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Synthesis, Spectroscopic Exploration, Biocidal Activities, and Crystal Structures of 3-(3-Fluorophenyl)-2-phenylpropenoic Acid and Trimethyltin(IV) Complex

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ABSTRACT: *The ligand, 3-(3-fluorophenyl)-2-phenylpropenoic acid, [$C_{15}H_{11}FO_2$] (**I**) was prepared by reacting equimolar amount of phenyl acetic acid with 3-fluorobenzaldehyde (1:1) using Perkin condensation method. The trimethyltin(IV) carboxylate, [$Me_3SnO_2FH_{10}C_{15}$] (**II**) was synthesized by refluxing an equimolar (1:1) mixture of trimethyltin chloride and silver salt of the ligand acid, [$C_{15}H_{10}FO_2Ag$] (**Ia**). The ligand and complex both were characterized by elemental analysis, IR, mass, ^1H NMR, and X-ray crystallographic data. On the basis of ^1H NMR data, ($^2J[^{117/119}Sn, ^1H]$ and C–Sn–C bond angle), it is concluded that the environment around the tin atom in solution is tetrahedral. The Infrared spectroscopic results showed that trimethyltin(IV) derivative has 5-coordinated polymeric structure with bridging carboxylate groups in the solid state, which has been confirmed by the X-ray crystallographic data. The crystal of ligand acid (**I**) is triclinic with space group Pbar1. However, the crystal of the complex (**II**) is monoclinic with space group $C_{2/c}$. The geometry around the tin atom is distorted trigonal bipyramid with O(1) and O(2) atoms in apical positions. The ligand (**I**) and complex (**II**) were also tested for their biocidal activities.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:398–406, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20032

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INTRODUCTION

Several series of organotin(IV) compounds were found to be active in vitro against the human cell lines of the A_{204} rhabdomyosarcoma, MCF-7 mammary carcinoma, T_{24} bladder carcinoma, WiDr colon carcinoma, and IgR-37 melanoma [1]. Furthermore, organotin(IV) complexes with ligands bearing fluorine, sulfur, nitrogen, and oxygen as substituents have widely been tested for their possible use in cancer chemotherapy, and a few of them proved to be active against tumors [2]. In view of the antitumor activity of organotin(IV) complexes with ligands having fluorine on organic moiety [3], we have synthesized a series of organotin(IV) compounds of analogous ligands. Since exploration of the structure–activity relationships of such systems provided numerous reports in literature [4–6], we therefore, present in this paper the synthesis, elemental analysis, infrared, ^1H NMR, mass spectrometric analysis,

and crystal structures of the 3-(3-fluorophenyl)-2-phenylpropenoic acid (**I**) and trimethyltin(IV) [3-(3-fluorophenyl)-2-phenylpropenoate] (**II**).

RESULTS AND DISCUSSION

The ligand was synthesized by a reported method [7]. The trimethyltin 3-(3-fluorophenyl)-2-phenylpropenoate complex was prepared by treating silver salt of the ligand acid with trimethyltin chloride in 1:1 molar ratio in dry chloroform [Eq. (1)]. The composition of ligand acid, complex, and nature of bonding were recognized by spectroscopic data and X-ray crystallography.

$$(CH_3)_3SnCl + AgL \rightarrow (CH_3)_3SnL + AgCl \qquad (1)$$

Both the compounds are stable and soluble in common organic solvents.

Infrared Spectroscopy

The infrared spectral data give important informations about the bonding behavior of ligand and hence the structure of compound. Particularly the frequency difference, $\Delta\nu = \nu_{asym}(COO) - \nu_{sym}(COO)$ is of the main importance. The bands attributed to $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ usually shift their positions rather significantly to lower and upper frequency region, respectively upon coordination to a metal and decrease the value of $\Delta\nu$. It may be due to conversion of the structure of complex from four- to five-coordinated symmetry [8,9]. In this case, value of $\Delta\nu$ for trimethyltin(IV) derivative is within the range of silver salt of the ligand acid. Thus, data in Table 1 suggest that the carboxyl group in the complex behaves as a bidentate ligand and may have carboxylate-bridged five-coordinated polymeric structure (Fig. 1). The absorption bands ν(Sn—C) at 552 cm^{-1} and ν(Sn—O) at 463 cm^{-1} are also important and support the formation of the compound [10,11]. Furthermore, another explicit feature in the spectra of the complex is the absence of the broad band in the region 2857–3400 cm^{-1}, which

TABLE 1 Infrared Data (cm^{-1}) for the Synthesized Compounds

Compound No.	ν(COO) Asym.	ν(COO) Sym.	$\Delta\nu$	ν(C–O)	ν(Sn–C)	ν(Sn–O)
I (LH)	1677 s	1420 s	257	1243	–	–
II	1571 s	1370 s	201	1245 w	552	463
Ia (AGL)	1581 s	1356 s	225	1243 w	–	–

s = strong, m = medium, w = weak.

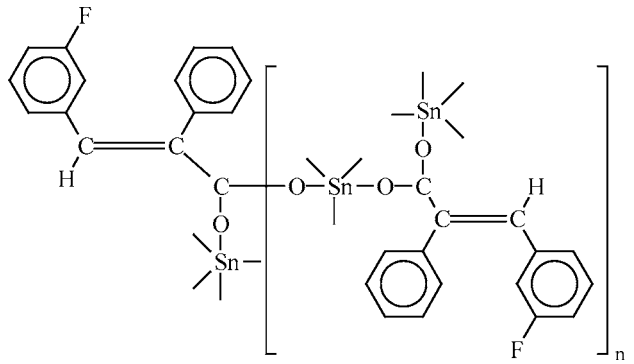


FIGURE 1 Polymeric structure for trimethyltin(IV)-3-(3-fluorophenyl)-2-phenyl-propenoate.

appears in the free ligand (**I**) as the ν(O—H) vibration, thus indicating metal–ligand bond formation through this site.

^{1}H NMR Spectroscopy

^{1}H NMR data in $CDCl_3$ solution of the ligand acid and its trimethyltin(IV) derivative are given in Table 2. In the spectrum of the ligand, a signal at 7.91 ppm is due to olefinic proton [12]. The resonance signals for aromatic protons were assigned with their distinct multiplicity and J values, $^3J(^1H,^1H)$ and $^nJ(^1H,^{19}F)$. The analogous pattern of the signals at rather similar positions has been observed for the protons on the ligand in the trimethyltin(IV) derivative (Table 2). However, the methyl protons of the $Sn(CH_3)_3$ moiety appear as a sharp singlet at 0.58 ppm with well-resolved coupling constant, $^2J[^{119}Sn,^1H]$ = 57.6 Hz that reflects a tetrahedral geometry of the complex

TABLE 2 ^{1}H NMR Data[a–e] (in ppm) of the 3-(3-Fluorophenyl)-2-phenylpropenoic Acid and Trimethyltin(IV) Derivative

^1H No.	*Ligand Acid*	*Me_3SnL*
3	7.91 (s)	7.80 (s)
5	6.89–6.90 (d, 7.8)	6.83–6.84 (d, 7.7)
7	6.69–6.71 (d, 10.2)	6.65–6.67 (d, 10.5)
8	7.13–7.17 (dd, 8.0)	7.07–7.12 (dd, 7.9)
9	6.92–6.93 (d, 2.03)	6.86–6.87 (d, 2.3)
11	7.37–7.42 (m)	7.30–7.35 (m)
12	7.37–7.42 (m)	7.30–7.35 (m)
13	7.23–7.25 (m)	7.19–7.21 (m)
α	–	0.58 (s), ^2J [57.6]

[a] In $CDCl_3$ at 300 K.
[b] Chemical shift (δ) in ppm. $^2J[^1H, ^1H]$, $^2J[^{119}Sn, ^1H]$ in Hz are listed in parenthesis.
[c] Multiplicity is given as s = singlet, d = doublet, dd = doublet of doublet, and m = multiplet.
[d] For numbering scheme, see Fig. 2.
[e] Sn—CH_3^{α}.

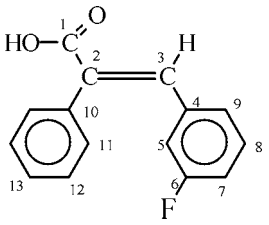
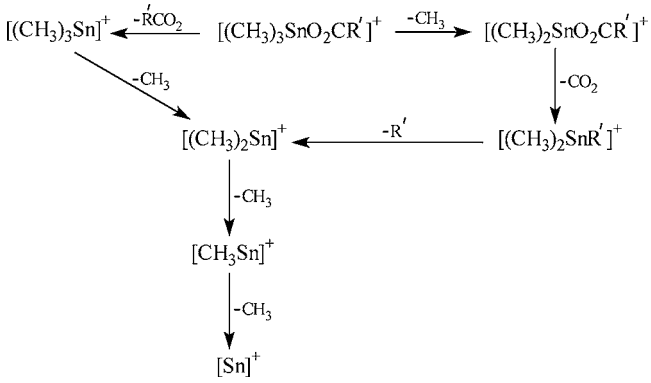


FIGURE 2 Numbering scheme of 3-(3-fluorophenyl)-2-phenylpropenoic acid.

in solution [9]. The C—Sn—C bond angle calculated by Lockhart's equation (110.8°), further confirm the proposed slightly distorted tetrahedral geometry around the tin atom in solution [13].

Mass Spectrometry

The important ions observed in the mass spectra of ligand acid and its trimethyltin(IV) derivative are given in Table 3, and the fragmentation pattern for the complex is described in Scheme 1. The molecular ion peak is perceived for both compounds. The observed fragmentation pattern follows the expected pathway and is in good agreement with the structures of the compounds. For trimethyltin(IV) derivative the base peak is derived from $(C_6H_5)CCH(C_6H_4F)$=R′ part of the ligand in the complex, whereas, in ligand acid M^+ ion appears as a base peak. The primary fragmentation in the ligand acid involves loss of COOH or F group. In trimethyltin(IV) derivative the primary fragmentation is due to elimination of CH_3 group or ligand (R′COO). If primary fragmentation is due to the release of CH_3 group, then secondary and tertiary fragmentations involve loss of CO_2 and R′, respectively. The other pathway involves loss of R group in the secondary fragmentation. However, the next fragmentation behaviour is similar in both routes and occurs through successive elimination of CH_3 groups, which finally ends to [Sn^+], (see Scheme 1).



$R'CO_2$ = Acid anion ($C_{15}H_{10}FO_2^-$)

SCHEME 1 Fragmentation pattern of $(CH_3)_3SnL$.

X-ray Structures

Crystal Structure of (I). The ORTEP plot of molecular structure for (**I**) is shown in Fig. 3 with atomic labeling scheme while the selected bond lengths, bond angles, and torsion angles are shown in Table 4.

The crystal data obtained and Fig. 3 reveal that the configurations around the C(2) and C(3) are distorted trigonal planes with compressed C(10)—C(2)—C(1) (116.81(13) Å), and expanded C(3)—C(2)—C(10) (124.18(12) Å), and C(2)—C(3)—C(4) (129.30(13) Å) bond angles, respectively. It is due to the steric interaction between the two phenyl rings that acquire a position almost perpendicular to each other. It is further supported by the values of torsion angles O(1)—C(1)—C(2)—C(10) (−3.9°(2)),

TABLE 3 Fragmentation Pattern and Relative Abundance of 3-(3-Fluorophenyl)-2-phenylpropenoic acid (**I**) and Its Trimethyltin(IV) Derivative

Fragment Ion	(**I**) *Intensity (%) (Acid)*	*Fragment Ion*	(**II**) *Intensity (%) (R=CH₃)*
$[R'COOH]^+$	242 (100)	$[R_3SnOOCR']^+$	406 (8)
$[R''COOH]^+$	223 (16)	$[R_2SnOOCR']^+$	391 (97)
$[R']^+$	197 (87)	$[R_2SnR']^+$	347 (65)
$[R'']^+$	177 (22)	$[R_3Sn]^+$	165 (90)
–	–	$[R_2Sn]^+$	150 (60)
–	–	$[RSn]^+$	135 (66)
–	–	$[Sn]^+$	120 (42)
–	–	$[SnOOCR']^+$	361 (3)
–	–	$[R'COO]^+$	241 (2)
–	–	$[R']^+$	197 (100)

R′ = $(C_6H_5)CCH(C_6H_4F)$ and R″ = $(C_6H_5)CCH(C_6H_4)$.

TABLE 4 Selected Bond Distances (Å), Bond Angles (°), and Torsion Angle (°) for (**I**) and (**II**)

(**I**) *Ligand Acid*		(**II**) *Trimethyltin (IV) Derivative*	
Atoms	*Distance (Å)*	*Atoms*	*Distance (Å)*
O(1)–C(1)	1.232(2)	Sn(1)–O(1)	2.147.(2)
O(2)–C(1)	1.320(2)	Sn(1)–C(1)	2.123(3)
C(1)–C(2)	1.491(2)	Sn(1)–C(2)	2.130(4)
C(2)–C(3)	1.336(2)	Sn(1)–C(3)	2.113(3)
C(2)–C(10)	1.488(2)	Sn(1)–O(2)	2.505(2)
C(3)–C(4)	1.477(2)	O(1)–C(4)	1.282(4)
C(4)–C(9)	1.392(2)	O(2)–C(4)	1.236(4)
C(5)–C(6)	1.384(2)	C(4)–C(5)	1.510(4)
C(6)–C(7)	1.371(2)	C(5)–C(6)	1.339(5)
C(10)–C(11)	1.395(2)	C(5)–C(13)	1.494(4)
C(11)–C(12)	1.387(2)	C(6)–C(7)	1.478(4)
C(12)–C(13)	1.381(2)	C(7)–C(8)	1.389(5)
Atoms	*Angles(°)*	C(8)–C(9)	1.374(5)
O(1)–C(1)–O(2)	123.19(13)	C(9)–C(10)	1.375(5)
O(1)–C(1)–C(2)	121.56(13)	C(13)–C(14)	1.395(4)
O(2)–C(1)–C(2)	115.22(13)	C(13)–C(18)	1.392(4)
C(2)–C(3)–C(4)	129.30(13)	C(14)–C(15)	1.389(5)
C(3)–C(2)–C(10)	124.18(12)	C(15)–C(16)	1.379(5)
C(5)–C(4)–C(3)	123.02(13)	*Atoms*	*Angles(°)*
C(6)–C(7)–C(8)	117.85(13)	O(1)–Sn(1)–O(2)	166.83(8)
C(7)–C(6)–C(5)	123.15(14)	C(1)–Sn(1)–O(1)	94.38(12)
C(9)–C(4)–C(3)	118.28(13)	C(2)–Sn(1)–O(1)	99.65(12)
C(9)–C(4)–C(5)	118.60(13)	C(3)–Sn(1)–O(1)	88.12(12)
C(11)–C(10)–C(2)	119.73(13)	C(1)–Sn(1)–O(2)	82.40
C(11)–C(11)–C(10)	120.14(14)	C(2)–Sn(1)–O(2)	92.97(12)
C(12)–C(13)–C(14)	119.97(13)	C(3)–Sn(1)–O(2)	82.64(12)
C(15)–C(10)–C(2)	121.34(13)	C(1)–Sn(1)–C(2)	120.21(15)
C(15)–C(10)–C(11)	118.89(13)	C(3)–Sn(1)–C(2)	117.65(16)
C(15)–C(14)–C(13)	119.77(15)	C(3)–Sn(1)–C(1)	120.66(15)
Atoms	*Torsion Angles(°)*	C(4)–O(1)–Sn(1)	128.51(19)
O(1)–C(1)–C(2)–C(10)	-3.9(2)	C(4)–O(2)–Sn(1*)	162.3(2)
C(1)–C(2)–C(3)–C(4)	-171.39(14)	O(2)–C(4)–O(1)	123.8(3)
C(2)–C(3)–C(4)–C(5)	27.6(2)	O(1)–C(4)–C(5)	114.1(3)
C(2)–C(3)–C(4)–C(9)	-156.08(16)	O(2)–C(4)–C(5)	122.0(3)
C(3)–C(2)–C(10)–C(11)	62.9(2)	C(5)–C(6)–C(7)	130.5(3)
C(10)–C(2)–C(3)–C(4)	7.6(3)	C(6)–C(5)–C(13)	124.7(3)
–	–	C(8)–C(7)–C(6)	117.4(3)
–	–	C(8)–C(7)–C(12)	118.5(3)
–	–	C(8)–C(9)–C(10)	120.3(3)
–	–	C(11)–C(10)–C(9)	118.4(3)
–	–	C(11)–C(12)–C(7)	118.7(3)
–	–	C(12)–C(7)–C(6)	124.0(3)
–	–	C(13)–C(5)–C(4)	117.3(3)
–	–	C(14)–C(13)–C(5)	119.9(3)
–	–	C(15)–C(14)–C(15)	119.9(3)
–	–	C(15)–C(16)–C(17)	119.8(3)
–	–	C(18)–C(13)–C(14)	118.7(3)
–	–	C(18)–C(17)–C(16)	119.9(3)
		Atmons	*Torsion Angles (°)*
		O(1)–C(4)–C(5)–C(13)	13.6(4)
–	–	O(2)–C(4)–C(5)–C(6)	16.6(5)
–	–	C(4)–C(5)–C(6)–C(7)	−179.3(3)
–	–	C(4)–C(5)–C(13)–C(18)	66.6(4)
–	–	C(5)–C(6)–C(7)–C(12)	22.6(6)
–	–	C(6)–C(5)–C(13)–C(14)	63.2(4)
–	–	C(13)–C(5)–C(6)–C(7)	4.8(5)

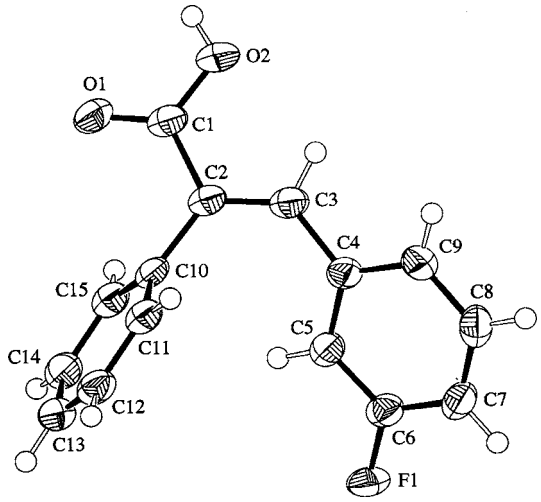


FIGURE 3 ORTEP drawing of the X-ray structure of $[C_{15}H_{11}FO_2]$ (**I**).

C(2)—C(3)—C(4)—C(9) (−156.08 (16)°), and C(10)—C(2)—C(3)—C(4) (7.6 (3)°). It is also substantiated by the fact that C(2)=C(3) bond is not coplanar with the phenyl moieties with C(2)—C(3)—C(4)—C(5), and C(3)—C(2)—C(10)—C(11) dihedral angles of 27.6°(2) and 62.9°(2), respectively. However, C(2)=C(3) bond is normal in bond length (1.336(2) Å).

The carboxyl group displays an interesting feature in the crystal structure of (**1**) and O(2)—O(1) are at a distance of 2.6482(16) Å. The carboxyl group interacts with its counterpart in the adjacent molecule and forms cyclic carboxyl dimer via hydrogen bonding, O(2)—H(2)—O(1). The data are given in Table 5. These hydrogen bonds shown in the unit cell packing of compound (**I**) increase the crystal stability, compactness, and hold the structure in two-dimensional space (Fig. 4).

Crystal Structure of (II). Figure 5 shows a one-dimensional view of the molecule and also gives the atomic numbering scheme different from that used for structural nomenclature. Selected bond distances, bond angles, and torsion angles are given in Table 4.

The crystal structure shows that the tin atom is coordinated with two oxygen atoms of the 3-(3-fluorophenyl)-2-phenylpropenoate ligand via carboxylate moieties and acquires a polymeric chain structure, shown in Fig. 2. The Sn(1)—O(1) bond distance, 2.147(2) Å is significantly different from Sn(1)—O(2) bond distance 2.505(2) Å, indicating that the former is a covalent bond and the latter is acting as a weak coordinate covalent bond corresponding to an anisobidentate ligand. The Sn—C bond distances are almost identical within the experimental error [2.113(3), 2.123(3), 2.130(4) Å] and lie in the range reported earlier for the related compounds [14]. The angles C(3)—Sn(1)—C(1) and C(1)—Sn(1)—C(2) with values 120.66(15) and 120.21(15) Å, respectively are in close agreement with angle 120° of a regular trigonal plane. However, the angle C(3)—Sn(1)—C(2) [117.65(16) Å] slightly deviates from the ideal value of 120°. Similarly, the C—Sn—O angles lie in the range 82.40(12) to 99.65(12)° and O(1)—Sn(1)—O(2) angle is 166.83(8)°. All these evidences might suggest description of the tin environment as a trigonal bipyramid with O(1) and O(2) in the apical positions and the three methyl groups in the equatorial positions.

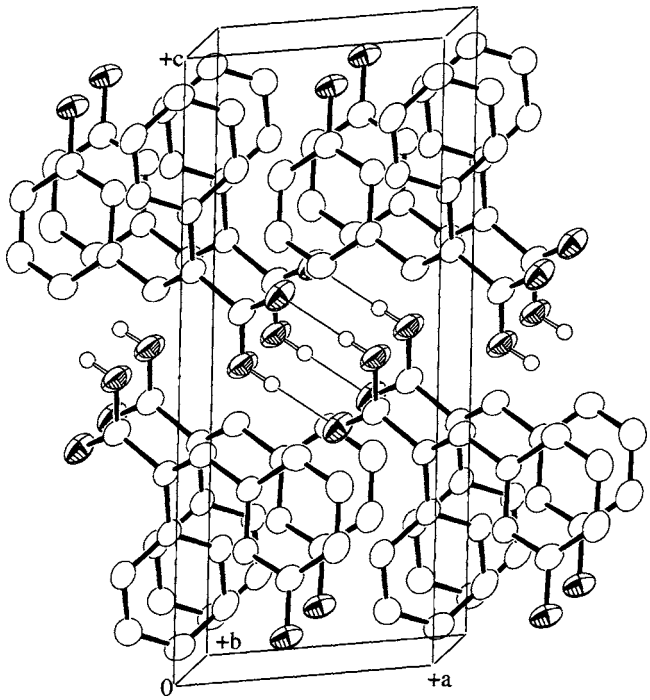


FIGURE 4 Unit cell packing of Compound (**I**).

TABLE 5 Hydrogen-Bonding Geometry (Å, °)[a]

D—H- - -A	d(D—H)	d(H- - -A)	d(D- - -A)	<DHA
O(2)—H(2)- - -O(1)#1	0.84	1.81	2.6482(16)	176

[a]Symmetry transformation used to generate equivalent atoms: #1 $-x+1, -y, -Z+1$.

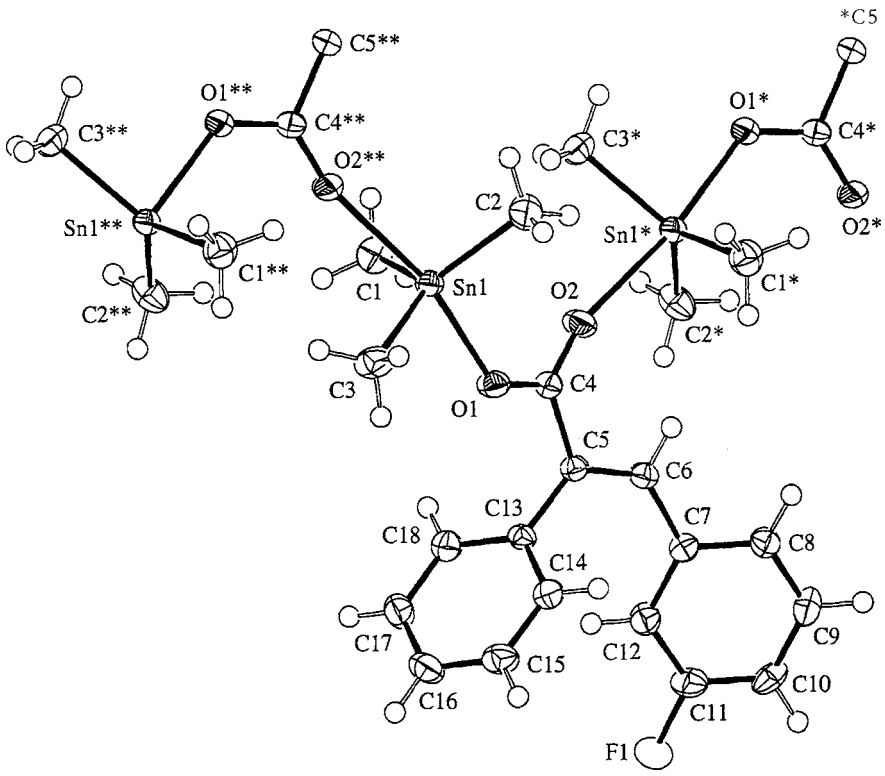


FIGURE 5 PRTEP drawing of the X-ray structure of [$C_{18}H_{19}FO_2SnJ$] (**II**).

The sum of the equatorial angles is 358.52° instead of the ideal 360° and the tin lies 0.358 Å out of the equatorial plane toward the more strongly bonded O(1) atom. This indicates the slightly distorted bipyramidal geometry, which is compatible with the earlier reports [9,15]. The structure of the ligand (bond distances and angles) on complexation remains almost unchanged.

Biological Activity

The synthesized ligand acid (3-(3-fluorophenyl)-2-phenylpropenoic acid) and derivative [trimethyltin(IV)] were tested for their microbial toxicity against a set of bacterial and fungal populations. The results are summarized in Tables 6 and 7, respectively. The compounds were also

TABLE 6 Bactericidal Data[a,b] of 3-(3-Fluorophenyl)-2-phenylpropenoic Acid and Its Trimethyltin(IV) Derivative

		Zone of Inhibition (mm)		
Name of Bacterium	*Clinical Implication*	(**I**) *Acid*	(**II**)	*References Drug*
Escherichia coli	Infection of wounds, urinary tract, and dysentery	–	–	30
Bacillus subtilis	Food poisoning	9	9	31
Shigella flexenari	Blood diarrhea with fever and severe prostration	–	–	33
Staphylococcus aureus	Food poisoning, scaled skin syndrome, endocarditis	10	14	43
Pseudomonas aeruginosa	Infection of wounds, eyes, septicemia	11	14	25
Salmonella typhi	Typhoid fever, food poisoning, localized infection	10	–	41

[a] *In vitro*, agar well diffusion method, concentration 1 mg/ml of DMSO.
[b] Reference drug, Imipenum.

TABLE 7 Antifungal Activity[a] of 3-(3-Fluorophenyl)-2-phenylpropenoic Acid and Its Trimethyltin(IV) Derivative

	Percent Inhibition				
Name of Fungus	(**I**) *Acid*	(**II**)	*Standard Drug*	*Percent Inhibition*	*MIC μg/ml*
Trichophyton longifusus	50	90	Miconazole	100	70
Candida albicans	55	65	Miconazole	100	110.8
Aspergillus flavus	50	75	Amphotericin-B	100	20
Microsporum canis	90	90	Miconazole	100	98.4
Fusarium solani	65	70	Miconazole	100	73.25
Candida glaberata	0	0	Miconazole	100	110.8

[a]Concentration: 200 μg/ml of media.

evaluated for their cytotoxicity using Brine–Shrimp method [16] and results are listed in Table 8.

The ligand acid and complex were screened for their antibacterial activity against *Escherichia coli, Bacillus subtilis, Shigella flexenari, Staphylococcus aureus, Pseudomonas aeruginosa*, and *Salmonella typhi* using "agar well diffusion method" [17] and the results obtained were compared with a standard reference drug (imipenum). The ligand acid was found to be inactive against *Escherichia coli* and *Shigella flexenari* while showed some activity against *Bacillus subtilis, Staphylococcus aureus, Pseudomonas aeruginosa*, and *Salmonella typhi*, which is nonsignificant as compared to standard drug. Similarly, the complex Me_3SnL was found to be inactive against *Escherichia coli, Shigella flexenari*, and *Salmonella typhi* and showed low activity against other tested bacteria. Both of the compounds were found to have lower activity against different bacteria than the reference drug had.

The compounds were also screened against various fungal strains using the "agar tube dilution protocol test" [18]. Miconazole and amphotericin B were used as standard drugs. It was observed that the ligand and its complex are inactive against *Candida glaberata*. The ligand acid was found to have significant activity against *Microsporum canis* only and showed moderate activity against the other tested fungi. However, trimethyltin(IV) derivative in addition to showing activity against *Microsporum canis* is also significantly active against *Trichophyton longifusus* and gave moderate activity against the other examined fungal strains. The results given in Table 7 indicate that the complex is more active than the free ligand against different fungi.

TABLE 8 Cytotoxicity Data[a–d] of 3-(3-Fluorophenyl)-2-phenylpropenoic Acid and Its Trimethyltin(IV) Derivative

Compound	(**I**) *Acid*	(**II**)	*Reference Drug*
LD_{50}	–	1.7248	7.4625

[a]Concentration: 1, 10, 100 μg/ml of media.
[b]Against brine-shrimp(in vitro).
[c]No cytotoxicity for acid (**I**).
[d]Reference drug, Etoposide.

For both compounds LD_{50} data have been collected by "Brine–Shrimp lethality bioassay method" [16]. It was observed that the ligand acid is absolutely nontoxic, whereas trimethyltin(IV) derivative showed positive lethality with LD_{50} value 1.7248 μg/ml. Thus the compound, trimethyltin(IV) 3-(3-flurophenyl)-2-phenylpropenoate is more toxic in comparison to the standard drug etoposide.

EXPERIMENTAL

Materials

The ligand 3-(3-flurophenyl)-2-phenylpropenoic acid was prepared, following the procedure reported in literature [7]. Trimethyltin chloride was purchased from Aldrich Chemicals (USA). The solvent used were dried *in situ* using standard methods [19].

General Procedure for Synthesis

The silver salt (2.0 g, 6.0 mmol) was suspended in 60 ml of dry chloroform in a 250 ml two-necked round bottom flask equipped with a magnetic bar and a condenser. Trimethyltin chloride (1.2 g, 6.0 mmol) dissolved in chloroform was added slowly with constant stirring. The reaction mixture was refluxed for 7–8 h and allowed to stand overnight at room temperature. The silver chloride formed was filtered off and solvent was removed under reduced pressure. The solid obtained was recrystallized from chloroform/*n*-hexane (80:20). Melting point 153–155°C. Anal Cald for $C_{18}H_{19}FO_2Sn$: C, 53.33; H, 4.69. Found: C, 53.33; H, 4.65.

Instrumentation

Melting points were measured on a MPD Mitamura Riken Kogyo (Japan) electrothermal melting point apparatus. Infrared spectra were obtained using a

Bio-Rad Excaliber FTIR, model FTS 300 MX spectrometer (USA), in the 4000–400 cm^{-1} range with the samples as KBr discs. ^1H NMR spectra were recorded on a Bruker apparatus at 500 MHz, using $CDCl_3$ as an internal reference [δ ^1H ($CDCl_3$) = 7.25 ppm]. Mass spectral data were determined on a Mat 311A mass spectrometer. X-ray single crystal analysis measurements were made on a Nonius KappaCCD diffractometer with graphite monomchromated M_o–K_α radiation.

Crystal Structure Determination

The ligand acid (**I**) and its trimethyltin(IV) derivative (**II**) were recrystallized from chloroform/*n*-hexane (80:20) on slow evaporation at room temperature.

A suitable crystal of the 3-(3-fluorophenyl)-2-phenylpropenoic acid with dimensions $0.18 \times 0.15 \times 0.14$ mm^3 was used for crystal data collection. X-ray data were collected [20] at a temperature of 173(2)K on a Nonius KappaCCD diffractometer with graphite monochromated M_o–K_α radiation, using ω and φ scans to a maximum θ value of 27.4°. Cell constants from the refinement of 4956 reflections in the range $3.6 < \theta < 27.4°$ corresponded to a primitive triclinic cell.

For trimethyltin(IV) derivative of 3-(3-fluorophenyl)-2-phenylpropenoic acid ($C_{18}H_{19}FO_2Sn$) (Fig. 4), a colourless block crystal ($0.12 \times 0.12 \times 0.05$ mm^3) was used for data collection on a Nonius KappaCCD diffractometer. X-ray measurements were carried out at 173(2)K using the ω and φ scans to a maximum

TABLE 9 Crystal Data, Data Collection, Structural Solution and Refinement of Compounds C_{15} H_{11} FO_2 (**I**) and C_{18} H_{19} FO_2Sn (**II**)

	(**I**)	(**II**)
Empirical formula	$C_{15}H_{11}FO_2$	$C_{18}H_{19}FO_2Sn$
Formula weight	242.24	405.02
Temperature (K)	173 (2)	173 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	*P* bar1	C_2/c
Unit cell dimensions		
a (Å)	5.773 (2)	17.838 (7)
b (Å)	7.474 (3)	10.444 (5)
c (Å)	14.140 (6)	19.777 (7)
α (°)	77.14 (2)	–
β (°)	84.55 (3)	112.97 (2)
γ (°)	84.86 (2)	–
Volume $(Å)^3$	590.6 (4)	3392 (2)
Z	2	8
D_{calc} (g cm^{-3})	1.362	1.586
Absorption coefficient (mm^{-1})	0.10	1.52
F(OOO)	252	1616
Crystal size (mm^{-3})	$0.18 \times 0.15 \times 0.14$	$0.12 \times 0.2 \times 0.05$
Theta range for data collection (°)	3.6–27.4	4.0–27.5
Index ranges	$-7 <= h <= 7$	$-23 <= h <= 23$
	$-9 <= k <= 9$	$-13 <= k <= 12$
	$-17 <= l <= 18$	$-25 <= l <= 25$
Reflections collected	4956	6249
Independent reflections	2685 [R(int) = 0.027]	3872 [R(int) = 0.032]
Refinement method	Full-matrix least-squares on F_2	Full-matrix least-squares on F_2
Data/restraints/parameters	2685/0/174	3872/0/212
Goodness-of-fit on F_2	1.03	1.02
Final *R* indices [I > 2 sigma (I)]	$R_1 = 0.044$	$R_1 = 0.035$
	$wR_2 = 0.107$	$wR_2 = 0.073$
R indices (all data)	$R_1 = 0.79$	$R_1 = 0.060$
	$wR_2 0.126$	$wR_2 = 0.082$
Weighting scheme	$W = 1/[\sigma^2(Fo_2) + (0.067\,P)^2 + 0.020\,P]$	–
	Where $P = (Fo^2 + 2Fc^2)/3$	–
(Δ/θ) max	0.00	–
Largest diff.peak and hole (e $Å^{-}3$)	0.17 and −0.21	0.91 and −0.86

θ value of 27.5° and M_o–K_α radiation monochromated with a graphite.

The data were corrected for Lorentz and polarization effects and for absorption using multiscan method [21]. The structures were solved by the Direct methods [22] and expanded using Fourier techniques [23]. They were refined by full-matrix least-squares calculation with SHELXL 97 [24]. The nonhydrogen atoms were refined anisotropically while hydrogen atoms bonded to carbon atoms were included at geometrically idealized positions and were not refined. The hydrogen atoms bonded to carboxyl oxygen atoms in **I** were found from the difference density map and were included during structure refinement. Crystallographic data, details of the data collection, structure solution, and refinements are listed in Table 9.

Supplementary Data

A complete list of crystallographic data and parameters including atomic coordinates are deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44-1223-336033; e-mail: linstead@ccdc.cam.ac.uk; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk. The deposition (CCDC) numbers allocated to the crystal structures of $C_{15}H_{11}FO_2$ (**I**) and $C_{18}H_{19}FO_2Sn$ (**II**) are 218975 and 218976, respectively.

CONCLUSION

The results obtained from spectroscopic and X-ray single crystal analysis led to the conclusion that the carboxylate moiety of the complex in the solution behaves as a monodentate ligand, while in the solid state it adopts an orientation to act as an anisobidentate donor group.

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