alkyl as anticipated from the structures validate formation of **1**–**7**. Furthermore, signal of the carboxylic carbon of the ligand shifted downfield upon complexation. Greater downfield shift of C-1 in dialkyltin derivatives shows higher coordination number of tin and corresponds to deshielding of C-1. The ^1J [$^{119/117}Sn$, ^{13}C] coupling constant can be used to assess the coordination number of Sn in organotin compounds. The calculated coupling constants were 359/342 Hz for tributyltin **5**, 398/380 Hz for trimethyltin **6**, and

642 Hz for triphenyltin **7**, consistent with the range reported for four-coordinate Sn [30]. The ^{1}H and ^{13}C-NMR spectra of the complexes were found to exhibit no additional resonances and thus reflect the purity of complexes. The $\delta(^{119}\text{Sn})$ values define the coordination number of tin [7]. For **1**–**4**, the $\delta(^{119}\text{Sn})$ values fall in the range +200 to −60 ppm, showing five-coordinate tin. $\delta(^{119}\text{Sn})$ signals for **5**–**7** show a four-coordinate tetrahedral geometry in solution.

3.4. *Crystal structure of 6*

Compound **6** crystals were obtained from chloroform and *n*-hexane (4 : 1) mixture, and the structure is shown in figure 1. Crystal data and selected interatomic parameters are collected in tables 1 and 2, respectively. X-ray diffraction investigation of **6** shows that it

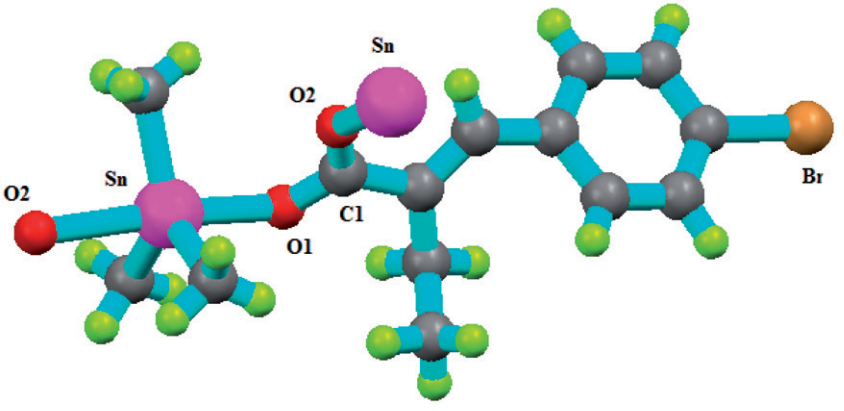


Figure 1. Molecular structure of **6**.

Table 1. Crystal data and structure refinement parameters for **6**.

Empirical formula	$C_{14}H_{19}BrO_2Sn$
Formula weight	417.92
Temperature (K)	100(1)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	6.8387(6)
b	9.7596(8)
c	23.547(2)
β	95.4929(14)
Volume (Å^3), *Z*	1564.4(2), 4
τ	0.82
Calculated density (g cm^{-3})	1.774
F(000)	816
Crystal size (mm^3)	0.44 × 0.20 × 0.13
θ range for data collection (°)	2.72–28.28
Limiting indices	$-9 \le h \le 8$; $-13 \le k \le 13$; $-26 \le l \le 31$
Total data	14,003
Unique data	3870[*R*(int) = 0.0291]
Final *R* indices [$F_o > /4\sigma(F_o)$]	$R_1 = 0.0301$, $wR_2 = 0.0737$

is an infinite zigzag polymeric chain with trimethyltin centers being linked by bridging carboxylates. Each tin is five-coordinate, axially by two oxygen atoms and equatorially by three methyl groups, thus resulting in a distorted trigonal bipyramidal geometry. Each O–Sn–O unit is associated with unequal Sn–O bond distances (2.1795(19), 2.411(2) Å). These values are closer to the Sn–O covalent bond length (2.13 Å), but are much shorter than the sum of the van der Waals radii of connected atoms (3.68 Å) [31]. This asymmetry may be due to involvement of oxygen in inter- and intramolecular Sn–O non-covalent interactions (3.287 Å). These interactions also render a supramolecular cage-like structure to **6** (figure 2). The interactions are 0.1 Å less than the van der Waals radii and were drawn by using Hg-2.2 software. The dissimilarity in Sn–O bonds is clearly evident in the associated C–O bond lengths: the longer C–O bond is associated with shorter Sn–O interaction and vice versa. Sn–C bond lengths (2.119(3)–2.125(3) Å) are consistent with those reported for other triorganotin derivatives [7].

Table 2. Selected bond lengths (Å) and angles (°) of **6**.

Sn–O1	2.1795(19)	Sn–C13	2.119(3)
Sn–O2	2.411(2)	Sn–C14	2.125(3)
Sn–C12	2.131(3)	O1–C1	1.288(3)
O2–C1	1.252(3)		
O1–Sn–C12	92.22(10)	C12–Sn–O2	90.65(10)
O1–Sn–C13	87.90(10)	C13–Sn–C14	122.48(13)
O1–Sn–C14	99.35(10)	C13–Sn–O2	84.1(10)
O1–Sn–O2	171.96(7)	C14–Sn–O2	85.62(10)
C12–Sn–C13	116.07(13)	Sn–O1–C1	123.79(17)
C12–Sn–C14	120.48(13)		

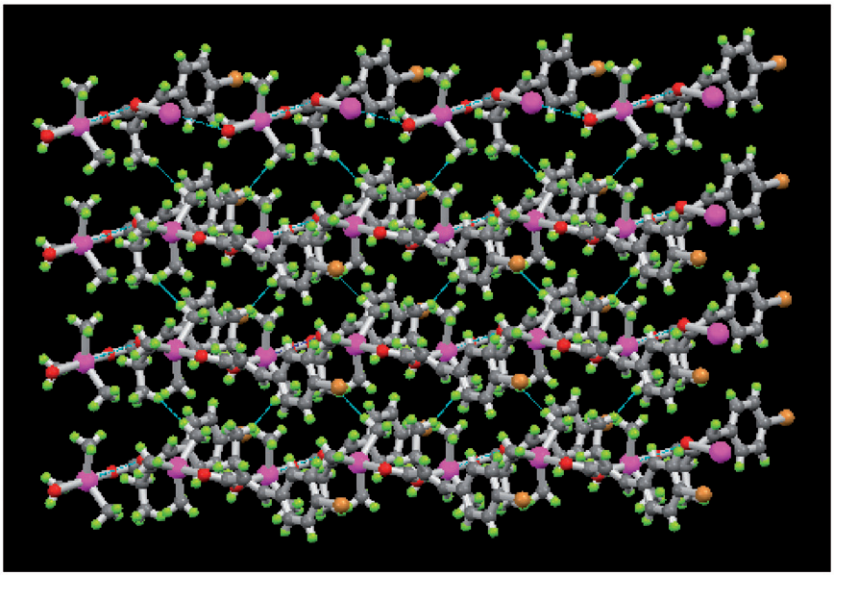


Figure 2. Cage-like supramolecular structure of **6** mediated by intermolecular Sn–O interaction (3.287 Å).

Table 3. Antibacterial activity data of organotin(IV) derivatives of 3-(4-bromophenyl)-2-ethylacrylic acid (HL).[a,b]

	Zone of inhibition (mm)								Ref. drugs		
Name of bacterium	HL	**1**	**2**	**3**	**4**	**5**	**6**	**7**	A	B	C
E. coli	14	10	12	26	12	13	20	7	28	40	32
B. subtilis	12	13	15	20	11	52	24	12	35	26	21
Erwenia sp.	25	23	20	33	09	30	33	14	30	33	35

[a]Concentration: 1 mg mL^{-1} of DMSO; [b]Reference drugs: Ofloxacin (A), Ciprofloxacin (B), and Ampicillin (C).

3.5. *Antimicrobial studies*

3.5.1. Antibacterial activity. The parent acid and complexes were evaluated for their antibacterial activities using the agar well diffusion method [32]. The *in vitro* antibacterial activity was performed against *Bacillus subtilis*, *Escherichia coli*, and *Erwenia* sp. and the activity is shown in terms of zone of inhibition (mm) in table 3. In order to compare the results obtained, Ofloxacin, Ciprofloxacin, and Ampicillin were used as standard drugs. A comparative study of the ligand acid and its organotin(IV) derivatives indicates that complexes exhibit higher or comparable antibacterial activity than the free ligand, in general. In some cases activity is higher than standard drug, especially for **5** against *B. subtilis*.

Improved activity of the complexes can be explained on the basis of Overtone's concept [33] and Tweedy's chelation theory [34–36], which requires increased lipophilicity for antimicrobial activity. The observed variation in activity of the synthesized complexes against the tested bacteria may be due to differences in cell wall and/or membrane construction, nature of complex, number, and lengths of alkyl groups attached to tin. Triorganotin(IV) derivatives are more active than the diorganotin(IV) derivatives, attributed to greater lipophilic character. Also, activity decreases with increasing length of alkyl group, which may be due to slow movement and greater hydrophobic character of bulky groups. This trend shows dependence of antibacterial activity on number and nature of alkyl group attached to tin.

3.5.2. Antifungal activity. The complexes were checked for antifungal activity against different pathogens by using Agar tube dilution protocol [32] and the data collected are listed in table 4. Generally, complexes show markedly higher antifungal activity than the ligand. Like antibacterial activities no clear patterns were observed for complexes against fungal strains.

Antimicrobial results of this study are almost comparable with the promising findings of Amin *et al.* [37].

4. Conclusion

The outcome of this study is that the di- and triorganotin(IV) 3-(4-bromophenyl)-2-ethylacrylates demonstrated different structural motifs in solution and solid states.

Table 4. Antifungal activity data of organotin(IV) derivatives of 3-(4-bromophenyl)-2-ethylacrylic acid (HL).[a,b]

	Percent inhibition								
Name of fungus	HL	**1**	**2**	**3**	**4**	**5**	**6**	**7**	Standard drug
Saccharomyces cerevisiae	47	43	50	43	40	37	40	40	100
Kluyveromyces fragilis	27	24	82	73	30	42	30	30	100
Aspergillus niger	33	40	47	40	33	60	43	40	100
Aspergillus oryzae	18	50	55	63	25	50	70	75	100

[a]Concentration: 400 μg mL^{-1} of DMSO; [b]Standard drug: Travogen.

These compounds are active biologically; however, this property not only depends on structure of complex but also on type of antimicrobial study in consideration. Difference in behavior toward bacterial and fungal strains suggests a different mode of action and activity controlling factors in either case.

Supplementary material

Crystallographic data for the structural analysis are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 882 214.

Acknowledgments

We thank the Higher Education Commission of Pakistan for the financial support.

References

[1] R. Rogers. *Int. J. Antimicrob. Agents*, **27**, 7 (2006).
[2] G. Chamilos, D.P. Kontoyiannis. *Drug Resist. Updates*, **8**, 344 (2005).
[3] E. Francois, A.M. Aerts, B.P. Cammue, K. Thevissen. *Curr. Drug Targets*, **6**, 895 (2005).
[4] N. Zetola, J.S. Francis, E.L. Nuermberger, W.R. Bishai. *Lancet Infect. Dis.*, **5**, 275 (2005).
[5] E.A. Simor, M. Ofner-Agostini, E. Bryce. *Can. Med. Assoc. J.*, **165**, 21 (2001).
[6] J.W. Gray. *Arch. Dis. Child.*, **89**, 297 (2004).
[7] N. Muhammad, Zia-ur-Rehman, S. Ali, A. Meetsma, F. Shaheen. *Inorg. Chim. Acta*, **362**, 2842 (2009).
[8] S. Tabassum, C. Pettinari. *J. Organomet. Chem.*, **691**, 1761 (2006).
[9] D.K. Demertzi. *J. Organomet. Chem.*, **691**, 1767 (2006).
[10] M. Gielen, A.E. Khloufi, M. Biesemans, F. Kaysert, R. Willem. *Appl. Organomet. Chem.*, **7**, 201 (1993).
[11] M. Gielen. *Coord. Chem. Rev.*, **151**, 41 (1996).
[12] W. Kang, X. Wu, J. Huang. *J. Organomet. Chem.*, **694**, 2402 (2009).
[13] S.L. Cai, Y. Chen, W.X. Sun, H. Li, Y. Chen, S.S. Yuan. *Bioorg. Med. Chem. Lett.*, **20**, 5649 (2010).
[14] Y.F. Win, S.G. Teoh, M.R. Vikneswaran, Y. Sivasothy, S.T. Ha, P. Ibrahim. *Aust. J. Basic Appl. Sci.*, **4**, 5923 (2010).
[15] X. Wua, W. Kang, D. Zhu, C. Zhu, S. Liu. *J. Organomet. Chem.*, **694**, 2981 (2009).

[16] N. Muhammad, A. Shah, Z. Rehman, S. Shuja, S. Ali, R. Qureshi, A. Meetsma, M.N. Tahir. *J. Organomet. Chem.*, **694**, 3431 (2009).
[17] D.D. Perrin, W.L.F. Armengo. *Purification of Laboratory Chemicals*, 3rd Edn, Pergamon Press, Oxford (2003).
[18] N. Muhammad, Z. Rehman, S. Ali, A. Meetsma. *Acta Cryst.*, **E63**, o2557 (2007).
[19] Bruker. *SMART, SAINTPLUS and XPREP. Area Detector Control and Integration Software. Smart Apex Software Reference Manuals*. Bruker Analytical X-ray Instruments Inc., Madison, WI, USA (2006).
[20] P.T. Beurskens, G. Beurskens, R. de Gelder, S. García-Granda, R.O. Gould, R. Israël, J.M.M. Smits. *The DIRDIF-99 Program System*, Crystallography Laboratory, University of Nijmegen, The Netherlands (1999).
[21] R.R. Holmes, C.G. Schmid, V. Chandrasekhar, R.O. Day, J.M. Homels. *J. Am. Chem. Soc.*, **122**, 5158 (2000).
[22] G.K. Sandhu, R. Hundal. *J. Organomet. Chem.*, **436**, 287 (1992).
[23] G. Eng, X. Song, A. Zapata, A.C. de Dios, L. Casabianca, R.D. Pike. *J. Organomet. Chem.*, **692**, 1398 (2007).
[24] O.L. Chapman, W.R. Adams. *J. Am. Chem. Soc.*, **90**, 2333 (1968).
[25] H. Xin, M.Y. Li, L.Y. Zi, Z.Y. Li, L.T. Xiao. *Chin. Chem. Lett.*, **8**, 883 (1997).
[26] M. Bartök, G. Wittmann, G. Göndös, G.V. Smith. *J. Org. Chem.*, **52**, 1136 (1987).
[27] Zia-ur-Rehman, M. Barsan, I. Wharf, N. Muhammad, S. Ali, A. Meetsma, I.S. Butler. *Inorg. Chim. Acta*, **361**, 3322 (2008).
[28] S. Shahzadi, S. Ali, M.H. Bhatti, M. Fettouhi, M. Akhtar. *J. Organomet. Chem.*, **691**, 1797 (2006).
[29] T.P. Lockhart, W.F. Manders. *Inorg. Chem.*, **25**, 892 (1986).
[30] M.K. Rauf, M.A. Saeed, Imtiaz-ud-Din, M. Bolte, A. Badshah, B. Mirza. *J. Organomet. Chem.*, **693**, 3043 (2008).
[31] A. Bondi. *J. Phys. Chem.*, **68**, 441 (1964).
[32] A. Rahman, M.I. Choudry, W.J. Thomsen. *Bioassay Techniques for Drug Development*, Harwood Academic, The Netherlands (2001).
[33] Y. Anjaneyula, R.P. Rao. *Synth. React. Inorg. Met.-Org. Chem.*, **16**, 257 (1986).
[34] N. Dharamaraj, P. Viswanathamurthi, K. Natarajan. *Trans. Met. Chem.*, **26**, 105 (2001).
[35] K. Nagashri, J. Joseph, C.J. Dhanaraj. *Appl. Organomet. Chem.*, **25**, 25 (2011).
[36] Zia-ur-Rehman, N. Muhammad, S. Ali, I.S. Butler, A. Meetsma. *Inorg. Chim. Acta*, **373**, 187 (2011).
[37] M.M. Amin, S. Ali, S. Shahzadi, S.K. Shama, K. Qanungo. *J. Coord. Chem.*, **64**, 337 (2011).