

## Synthesis, Multinuclear ( $^1\text{H}$ , $^{13}\text{C}$ and $^{119}\text{Sn}$ ) NMR, Mass, Mossbauer, and Crystal Structure of Diethyltin(IV) bis-[2-(2-fluoro-4-biphenyl)]propanoate

$^1\text{S. MAHMOOD}$ ,  $^1\text{S. SHAHZADI}$ ,  $^1\text{S. ALI}^*$ ,  $^2\text{M. PARVEZ}$ ,  $^1\text{M. MAZHAR}$  AND  $^1\text{A. BADSHAH}$

$^1$ Department of Chemistry

Quaid-i-Azam University, Islamabad – 45320, Pakistan

$^2$ Department of Chemistry

University of Calgary, 2500 University Drive,

N. W. Calgary, Alberta, Canada T2N 1N4

(Received 31<sup>st</sup> March, 2005, revised 11<sup>th</sup> October, 2005)

**Summary:** Diethyltin(IV) bis[2-(2-fluoro-4-biphenyl)]propanoate was synthesized and characterized by IR, elemental analysis, mass spectrometry, mossbauer and multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$ ) spectroscopy. The crystal structure of reported compound was determined by X-ray diffraction method. A colourless prismatic crystal of the title compound displayed in the triclinic space group  $P\bar{1}$  (#2), with  $a = 9.906(8)\text{\AA}$ ,  $b = 18.387(15)\text{\AA}$ ,  $c = 8.715(9)\text{\AA}$ ,  $\alpha = 97.88(8)^\circ$ ,  $\beta = 105.74(8)^\circ$  and  $\gamma = 80.21(7)^\circ$ .

### Introduction

Organotin compounds are widely distributed toxicants. These compounds are used as stabilizers or glass coatings, as catalysts for the formation of polyurethane foams, as biocides for the agricultural applications and as preservatives for timber, wood, textiles, paper and leather [1,2].

Organotin(IV) compounds  $\text{R}_n\text{SnX}_{4-n}$  exhibit a variety of pharmaceutical applications depending on the number  $n$ , on the type of organic groups  $\text{R}$  bound to tin and the ligand  $\text{X}$ . Organotin compounds have been studied as possible candidates for antitumor activity, chemotherapy, leishmaniasis and helminthes, and parasitic infection of the skin [3,4].

In this paper, we report the crystal structure and spectroscopic characterization of diethyltin(IV) bis[2-(2-fluoro-4-biphenyl)]propanoate. Flurbiprofen is used as ligand acid. It is non-steroidal anti-inflammatory drug that may have certain significant drug interaction.

As contradiction, its very abrupt use may also have the risk of bleeding on the antiplatelet action. It has 3-4 hours half life. Its mode of action is considered to be mild to moderate [5,6]. The crystal structure of the title compound (Fig. 1) was studied by X-ray crystallography.

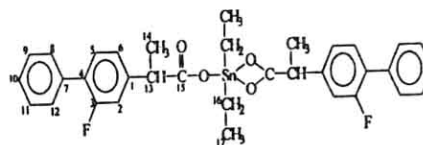


Fig. 1: Numbering Scheme of the Diethyltin(IV)bis-[2-(2-fluoro-4-biphenyl)]propanoate.

### Results and Discussion

#### Physical data

White, solid. Yield = 81.7%, m.p. = 154-155 °C, Mol. Wt = 663.33, anal. calcd. for  $\text{C}_{34}\text{H}_{34}\text{O}_4\text{F}_2\text{Sn}$ : %C = 61.45, %H = 5.12. Found: %C = 61.13, %H = 4.97.

#### IR data

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{COO})_{\text{asym}}$  1597,  $\nu(\text{COO})_{\text{sym}}$  1381,  $\Delta\nu$  216,  $\nu(\text{Sn}-\text{C})$  528,  $\nu(\text{Sn}-\text{O})$  470.

The IR spectra was recorded as KBr disc in the solid state within the range 4000-400  $\text{cm}^{-1}$ . The specificity of the bands for the structure assignment are  $\nu(\text{COO})_{\text{asym}}$ ,  $\nu(\text{COO})_{\text{sym}}$ ,  $\nu(\text{Sn}-\text{C})$  and  $\nu(\text{Sn}-\text{O})$ . The  $\nu(\text{Sn}-\text{C})$  band appeared at 528  $\text{cm}^{-1}$ . The  $\nu(\text{Sn}-\text{O})$  band was observed at 470  $\text{cm}^{-1}$  which confirmed the formation of the complex.

\*To whom all correspondence should be addressed.

**Mass spectral data**

Mass spectral data (*m/z*, %):  $[C_{14}H_{12}FSn]^+$  (319, 2),  $[C_{18}H_{22}FSn]^+$  (178, 23),  $[Sn/SnH]^+$  (121, 2),  $[C_{14}H_{12}F]^+$  (199, 100).

Mass spectral data showed that base peak was due to  $[C_{14}H_{12}F]^+$  (100%). The fragments  $[C_{14}H_{12}FSn]^+$  and  $[C_{18}H_{22}FSn]^+$  appeared at *m/z* 319 and 178, which showed that the main fragmentation was observed due to the loss of a ligand followed by the loss of CO<sub>2</sub> from the ligand. The successive loss of R group proceeded with the loss of the remaining part of the ligand until Sn<sup>+</sup> and SnH<sup>+</sup> was observed.

Table 1. <sup>1</sup>H and <sup>13</sup>C NMR Data<sup>1</sup>

Proton/ Carbon no.	<sup>1</sup> H δ (ppm)	<sup>13</sup> C δ (ppm)
1	-	142.4, 142.5 {8}
2	7.28 (d 8.2)	115.5, 115.9 {24}
3	7.40 (m)	158.4, 162 {249}
4	-	128.1, 128.3 {24}
5	7.40 (m)	131.2 {8}
6	7.22 (m)	124.0
7	-	136.0 {4}
8,12	7.61 (m)	129.4
9,11	7.45 (m)	128.9
10	7.45 (m)	128.1
13	3.91 (q)	45.5
14	1.66 (d 7.1)	18.2
15	-	184.8
16	1.26 (t)	19.3 [566, 540]
17	0.85 (t)	9.2 [37]

<sup>1</sup> Coupling constant in ( ) <sup>n</sup>J (<sup>1</sup>H,<sup>1</sup>H); in [ ] <sup>l</sup>J [<sup>13</sup>C,<sup>119</sup>Sn]; in { } <sup>n</sup>J (<sup>13</sup>C,<sup>19</sup>F)

In the <sup>1</sup>H NMR data (Table-1) the signals were assigned by their peak multiplicity, intensity pattern, integration and satellites. The ethyl groups attached to tin atom give signals at expected range, thus confirming the complexation.

In the <sup>13</sup>C NMR data (Table-1) the aromatic carbon's resonance peaks were assigned by comparison of the experimental chemical shifts with those calculated by the incremental method [7]. The resonance of carbonyl carbon was observed at δ 184.4 ppm [8], suggesting the coordination of the ligand through the carboxylic oxygen to organotin(IV) moiety [9].

<sup>119</sup>Sn NMR data: -144.6 (ppm).

The <sup>119</sup>Sn NMR spectra was recorded in CDCl<sub>3</sub> solution and exhibited a single resonance in the range characteristic for coordination number higher than four.

**Mossbauer data**

IS = 1.45; QS = 3.53; QS/IS = 2.43

Mossbauer data showed that there is distortion from perfect octahedral geometry in the reported complex which is apparently due to high electronegativity of oxygen atoms which gives values closer to trigonal bipyramid [10-13].

**Crystallographic data**

The crystal structure of diethyltin(IV)bis-[2-(2-fluoro-4-biphenyl)]propanoate is given in Figure 2.

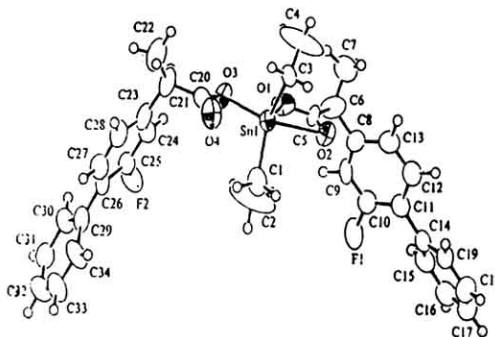


Fig. 2: Molecular structure of diethyltin(IV)bis[2-(2-fluoro-4-biphenyl)]-propanoate in the crystal showing the atom numbering scheme.

Details concerning data collection and refinement are given in Table-3. Selected bond lengths and angles are given in Table-2. Final atomic coordinate and equivalent isotropic displacement parameters are presented in Table-4.

The crystal structure showed two carboxylate groups attached around the tin moiety. One carboxylate group acts as bidentate with bond angle O1-Sn1-O2 53.6(3) and torsion angle Sn1-O1-C5-C6 -179.4(10). Whereas other carboxylate group acts as monodentate with bond angle O1-Sn1-O3 80.4(4) and torsion angle Sn1-O3-C20-C21 -179.3 (10). It showed distorted trigonal bipyramidal geometry which is consistent with earlier reports [9-12]. All other bond lengths fall within the expected range.

**Experimental****Instrumentation**

Melting points were determined on a digital melting point instrument MPD Mitamura Riken

Table-2: Crystal data and structure refinement of the reported compound.

Empirical formula	C <sub>14</sub> H <sub>14</sub> F <sub>2</sub> O <sub>4</sub> Sn
Formula weight	665.33
Lattice parameters	a = 9.906(8) Å α = 97.88(8)° b = 18.387(15) Å β = 105.74(8)° c = 8.715(9) Å γ = 80.21(7)°
Crystal system	Triclinic
Space group	P 1̄(#2)
μ(MoKα)	2.01 cm <sup>-1</sup>
Z	2
Volume	1498.6(24) Å <sup>3</sup>
Density (calculated)	1.470g/cm <sup>3</sup>
Crystal dimensions	0.43 x 0.42 x 0.42 mm
F(000)	676.00
Temperature	-103.0°C
2θ <sub>max</sub>	50.1°
No. of reflections measured	Total: 5636 Unique: 5307 (R <sub>int</sub> = 0.070)
No. of observations (I > 3.00 σ(I))	2974
Residuals: R, R <sub>w</sub>	0.072, 0.075
Maximum peak in Final Diff. Map	1.43 e/Å <sup>-3</sup>

Table 3: Selected bond length (Å) and bond angles (°).

Bond lengths	Bond angles
Sn1-O1 2.143(8)	O1-Sn1-O2 53.6(3)
Sn1-O3 2.074(8)	O1-Sn1-O3 80.4(4)
Sn1-O2 2.50(9)	Sn1-O1-C5 100.3(9)
Sn1-C1 2.034(16)	Sn1-O2-C5 82.1(8)
Sn1-C3 2.132(13)	Sn1-O3-C20 104.8(9)
F1-C10 1.364(16)	Sn1-C1-C2 113.7(12)
F2-C25 1.355(13)	Sn1-C3-C4 114.2(13)

Table 4: Atomic coordinates and B<sub>iso</sub>/B<sub>eq</sub>.

Atom	x	y	z	B <sub>eq</sub>
Sn(1)	0.13958(11)	0.10214(6)	0.13460(13)	3.15(2)
F(1)	0.3490(10)	-0.14775(5)	-0.5382	6.5(3)
F(2)	0.4603(8)	0.3278(4)	-0.1051(10)	5.2(2)
O(1)	0.3276(9)	0.0289(6)	0.1123(11)	4.5(3)
O(2)	0.1523(9)	-0.0316(5)	0.0084(11)	4.2(3)
O(3)	0.2891(9)	0.1732(5)	0.2334(11)	4.4(3)
O(4)	0.0869(11)	0.2398(6)	0.2504(13)	5.3(3)
C(1)	0.0482(14)	0.1372(8)	-0.0863(19)	4.6(4)
C(2)	0.146(3)	0.1254(14)	-0.193(2)	14.6(10)
C(3)	0.0897(18)	0.0704(8)	0.3370(16)	5.1(4)

Kogyo (Japan) and are incorreced. IR spectra was recorded as KBr pellets on model 270-50 Hitachi IR Spectrophotometer (Japan); multinuclear (<sup>1</sup>H and <sup>13</sup>C). NMR spectra were recorded on a Bruker AM-500 Spectrometer (Germany) using CDCl<sub>3</sub> as internal reference δ <sup>1</sup>H (CDCl<sub>3</sub> = 7.14), δ <sup>13</sup>C (CDCl<sub>3</sub> = 77.0). <sup>119</sup>Sn NMR spectra was obtained on Bruker 250 ARX (Germany); with Me<sub>4</sub>Sn (Ξ <sup>119</sup>Sn = 37.290665 MHz) as external reference. Mass spectra was recorded on a MAT 8500 Finnigan (Germany). Elemental analysis was performed with an organic elemental analyzer, mode EA 1110, CE Instrument, Italy. Single crystal X-ray data were collected on a Rigaku AFC6S

diffractometer with monochromated MoK<sub>α</sub> radiation at -103 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 50.1°. Omega scan of several intense reflections, made prior to data collection, had an average width at half-height of 0.42° with takeoff angle of 6.0°.

The structure was solved by Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but no refined. The final cycle of full matrix least squares refinement was based on 2974. Observed reflections (I > 3.00 σ(I)) and 370 variable parameters and converged (large parameter shift was 0.09 times its used) with unweighted and weighted agreement factors of

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.072$$

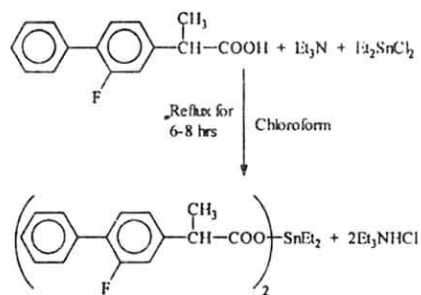
$$R_w = \sqrt{\frac{\sum_w (|F_o| - |F_c|)^2 / \sum_w F_o^2}{\sum_w F_o^2}} = 0.075$$

Neutral atom scattering factors were taken from Cromer and Weber [14].

All calculations were performed using the X-scan [15] Crystallographic Software Package of Molecular Structure Corporation.

#### Synthesis of the Complex

2-(2-Fluoro-4-biphenyl)propanoic acid with Et<sub>3</sub>N was dissolved in 50 mL dried chloroform in 250 mL two neck flask having magnetic bar. The flask was well equipped with water condenser and placed on magnetic stirrer with controlled heating system. Then diethyltin(IV) dichloride was added to the reaction mixture at ambient temperature. The reaction was refluxed for 6-8 hours and was filtered after cooling to room temperature. The filtrate was treated with charcoal and the solvent was removed under vacuum on rotary evaporator. The solid product was recrystallized from dichloromethane at low temperature (-20°C).



**Acknowledgment**

Saqib Ali is thankful to Quaid-i-Azam University for financial support.

**References**

1. I.J. Boyer, *Toxicology*, **55**, 253 (1989).
2. K. Freut, *Crit. Rev. Toxicol.*, **26**, 1 (1996).
3. W. Peters, E.R. Trotter and B.L. Robinson, *Ann. Trop. Med. Parasitol.*, **74**, 321 (1980).
4. L. Pellerito and L. Nagy, *Coord. Chem. Rev.*, **224**, 111 (2002).
5. R. Laurence and P.N. Bennet, *Clinical Pharmacology*, Ed. 7<sup>th</sup>, ELBS, UK (1993).
6. B.G. Katzung, *Basic and Clinical Pharmacology International*, Ed. 6<sup>th</sup> (1995).
7. H. O. Kalinowski, S. Berger and S. Brown, <sup>13</sup>C NMR Spektroskopie, Thieme Verlag, Stuttgart, Germany (1984).
8. C. J. Pouchert and J. Behnke; The Aldrich Library of <sup>13</sup>C and <sup>1</sup>H FT NMR Spectra, Aldrich Chemical Company, Wisconsin, I, 273, 892 (1993).
9. G. Domazetis, R. J. Magee and B. D. James, *J. Organomet. Chem.*, **162**, 239 (1978).
10. S.W. Ng and V.G. Kumar Das, *Acta Cryst. C53*, 546 (1997).
11. M. K. Lo, S.W. Ng and V.G. Kumar Das, *Acta Cryst. C53*, 545 (1997).
12. E.C. Holloway and M. Melnik, *Main Group Met. Chem.*, **23**, 331 (2000).
13. M. Parvez, M.H. Bhatti, S. Ali, M. Mazhar and S.I. Qureshi, *Acta Cryst. C56*, 327 (2000).
14. D.T. Cromer and J.T. Weber, "International Tables for X-ray Crystallography", Vol. 4, The Kynoch Press, Birmingham, England.
15. Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).