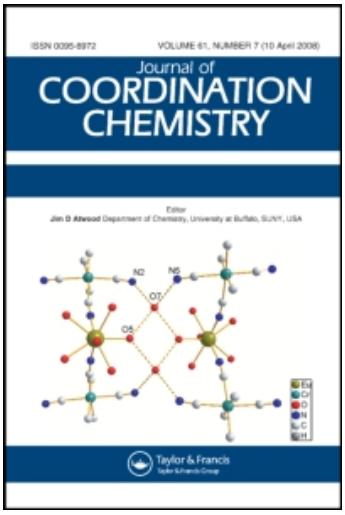

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and coordination chemistry of organotin(IV) complexes of 2,3-methylenedioxyphenylpropenoic acid

Mukhtiar Hussain[a]; Muhammad Hanif[b]; Saqib Ali[a]; Saira Shahzadi[b]; Muhammad Sheeraz Ahmad[c]; Bushra Mirza[c]; Helen S. Evans[d]
[a] Department of Chemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan [b] Department of Chemistry, GC University, Faisalabad, Pakistan [c] Department of Biochemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan [d] Institute of Microtechnology, University of Neuchatel, CH-2009 Neuchatel, Switzerland

To cite this Article Hussain, Mukhtiar , Hanif, Muhammad , Ali, Saqib , Shahzadi, Saira , Ahmad, Muhammad Sheeraz , Mirza, Bushra and Evans, Helen S.(2009) 'Synthesis and coordination chemistry of organotin(IV) complexes of 2,3-methylenedioxyphenylpropenoic acid', Journal of Coordination Chemistry, 62: 13, 2229 — 2238
To link to this Article: DOI: 10.1080/00958970902803325
URL: http://dx.doi.org/10.1080/00958970902803325

Journal of Coordination Chemistry
Vol. 62, No. 13, 10 July 2009, 2229–2238

Taylor & Francis
Taylor & Francis Group

Synthesis and coordination chemistry of organotin(IV) complexes of 2,3-methylenedioxyphenylpropenoic acid

MUKHTIAR HUSSAIN†, MUHAMMAD HANIF†,
SAQIB ALI*†, SAIRA SHAHZADI‡, MUHAMMAD SHEERAZ AHMAD§,
BUSHRA MIRZA§ and HELEN S. EVANS¶

†Department of Chemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan
‡Department of Chemistry, GC University, Faisalabad, Pakistan
§Department of Biochemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan
¶Institute of Microtechnology, University of Neuchatel, Rue Emile-Argand 11,
CH-2009 Neuchatel, Switzerland

(*Received 2 June 2008; in final form 5 November 2008*)

The synthesis, spectroscopy, and antitumor behavior of organotin(IV) complexes of 2,3-methylenedioxyphenylpropenoic acid are described. The spectroscopic data indicate 1 : 2 and 1 : 1 metal to ligand stoichiometry in case of di- and trioganotin(IV) compounds and hypervalency of Sn(IV) in trigonal bipyramidal and octahedral modes. Mass spectrometric and elemental analysis data support the solid and solution spectroscopic results. The complexes have been evaluated *in vitro* against crown gall tumor and bio-activity screenings showed *in vitro* biological potential. The nature of covalent attachments (methyl, ethyl, *n*-butyl, phenyl, and *n*-octyl) of Sn(IV) played a decisive role for bioactivity. All the compounds have been studied in solution by NMR (^{1}H, ^{13}C) and also in solid state using FTIR, mass spectrometry, and by X-ray crystallography. The molecular structure of Et_2Sn(IV) and Me_3Sn(IV) derivatives confirm the behavior of di- and tri-organotin(IV) compounds in solid state. Mono-organotin derivatives are octahedral both in solid and solution.

Keywords: 2,3-Methylenedioxyphenylpropenoic acid; Organotin(IV) complexes; NMR; Mass spectrometry; Antitumor activity; XRD

1. Introduction

The chemistry of organotin(IV) complexes [1] and especially organotin carboxylates of substituted benzoic acids has been prompted by their structural diversity [2] and broad therapeutic activity [3]. Organotin(IV) carboxylates also have potential biocidal activity [4] and cytotoxicity [5] as well as their industrial and agricultural applications [6].

Biocidal activity of organotin complexes is influenced by molecular structures and coordination number of the tin [7]. Crystallographic studies have revealed that

*Corresponding author. Email: drsa54@yahoo.com

ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902803325

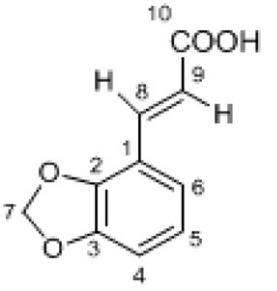

Figure 1. The structure and numbering scheme of 2,3-methylenedioxyphenylpropenoic acid.

organotin carboxylates adopt structures dependent on the nature of the substituent bonded to tin and on the type of carboxylate [8, 9]. Organotin(IV) derivatives containing carboxylate ligands with additional donors, such as oxygen, have new structural types.

Increasing interest in the chemistry of organotin(IV) compounds has led to studies of their reactions with different biomolecules, e.g. carbohydrates [10], nucleic acid derivatives [11], amino acids [12], and peptides [13].

Triorganotin(IV) compounds display a larger array of biological activity than their diorganotin and mono organotin analogues, attributed to their ability to bind proteins [14]. Many organotin(IV) carboxylates characterized in solid and solution have been found to possess anticancer activity in a variety of tumor cells [15]; dialkyltin(IV) compounds are selective for lymphocytes [16]. Easily dissociable chelating ligands give intermediates such as $RnSn^{+(4-n)}$ ($n = 2$ or 3), which may bind to DNA [17] or high affinity site ATPase (histidine) or low affinity site ATPase and hemoglobin (cystine) [18]. Coordination behavior of these compounds may give insight as to how the metallic species behave inside biological systems and also help to formulate structure-activity correlations for biocidal activities.

In continuation of our interest in the synthesis, characterization, and biological studies of organotin(IV) carboxylates [19–21], we synthesized organotin(IV) complexes of 2,3-methylenedioxyphenylpropenoic acid (figure 1) and characterized them by multinuclear NMR (^1H, ^{13}C), FTIR, mass spectrometry, and X-ray crystallography. These compounds were tested for their *in vitro* antitumor activity.

2. Experimental

2.1. *Material and methods*

The *o*-piperonal was synthesized by reported method [22], malonic acid, pyridine, piperidine, organotin(IV) oxides/hydroxides, and organotin(IV) chlorides used during the synthesis of ligand and complexes were purchased from Aldrich Chemicals (USA). The organic solvents (toluene, chloroform, etc.) used were purchased from Merck (Germany) and dried by standard procedures [23]. All other chemicals were of analytical grade and used without purification.

Melting points were determined in a capillary tube using a MPD Mitamura Riken Kogyo (Japan) electro thermal melting point apparatus. The infrared (IR) spectra were recorded as KBr pellets (for solid compounds) on a Bio-Rad *Excaliber* FT-IR, model FTS 300 MX spectrophotometer (USA), in the frequency range 4000–400 cm^{-1}. Multinuclear NMR (^1H and ^{13}C) spectra were recorded on a Bruker ARX 300 MHz FT-NMR spectrometer using $CDCl_3$ as an internal reference [δ ^1H ($CDCl_3$) = 7.25 and δ ^{13}C ($CDCl_3$) = 77.0]. Chemical shifts (δ) are given in ppm and coupling constants J are given in Hz. The multiplicities of signals in ^1H NMR are given with chemical shifts. Mass spectral (APCI and ESI mode) data were taken on a LCQ Finnigan MAT ion trap (USA). The m/z values were evaluated assuming that H = 1, C = 12, N = 14, O = 16, Cl = 35, and Sn = 120. X-ray single crystal analyses were made on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation. The structures were solved by direct methods and expanded using Fourier techniques. The figures were plotted with the aid of ORTEPII [24].

2.2. *Synthesis of* 2,3-*methylenedioxyphenylpropenoic acid*

2,3-*methylenedioxyphenylpropenoic acid* (HL) was prepared by reported method [25]. A mixture of 2,3-methylenedioxybenzaldehyde (5 g, 3.3 mmol), malonic acid (7.5 g, 7.2 mmol), and 15 mL of pyridine was heated below 100°C for 2 h in a round bottom flask. A few drops of piperidine (0.25 mL) were added to the mixture. After that, the mixture was poured into excess of water containing enough HCl to neutralize the basic medium. The precipitated ligand acid was washed and dried. The dried solid was converted to its sodium salt by dissolving the acid (3.0 g, 1.56 mmol) in absolute ethanol and treating it with sodium hydrogen carbonate (1.3 g, 1.56 mmol). After one hour stirring, the solvent was evaporated under reduced pressure. The solid product was dried over CaO/P_2O_5.

2.3. *General procedure for synthesis of complexes*

2.3.1. Procedure (a). Sodium salt of acid and corresponding organotin(IV) chlorides (R_2SnCl_2 and R_3SnCl) were added to 100 mL of dry toluene in 2 : 1/1 : 1 molar ratio in a round bottom two-necked flask (250 mL). The mixture was refluxed for 5–6 h. On cooling, sodium chloride was filtered off and filtrate evaporated under reduced pressure. The solid product obtained was recrystallized from chloroform and *n*-hexane mixture (4 : 1).

2.3.2. Procedure (b). The synthesized carboxylic acid and analogous organotin(IV) oxide (R_2SnO), organotin(IV) hydroxide (R_3SnOH), and organotin(IV) hydroxide chloride (RSn(OH)Cl) in 2 : 1, 1 : 1, and 2 : 1 ratio, respectively, were suspended in dry toluene (100 mL) in a reaction flask with constant stirring and refluxed for 6 h. The azeotropic mixture formed was continuously removed via Dean and Stark trap. After that, the reaction mixture was cooled at room temperature; solvent was removed through rotary apparatus under reduced pressure. The solid was recrystallized from $CHCl_3$ and *n*-hexane (4 : 1).

3. Results and discussion

Organotin derivatives **1**–**9** were obtained by heating at reflux the stoichiometric amount of 2,3-methylenedioxyphenylpropenoic acid or its sodium salt with the corresponding organotin oxide/hydroxide/hydroxide chloride or organotin chloride in anhydrous toluene (equations 1–5).

$$R_2SnCl_2 + 2NaL \longrightarrow R_2SnL_2 + 2NaCl \quad (1)$$
$$R = \text{Me } (\mathbf{1}), \text{Et } (\mathbf{2}), \text{Ph } (\mathbf{5})$$

$$R_2SnO + 2HL \longrightarrow R_2SnL_2 + H_2O \quad (2)$$
$$R = n\text{-Bu } (\mathbf{3}), n\text{-Oct } (\mathbf{4})$$

$$R_3SnOH + HL \longrightarrow R_3SnL + H_2O \quad (3)$$
$$R = \text{Ph } (\mathbf{8})$$

$$R_3SnCl + NaL \longrightarrow R_3SnL + NaCl \quad (4)$$
$$R = \text{Me } (\mathbf{6}), n\text{-Bu } (\mathbf{7})$$

$$RSn(OH)_2Cl + 2HL \longrightarrow RSnL_2Cl + H_2O \quad (5)$$
$$R = n\text{-Bu } (\mathbf{9})$$

where L = ligand, NaL = sodium salt of ligand.

The nature of bonding in the complexes was studied by multinuclear NMR, IR, mass spectroscopy, and X-Ray crystallography. All the compounds are soluble in organic solvents and are stable in air at room temperature. The yield obtained for these complexes is 73–90%. Physical data are reported in table 1.

3.1. *Infrared spectroscopy*

IR spectra show a very sharp peak at 924–933 cm^{-1} indicating the presence of methylenedioxy group in all the compounds showing no change of this group during

Table 1. Experimental and physical data for the complexes studied

				Elemental analysis Calcd (found)	
Comp. No.	Molecular formula	Yield (%)	Melting point (°C)	% C	% H
1	$C_{20}H_{20}O_8Sn$	78	183–187	49.62 (49.53)	3.75 (3.48)
2	$C_{24}H_{24}O_8Sn$	75	210–212	51.42 (51.97)	4.28 (4.31)
3	$C_{28}H_{32}O_8Sn$	80	72–74	54.54 (54.42)	5.19 (5.23)
4	$C_{36}H_{48}O_8Sn$	81	180–182	59.34 (56.49)	6.59 (6.43)
5	$C_{36}H_{24}O_8Sn$	73	143–145	58.53 (59.01)	3.65 (3.72)
6	$C_{13}H_{16}O_4Sn$	75	173–175	43.82 (44.01)	4.49 (4.52)
7	$C_{22}H_{34}O_4Sn$	74	145–146	54.77 (54.92)	7.05 (7.12)
8	$C_{28}H_{22}O_4Sn$	82	101–102	61.99 (62.05)	4.05 (4.15)
9	$C_{24}H_{23}O_8Sn$	75	180–182	48.44 (48.52)	3.87 (3.98)
HL	$C_{10}H_8O_4$	90	194	–	–

the reaction. The IR spectra show the absence of υ(OH) absorption of 2,3-methylenedioxyphenylpropenoic acid, an indication of complex formation; υ(COO)asym and υ(COO)sym values are determined from sharp to medium peaks from spectra present at 1636–1630 and 1456–1443 cm^{-1}.

The $\Delta\nu$ values in the range 176–188 cm^{-1} indicate bidentate coordination of $-COO^-$ [26, 27]. The absorption bands (cm^{-1}) for structural assignments are given in Supplementary Material.

3.2. *NMR spectroscopy*

The ^{1}H NMR spectral data (in $CDCl_3$) identify almost all protons of the ligand and complexes by intensities and multiplicities. ^{1}H NMR chemical shifts and coupling constant values for investigated compounds are summarized in Supplementary Material. Signals at 6.48–7.61 ppm with a distinct multiplicity have been assigned to protons of benzene. A sharp singlet at 6.02–6.13 ppm is due to two methylene protons in all complexes.

The protons (H-8 and H-9) of –CH=CH– group show two doublets in the range 6.69–7.74 having $^3J(^1H–^1H)$ coupling constant values of 15.04–16.3 Hz. These coupling constants show that the protons are *trans* to each other. Compounds **5** and **8** having phenyl moieties show multiplets in the aromatic region at 7.12–7.77 ppm. Methyl protons in **1** and **6** are sharp singlets at 1.07 and 0.62 ppm, respectively. In **3**, **7**, and **9**, protons of α-carbons are a triplet at 0.86, 0.93, and 0.92 ppm, respectively, while a complex pattern is observed for other protons of *n*-butyl. In **2**, methylene protons are a quartet at 1.76 ppm with $^3J(^1H–^1H)$ 8.0 HZ and methyl protons a triplet at 1.37 ppm.

The $^2J(^{119}Sn–^1H)$ coupling constant values for **1** and **2** are 74 and 78 Hz, respectively, supporting six-coordinate tin [15]. In **6**, tetrahedral geometry around tin is observed as indicated from $^2J(^{119}Sn–^1H)$ coupling constant [28].

^{13}C NMR data (Supplementary Material) are useful for determination of coordination number of tin, its molecular geometry, and stereochemistry. For diorganotin dicarboxylates, the geometry around tin in solution could not be determined with certainty due to fluxional behavior of the carboxylate; however, earlier reports suggest six-coordinate tin.

The alkyl carbons attached to tin occur at the normal values for methyl, ethyl, and butyl tin compounds [29]. The aromatic carbon resonances were assigned by the comparison of experimental chemical shift with those calculated from the incremental method [30] and with literature values [15, 16]. The resonances of the carboxylate carbons in organotin compounds show downfield shift (176.2–177.9 ppm) as compared to ligand (169.0 ppm) suggesting coordination through the carboxylate oxygen. The methylene carbons resonate downfield. The measurement of coupling constants in ^{13}C NMR helps to determine the molecular structure of compounds. In **1** and **2**, the $^1J(^{119}Sn–^{13}C)$ coupling constants were 630 and 542 Hz, respectively, in agreement with literature values [31, 32] and corresponding to distorted octahedral geometry.

For **7**, with $^1J(^{119}Sn–^{13}C)$ being 350.6 Hz, use of the Holecek and Lycka equation [31] gave a C–Sn–C value of 111.6°, which corresponds to quasi-tetrahedral geometry in $CDCl_3$ solution. The tetrahedral geometry around tin in solution in **6** is also straightforward as confirmed by coupling value. For the diorganotin(IV) species, for which earlier results indicate distorted octahedral geometry, the calculated C–Sn–C

angles are consistent with this geometry [33], with the lower apparent coordination number arising from the asymmetric coordination of carboxylate.

3.3. *Mass spectrometry*

The mass spectral data of the title compounds are in good agreement with expected structures and generally have almost the same general fragmentation pattern with $[C_7H_5]^+$ as the base peak in most of the compounds. The 70 eV mass spectral data by using Electron Impact (EI) method for the reported complexes are given in Supplementary Material.

Fragment ions containing Sn are quite intense. In triorganotin(IV) and diorganotin(IV) carboxylates the primary fragmentation is due to loss of R. All diorganotin(IV) derivatives fragment via two pathways; the primary fragmentation may occur through loss of O_2CR' and secondary involves elimination of CO_2 with further fragmentations due to release of R and R′ groups generating $[RSn]^+$ and finally $[Sn]^+$. In the second pathway, primary fragmentation arises by loss of R and removal of CO_2 provides the secondary fragmentation. Successive release of CO_2, R′, and R makes SnR^+ which ends to $[Sn]^+$.

3.4. *X-Ray crystallography*

In order to support our discussion about the geometry around tin in these compounds, crystal data and the selected bond angles and bond lengths of **2** and **6** are given in tables 2 and 3, respectively.

Diorganotin(IV) dicarboxylates show somewhat different structures as shown in figure 2 for **2** due to fluxional behavior of carbonyl. In **2**, a discrete monomer with

Table 2. Crystal data and structure refinement parameters for **2** and **6**

Empirical formula	$C_{24}H_{24}O_8Sn$	$C_{13}H_{16}O_4Sn$
Formula weight	559.12	354.95
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimension (Å, °)		
a	7.5450(7)	11.6694(15)
b	11.8020(10)	10.5785(11)
c	13.0100(11)	11.9934(16)
α	95.824(7)	90.00
β	99.876(7)	108.192(10)
γ	93.451(7)	90.00
V(Å^3)	1131.87(17)	1406.5(3)
Z	2	4
D_{Caled} (g cm^{-3})	1.641	1.820
Crystal size (mm^3)	$0.46 \times 0.38 \times 0.31$	$0.50 \times 0.21 \times 0.15$
F(000)	564	704
Total reflections	6123	3797
Independent reflections	5438	2948
All indices (all data)	$R_1 = 0.0319$, $wR_2 = 0.0656$	$R_1 = 0.0429$, $wR_2 = 0.0713$
Final R indices [$I > 2(I)$]	$R_1 = 0.0261$, $wR_2 = 0.0632$	$R_1 = 0.0298$, $wR_2 = 0.0685$
Goodness-of-fit	1.053	0.913
θ Range for data collection (°)	1.60–29.25	1.84–29.23
Data/restraints/parameters	6123/0/370	3797/0/163

six-coordinate tin is observed. The geometry is highly distorted octahedral and can be described as skew-trapezoidal planar geometry. The Sn–C bond distances are identical within normal limits [2.11–2.12 Å] and the C–Sn–C bond angle is 116.14°, comparable to the corresponding angle in similar structures [34]. L is attached to tin with Sn–O distances significantly different, with shorter distances being 2.12(13) and 2.10(14) Å and longer Sn–O distances 2.54(14) and 2.49(17) Å.

Table 3. Bond lengths [Å] and angles [°] for **2** and **6**

Compound **2**					
Sn(1)–C(13)	2.113(3)	Sn(1)–C(12)	2.119(3)	Sn(1)–O(2)	2.188(19)
Sn(1)–O(1)	2.355(19)	O(1)–C(1)	1.257(3)	O(2)–C(1)	1.269(3)
O(2)–Sn(1)	2.188(19)	O(3)–C(9)	1.366(4)	O(3)–C(10)	1.411(4)
O(4)–C(8)	1.372(5)	O(4)–C(10)	1.407(6)	C(1)–C(2)	1.476(4)
C(13)–Sn(1)–C(11)	20.50(15)	C(13)–Sn(1)–C(12)	119.74(14)	C(11)–Sn(1)–C(12)	119.42(14)
C(13)–Sn(1)–O(2)	84.85(10)	C(11)–Sn(1)–O(2)	95.77(11)	C(12)–Sn(1)–O(2)	95.18(10)
C(13)–Sn(1)–O(1)	83.76(10)	C(11)–Sn(1)–O(1)	86.32(11)	C(12)–Sn(1)–O(1)	94.22(10)
Compound **6**					
Sn(1)–O(4)	2.105(14)	Sn(1)–C(33)	2.117(2)	Sn(1)–C(35)	2.120(2)
Sn(1)–O(5)	2.128(13)	Sn(1)–O(3)	2.497(17)	Sn(1)–O(6)	2.545(14)
Sn(1)–C(32)	2.668(2)	O(3)–C(32)	1.243(3)	O(4)–C(32)	1.293(3)
O(5)–C(37)	1.292(2)	O(6)–C(37)	1.245(2)	O(7)–C(46)	1.364(2)
O(8)–C(45)	1.414(3)	O(61)–C(69)	1.42(4)	O(62)–C(67)	1.33(2)
O(4)–Sn(1)–C(33)	103.93(7)	O(4)–Sn(1)–C(35)	102.26(8)	C(33)–Sn(1)–C(35)	144.19(8)
O(4)–Sn(1)–O(5)	80.26(5)	C(33)–Sn(1)–O(5)	102.90(7)	C(35)–Sn(1)–O(5)	105.26(8)
O(4)–Sn(1)–O(3)	56.05(6)	C(33)–Sn(1)–O(3)	86.02(7)	C(35)–Sn(1)–O(3)	88.74(8)
O(5)–Sn(1)–O(3)	136.17(5)	O(4)–Sn(1)–O(6)	135.14(5)	C(33)–Sn(1)–O(6)	89.76(7)
C(35)–Sn(1)–O(6)	88.62(7)	O(5)–Sn(1)–O(6)	54.95(5)	O(3)–Sn(1)–O(6)	168.80(5)
O(4)–Sn(1)–C(32)	28.45(6)	O(7)–C(46)–C(40)	127.7(17)	C(33)–Sn(1)–C(32)	95.90(8)
O(7)–C(46)–C(44)	109.8(17)	C(35)–Sn(1)–C(32)	95.60(8)	O(5)–Sn(1)–C(32)	108.68(6)
C(9)–O(1)–C(8)	104.5(3)	O(3)–Sn(1)–C(32)	27.60(6)	O(6)–Sn(1)–C(32)	163.59(6)

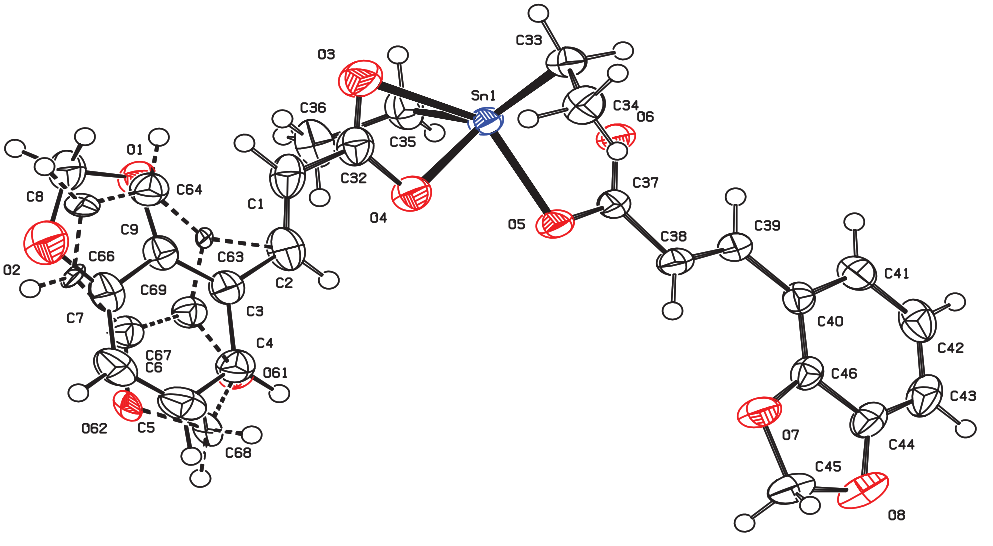

Figure 2. ORTEP drawing of the X-ray structure of **2**.

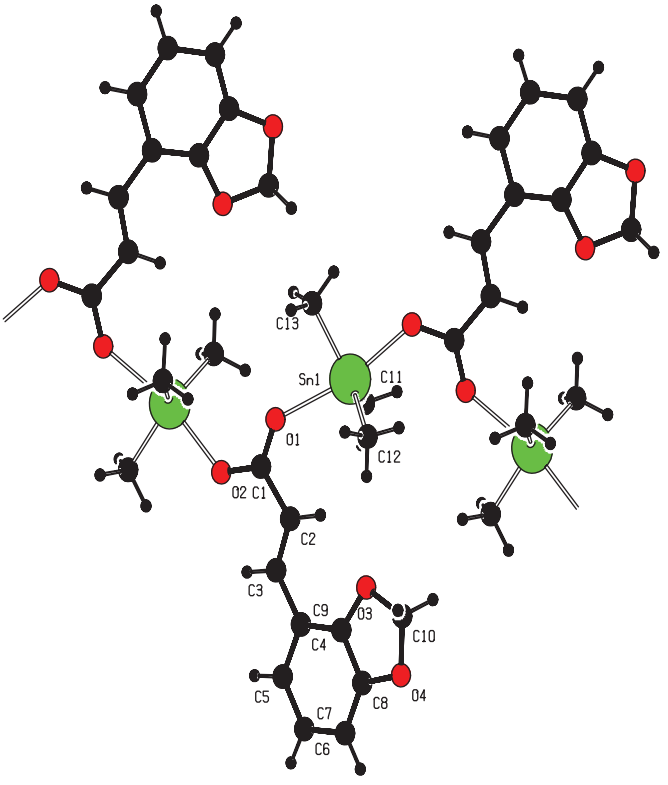

Figure 3. ORTEP drawing of the X-ray structure of **6**.

The structure of **6** shows typical polymeric behavior as observed in trimethyltin compounds in which oxygens of carboxylate are asymmetric with [Sn(1)–O(1) = 2.35(19) Å and Sn(1)–O(2) = 2.11(19) Å]. The geometry around tin is distorted trigonal bipyramidal. The carbonyl group C(1)–O(2) is not sterically encumbered by three methyl groups and is free for attachment with tin of neighboring molecule forming a polymeric chain. In this geometry, three methyl groups are equatorial while both oxygens are axial [28]. The Sn–C bonds with methyl are in the range 2.113(3)–2.119(3) Å. The O–Sn–O bond angle is 167.82°, showing the linearity. The C–Sn–C bond angles are in the range 119.42(14)–120.50(15)°, while C–Sn–O bond angles are given at 134.28(17)–126.21(16)°. The C(1)–O(1) and C(1)–O(2) bond lengths are 1.257(3) and 1.269(3) Å, indicating delocalized bonding with both bonds between single and double bonds. All the bond lengths and angles of benzene and methylenedioxy moiety are within the normal values [35]. Figure 3 shows the molecular structures and atomic numbering scheme of **6**.

3.5. *Microbial assay*

3.5.1. Antitumor assay. Organotin(IV) complexes were screened against *Agrobacterium tumefaciens* (At10) mediated tumor by crown gall tumor inhibition

Table 4. Antitumor assay of organotin complexes.[a]

Compound	Average number of tumors + SE	% Inhibition of tumors
1	0.0 ± 0.0	100.00
2	3.7 ± 0.49	47.88
3	5.5 ± 0.84	22.53
4	3.9 ± 0.56	45.07
5	1.0 ± 0.21	85.91
6	1.7 ± 0.26	76.05
7	3.0 ± 0.55	45.00
8	3.7 ± 0.39	47.88
cis-Cristine*	0.0 ± 0.00	100.00
–ve Control	7.1 ± 0.65	–

Notes: *Reference drug; *cis*-Cristine 1000 μg mL^{-1} of DMSO.
[a]Concentration: 1000 ppm of DMSO.

assay at 1000 μg L^{-1} for incubation of 21 days to determine their antitumor activity as described earlier [36]. The percent tumor inhibition was determined by using the formula:

$$\% \text{ inhibition of tumors} = 100 - (\text{ns/nc} \times 100)$$

ns = average number of tumors in test sample; nc = average number of tumors in negative control (DMSO).

For each test sample 15 replicates were used to study this activity and their average value was used to determine % tumor inhibition, more than 20% tumor inhibition was considered as significant activity [15, 16]. All the reported complexes show the significant antitumor activity. The data are given in table 4.

4. Conclusion

Organotin(IV) complexes of 2,3-methylenedioxyphenylpropenoic acid have been synthesized in anhydrous toluene and characterized by various analytical and spectroscopic techniques. The complexes in solution are tetrahedral for triorganotin(IV) complexes while polymeric structure was exhibited by triorganotin(IV) complex with five-coordinate tin. In diorganotin(IV) derivatives, tin is six-coordinate. These complexes have good antitumor activity against the tested bacterial strain (At10).

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 635321, and 635320 for **2** and **6**, respectively. Copies of these information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

M. Hussain, M. Hanif, and M.S. Ahmad are thankful to Higher Education Commission, Pakistan for financial support. M. Hanif is also thankful to PAEC (Pakistan Atomic Energy Commission) for study leave.

References

[1] M.J. Clarke, F. Zhu, D.R. Frasca. *Chem. Rev.*, **99**, 2511 (1999).
[2] T.S. Cameron, P.K. Bakshi, R. Thangarasa, T.B. Grindley. *Can. J. Chem.*, **70**, 1623 (1992).
[3] A. Jancso, L. Nagy, E. Moldrheim, E. Sletten. *J. Chem. Soc., Dalton Trans.*, 1587 (1999).
[4] S.U. Rehman, Z.H. Chohan, F. Gulnaz, C.T. Supuran. *J. Enzyme Inhib. Med. Chem.*, **20**, 333 (2005).
[5] M. Gielen. *Appl. Organomet. Chem.*, **16**, 481 (2002).
[6] J.A. Zubita, J.J. Zuckerman. *Inorg. Chem.*, **24**, 251 (1987).
[7] Q.L. Xie, X.H. Xu, H.G. Wang, X.K. Yao, R.J. Wang, Z.G. Zhang, J.M. Hu. *Acad. Chim. Sin.*, **49**, 1085 (1991).
[8] V. Chandrasekhar, S. Nagendran, V. Baskar. *Coord. Chem Rev.*, **1**, 235 (2002).
[9] M. Nath, S. Pokharia, R. Yadav. *Coord. Chem. Rev.*, **99**, 215 (2001).
[10] R. Barbieri, A. Silvestri, V. Piro. *J. Chem. Soc., Dalton Trans.*, 3605 (1990).
[11] M.J. Hynes, M.O. Dowd. *J. Chem. Soc., Dalton Trans.*, 563 (1987).
[12] G. Arena, R. Cali, A. Contino, A. Musumeci, S. Musumeci, R. Purello. *Inorg. Chim. Acta*, **237**, 187 (1995).
[13] P. Surdy, P. Rubini, N. Buzas, B. Henry, L. Pellerito, T. Gajda. *Inorg. Chem.*, **38**, 346 (1999).
[14] M. Gielen, E.R.T. Tiekink, in: M. Gielen, E.R.T. Tiekink (Eds.), *Metallotherapeutic Drug and Metal-based Diagnostic Agents*: *Tin Compounds and Their Therapeutic Potential*, Wiley, New York, Chapter 22, pp. 421–439 (2005).
[15] M. Hanif, M. Hussain, S. Ali, M.H. Bhatti, M.S. Ahmad, B. Mirza, H.S. Evans. *Turk. J. Chem.*, **31**, 349 (2007).
[16] M.S. Ahmed, M. Hussain, M. Hanif, S. Ali, B. Mirza. *Molecules*, **12**, 2348 (2007).
[17] R.B. Kelly, B.A. Beckett. *Can. J. Chem.*, **47**, 2501 (2001).
[18] M. Gielen, P. Lelieveld, D. de Vos, R. Willem. In *Metal Complexes in Cancer Chemotherapy*, B.K. Keppler (Ed.), pp. 369–384, VCH, Weinheim (1993).
[19] S. Shahzadi, K. Shahid, S. Ali, M. Mazhar, A. Badshah, E. Ahmed, A. Malik. *Turk. J. Chem.*, **29**, 273 (2005).
[20] K. Shahid, S. Shahzadi, S. Ali, M. Mazhar. *Bull. Korean Chem. Soc.*, **27**, 44 (2006).
[21] M.H. Bhatti, S. Ali, F. Huma, S. Shahzadi. *Turk. J. Chem.*, **29**, 463 (2005).
[22] P.L. Chen, C.C. Cheng. *J. Med. Chem.*, **13**, 867 (1970).
[23] W.L.F. Armaego, C.L.L. Chai. In *Purification of Laboratory Chemicals*, 5th Edn, Butterworth-Heinemann, London, New York (2003).
[24] C.K. Johnson. *ORTEPII*, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA (1976).
[25] R.B. Kelly, B.A. Beckett. *Can. J. Chem.*, **47**, 2501 (1969).
[26] Imtiaz-ud-din, M. Mazhar, K.M. Khan, M.F. Mahon, K.C. Molloy. *J. Organomet. Chem.*, **689**, 899 (2004).
[27] X.N. Fang, X.Q. Song, Q.L. Xie. *J. Organomet. Chem.*, **619**, 43 (2001).
[28] M. Hussain, M. Hanif, S. Ali, S. Shahzadi, H.S. Evans. *Turk. J. Chem.*, **32**, 25 (2008).
[29] Sadiq-ur-Rehman, S. Ali, A. Badshah. *Synth. React. Inorg. Met.-Org. Chem.*, **34**, 443 (2004).
[30] H.O. Kalinowski, S. Berger, S. Brown. *^{13}C NMR Spektroskopie*, Thieme, Verlag, Stuttgart, Germany (1984).
[31] J. Holecek, A. Lycka. *Inorg. Chim. Acta*, **118**, L15 (1986).
[32] M. Danish, S. Ali, A. Badshah, M. Mazhar, H. Masood, A. Malik, G. Kehr. *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 863 (1997).
[33] E.R.T. Tiekink. *Trends. Organomet. Chem.*, **1**, 71 (1994).
[34] Sadiq-ur-Rehman, H. Vienly, S. Ali, A. Badshah, M. Parvez. *Acta Cryst.*, **E60**, m1144 (2004).
[35] Sadiq-ur-Rehman, S.R. Shouldice, S. Ali, A. Badshah, M. Parvez. *Acta Cryst.*, **E60**, m670 (2004).
[36] A. Rehman, M.I. Choudhary, W.J. Thomsen. *Bioassay Techniques for Drug Development*, Harwood Academic Publishers, The Netherlands (2001).