# Synthetic, Spectroscopic, Thermal and Biological Studies of Tri-, Di- and Chlorodiorganotin(IV) 2-(4-isobutylphenyl)propanoate

[1]S. MAHMOOD, [1]S. ALI*, [1]M. H. BHATTI, [1]K. SHAHID, [1]S. SHAHZADI, [1]M. MAZHAR
[2]K. M. KHAN AND [2]G. M. MAHARVI
[1]*Department of Chemistry, Quaid-i-Azam University, 45320 Islamabad, Pakistan*
[2]*H.E.J. Research Institute of Chemisty, University of Karachi, Karachi-75720, Pakistan*

(Received 16th June, 2003, revised 25th October, 2003)

**Summary**: Certain new organotin(IV) compounds with general formulae $R_3SnL$, $R_2SnL_2$ and $R_2SnClL$ (where R = Me, Et, *n*-Bu, Ph and L = 2-(4-isobutylphenyl)propanoate) have been synthesized. For the characterization and structure elucidation, different physical methods (solubility, TLC, elemental analysis, and m.p.) and instrumental techniques [multinuclear NMR ($^1H$, $^{13}C$, $^{119}Sn$), $^{119m}Sn$ Mössbauer spectroscopy and mass spectrometry] have been used. In order to study the kinetic parameters such as energy of activation (E*) and order of reaction (n), thermogravimetric technique has been applied and the results were calculated by using Horowitz and Coats methods. Biological studies of the synthesized compounds were performed against various types of bacteria and fungi.

## Introduction

The applications of organotin(IV) compounds have grown significantly in the last few decades in many industrial [1-3] and biological [4-7] sectors. Organotin(IV) carboxylates are widely used as biocides and in industry as homogeneous catalyst [8-11]. The present work is the continuation of our interest in carboxylates studies reported earlier [12-16]. Here we report some newly synthesized organotin(IV) derivatives of 2-(4-isobutylphenyl) propanoic acid, (Fig. 1) commercially known as ibuprofen, the common antipyretic and anti-inflammatory drug [17]. These compounds have been characterized by elemental analysis, infrared, multinuclear NMR ($^1H$, $^{13}C$, $^{119}Sn$), Mössbauer and mass spectroscopies. Thermal behaviour of the complexes have been investigated using thermogravimetric analysis technique and some kinetic parameters were calculated. The investigated compounds were subjected to biological screening and their antibacterial (Gram positive and Gram negative) and antifungal activities are reported.

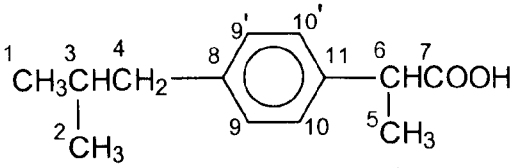



Fig. 1: 2-(4-Isobutylphenyl)propanoic Acid (HL)

## Results and Discussion

### *Infrared Spectroscopy*

Infrared data of 2-(4-isobutylphenyl)propanoic acid and its derivatives are given in Table 2. Several assignments for these complexes have been proposed on the basis of previous reports on organotin(IV) derivatives containing O-donor ligands [18-20]. The main changes observed in the spectra of the complexes with respect to that of neutral free ligands are: the absence of the broad absorption of ν(OH) at ~3200 $cm^{-1}$, and of Sn-Cl bond in the range from 330±10 $cm^{-1}$, various shifts of the carboxyl stretching frequencies ($\nu_{asym.}(COO)$, $\nu_{sym.}(COO)$), which have different patterns for the bands in 1600±50 and 1400±30 $cm^{-1}$, respectively. According to Lebl *et al.*, [21] the values of $\Delta\nu$ [$\Delta\nu = \nu_{asym.}(COO) - \nu_{sym.}(COO)$] can be divided into three groups; (a) In compounds where $\Delta\nu(COO) > 350$, hence these compounds contain, with high probability, the mono dentate carboxylate group. However, other very weak intra- and intermolecular interactions can not be excluded. (b) When $\Delta\nu(COO) < 200$, hence the carboxylate groups of these compounds can be considered to be practically bidentate. (c) In compounds where $\Delta\nu(COO) < 350$ and $> 200$ are considered as an intermediate state between monodentate and bidentate which is called anisobidentate. It has also been suggested that

*To whom all correspondence should be addressed.

Table-1:Physical Data of Organotin(IV) 2-(4-isobutylphenyl)propanoate

| No. | Compound | Emparical Formula Formula Wt. | M. P. (°C) | Yield (%) | % C Cald. (Found) | % H Cald.(Found) |
|---|---|---|---|---|---|---|
| | HL | $C_{13}H_{18}O_2$ 206 | 75-77 | - | - | - |
| I | $Me_3SnL$ | $C_{16}H_{26}O_2Sn$ 369 | 150-153 | 76.8 | 52.03 (52.42) | 7.05 (7.17) |
| II | $Bu_3SnL$ | $C_{25}H_{44}O_2Sn$ 495 | 78-79 | 73.6 | 60.61 (60.82) | 7.93 (7.95) |
| III | $Ph_3SnL$ | $C_{31}H_{32}O_2Sn$ 555 | 142-143 | 79.5 | 67.03 (66.89) | 5.77 (5.82) |
| IV | $Bz_3SnL$ | $C_{34}H_{38}O_2Sn$ 597 | 105 | 80.0 | 68.34 (68.52) | 6.37 (6.41) |
| V | $Me_2SnClL$ | $C_{15}H_{23}O_2ClSn$ 389.5 | 141-142 | 88.8 | 46.21 (46.05) | 5.91 (6.00) |
| VI | $Bu_2SnClL$ | $C_{21}H_{35}O_2ClSn$ 473.5 | 81-82 | 93.5 | 53.22 (53.41) | 7.39 (7.32) |
| VII | $Ph_2SnClL$ | $C_{25}H_{27}O_2ClSn$ 513.5 | 110-111 | 87.3 | 58.42 (58.50) | 5.26 (5.32) |
| VIII | $Me_2SnL_2$ | $C_{28}H_{40}O_4Sn$ 559 | 144-146 | 85.4 | 60.11 (59.92) | 7.16 (7.22) |
| IX | $Bu_2SnL_2$ | $C_{34}H_{52}O_4Sn$ 643 | 67-68 | 75.4 | 63.45 (63.52) | 8.09 (7.95) |
| X | $Oct_2SnL_2$ | $C_{42}H_{68}O_4Sn$ 755 | a | 88.0 | 66.75 (66.67) | 9.00 (8.89) |
| XI | $Ph_2SnL_2$ | $C_{38}H_{44}O_4Sn$ 683 | 123-125 | 73.5 | 66.76 (66.67) | 6.44 (6.41) |
| XII | $Bz_2SnL_2$ | $C_{40}H_{48}O_4Sn$ 711 | a | 78.2 | 67.51 (67.32) | 6.75 (6.80) |

[a]semisolid

**Table 2: Infrared Data[a] ($cm^{-1}$) of Organotin(IV) 2-(4-isobutyl-phenyl) propanoate.**

| No. | $\nu(COO)_{asym}$ | $\nu(COO)_{sym}$ | $\Delta\nu$ | $\nu$(Sn-Cl) | $\nu$(Sn-C) | $\nu$(Sn-O) |
|---|---|---|---|---|---|---|
| I | 1600 s | 1403 s | 197 | - | 530 w | 480 w |
| II | 1610 s | 1412 s | 198 | - | 534 m | 487 w |
| III | 1609 s | 1409 s | 200 | - | 526 m | 475 w |
| IV | 1612 s | 1411 s | 201 | - | 532 m | 472 m |
| V | 1600 s | 1420 s | 180 | 332 m | 530 w | 475 m |
| VI | 1598 s | 1416 s | 182 | 340 m | 547 w | 470 w |
| VII | 1600 s | 1415 s | 185 | 337 m | 518 m | 491 w |
| VIII | 1597 s | 1408 s | 198 | - | 540 m | 470 m |
| IX | 1605 s | 1415 s | 190 | - | 545 m | 490 m |
| X | 1592 s | 1400 s | 192 | - | 540 m | 478 m |
| XI | 1596 s | 1405 s | 191 | - | 525 w | 483 m |
| XII | 1593 s | 1403 s | 190 | - | 543 w | 482 m |
| HL | 1702 s | 1365 s | 337 | - | - | - |

[a]s, strong; m, medium; w, weak

$\Delta\nu$(COO) value in chelating mode is less than $\Delta\nu$(COO) in bridging [22].

From the preceding discussion and the data reported in Table 2, it is proposed that in the investigated series $R_2SnL_2$ and $R_2Sn(Cl)L$ have chelating type of carboxylates while $R_3SnL$ have bridging carbaxylate. The bands for $\nu$(Sn-C) and $\nu$(Sn-O) are assigned in the range 500-575$cm^{-1}$ and 400-450 $cm^{-1}$, respectively. In chlorodiorganotin(IV) carboxylates, $\nu$(Sn-Cl) band is observed in the region 330-340 $cm^{-1}$.

*Mass Spectrometry*

The matter of keen observation shows that molecular ion peak is casually observed in the case of organotmetallic compounds or with very low intensity [13,23,24]. This general behaviour of the compounds were also found in organotin(IV) carboxylates.

The mass fragmentation data of the tri-, di- and chlorodiorganotin(IV) carboxylates are given in Tables 3 and 4. The molecular ion peak of very low intensity was observed in some of the compounds whereas in some cases these were absent as reported earlier [23]. In triorganotin(IV) derivatives primary fragmentation is due to the stepwise loss of R groups and then ligand ending as $Sn^+$ or $SnH^+$ [13,23]. The second route is the loss of $CO_2$ from the ligand, elimination of remaining ligand and successive loss of R groups with end product $Sn^+$ or $SnH^+$. In case of diorganotin derivatives primary fragmentation is due to the loss of one ligand followed by $CO_2$ from the second ligand. If the first loss is due to the R group, then there is a successive elimination of two $CO_2$ molecules from the ligands. Chloro derivatives follow the same pattern as the triorganotin carboxylates. The first loss is due to an R group followed by $CO_2$ and then another R group and some fragments of the ligand. The peaks of $[C_{13}H_{18}O_2]^+$ ($m/z$ = 206) due to the ligand and one of its fragments i.e. $[C_{12}H_{17}]^+$ ($m/z$ = 161) are observed in all the compounds. The peaks for $[R_3Sn]^+$ and $[R_2Sn]^+$ have sometimes low

Table 3: Fragmentation Pattern of Tri- and Chlorodiorganotin(IV) 2-(4-isobutylphenyl) propanoate

| Fragment | I | % | II | % | III | % | IV | % | V | % | VI | % | VII | % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | m/z | Int. | m/z | Int. | m/z | Int. | m/z | Int. | m/z | Int. | m/z | Int. | m/z | Int. |
| $[R_3SnOCOR']^+$ | 370 | n.o. | 496 | 2 | 556 | 2 | 598 | 5 | - | - | - | - | - | - |
| $[R_2Sn(Cl)OCOR']^+$ | - | - | - | - | - | - | - | - | 391 | 10 | 475 | n.o. | 515 | 7 |
| $[R_2SnOCOR']^+$ | 355 | 4 | 439 | 100 | 479 | 9 | 507 | 15 | 355 | 52 | 439 | 67 | 479 | 35 |
| $[R_2SnR']^+$ | 311 | 4 | 395 | 3 | 435 | n.o. | 463 | n.o. | 311 | 100 | 395 | 39 | 435 | 43 |
| $[RSnR']^+$ | 296 | n.o. | 338 | n.o. | 358 | 40 | 372 | 4 | 296 | 60 | 338 | 100 | 358 | 72 |
| $[R_3Sn]^+$ | 165 | 37 | 291 | 40 | 351 | 100 | 393 | 3 | - | - | - | - | - | - |
| $[R_2Sn]^+$ | 150 | 3 | 234 | 12 | 274 | 2 | 302 | 3 | 150 | 22 | 274 | 43 | 234 | 100 |
| $[RSn]^+$ | 135 | 7 | 177 | 23 | 197 | 56 | 211 | 5 | 135 | 26 | 177 | 21 | 197 | 15 |
| $[SnR']^+$ | 281 | 10 | 281 | 20 | 281 | 16 | 281 | 5 | 281 | 39 | 281 | 32 | 281 | 45 |
| $[Sn/SnH]^+$ | 121 | 11 | 121 | 10 | 120 | 41 | 120 | 10 | 120 | 40 | 120 | 51 | 120 | 44 |
| $[R'COOH]^+$ | 206 | 69 | 206 | 5 | 206 | 5 | 206 | 10 | 206 | 69 | 206 | 80 | 206 | 62 |
| $[R']^+$ | 161 | 100 | 161 | 30 | 161 | 65 | 161 | 35 | 161 | 35 | 161 | 58 | 161 | 43 |
| $[C_6H_5]^+$ | 77 | 13 | 77 | 2 | 77 | 11 | 77 | 5 | 77 | 22 | 77 | 15 | 77 | 18 |
| $[R]^+$ | 15 | n.o. | 57 | 6 | - | - | 91 | 100 | - | - | - | - | - | - |

Table 4:Fragmentation Pattern of Diorganotin(IV) bis[2-(4-isobutylphenyl) propanoate]

| Fragment | VIII | % Int. | IX | % Int. | X | % Int. | XI | % Int. | XII | % Int. |
|---|---|---|---|---|---|---|---|---|---|---|
| | m/z | | m/z | | m/z | | m/z | | m/z | |
| $[R_2Sn(OCOR')_2]^+$ | 560 | n.o. | 644 | n.o. | 712 | 10 | 684 | 2 | 756 | 5 |
| $[R_2SnOCOR']^+$ | 355 | 100 | 439 | 100 | 507 | 3 | 479 | 12 | 551 | 100 |
| $[RSn(OCOR')_2]^+$ | 545 | 6 | 587 | 56 | 621 | 10 | 607 | n.o. | 643 | 10 |
| $[Sn(OCOR')_2]^+$ | 530 | n.o. | 530 | 5 | 530 | 5 | 530 | 2 | 530 | n.o. |
| $[R_2SnR']^+$ | 311 | n.o. | 395 | n.o. | 463 | 9 | 435 | n.o. | 507 | 4 |
| $[RSnR']^+$ | 296 | n.o. | 338 | n.o. | 372 | 5 | 358 | 8 | 394 | 4 |
| $[SnR']^+$ | 281 | 2 | 281 | 26 | 281 | 10 | 281 | n.o. | 281 | 5 |
| $[Sn/SnH]^+$ | 120 | 7 | 121 | 10 | 121 | 48 | 121 | 5 | 120 | 20 |
| $[R'COOH]^+$ | 206 | 16 | 206 | 18 | 206 | 75 | 206 | 64 | 206 | 5 |
| $[R']^+$ | 161 | 97 | 161 | 68 | 161 | 100 | 161 | 100 | 161 | 20 |
| $[C_6H_5]^+$ | 77 | 10 | 77 | 5 | 77 | 50 | 77 | 21 | 77 | n.o |
| $[R]^+$ | 15 | n.o. | 57 | 43 | 91 | 78 | - | - | 113 | 10 |

Table-5:$^1$H NMR Data[a-c] of Organotin(IV) 2-(4-isobutylphenyl) propanoate

| Proton | LH | I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $Me_3SnL$ | $Bu_3SnL$ | $Ph_3SnL$ | $Bz_3SnL$ | $Me_2SnClL$ | $Bu_2SnClL$ | $Ph_2SnClL$ | $Me_2SnL_2$ | $Bu_2SnL_2$ | $Oct_2SnL_2$ | $Ph_2SnL_2$ | $Bz_2SnL_2$ |
| 1,2 | 0.92 d (7.2) | 0.94 d (6.5) | 0.89 d (7.2) | 0.91 d (7.1) | 0.94 d (7.2) | 0.93 d (8.2) | 0.92 d (7.0) | 0.94 d (7.1) | 0.96 d (7.2) | 0.86 d (7.2) | 0.90 d (7.3) | 0.96 d (7.2) | 0.88 d (7.2) |
| 3 | 1.48 m | 1.52 m | 1.46 m | 1.51 m | 1.62 m | 1.82 m | 1.48 m | 1.57 m | 1.48 m | 1.50 m | 1.83 m | 1.52 m | 1.81 m |
| 4 | 2.44 d (7.2) | 2.49 d (7.1) | 2.36 d (7.2) | 2.51 d (7.2) | 2.50 d (7.1) | 2.41 d (7.1) | 2.48 d (7.0) | 2.41 d (7.0) | 2.41 d (7.1) | 2.40 d (7.2) | 2.44 d (7.3) | 2.40 d (7.2) | 2.40 d (7.6) |
| 5 | 1.50 d (7.4) | 1.53 d (7.1) | 1.65 d (7.1) | 1.55 d (7.1) | 1.50 d (7.2) | 1.67 d (8.2) | 1.64 d (7.3) | 1.55 d (6.9) | 1.54 d (7.1) | 1.68 d (7.1) | 1.51 d (7.2) | 1.60 d (7.4) | 1.52 d (7.3) |
| 6 | 3.71 q (7.2) | 3.78 q (7.0) | 3.61 q (7.0) | 3.87 q (7.0) | 3.62 q | 3.78 q (7.0) | 3.80 q (7.1) | 3.81 q (7.0) | 3.78 q (7.0) | 3.70 q (7.0) | 3.77 q | 3.65 q (7.2) | 3.48 q |
| 9,9' | 7.10 d (8.3) | 7.15 d (8.1) | 7.14 d (8.0) | 7.18 d (7.9) | 7.10 d (8.1) | 7.23 d (8.0) | 7.17 d (7.1) | 7.25 d (7.5) | 7.13 d (8.3) | 7.07 d (8.0) | 7.10 d (7.8) | 7.10 d (8.1) | 7.28 d (8.2) |
| 10,10' | 7.21 d (8.0) | 7.28 d (8.8) | 7.20 d (8.0) | 7.31 d (7.9) | 7.20 d (8.0) | 7.21 d (8.0) | 7.25 d (8.2) | 7.29 d (8.1) | 7.21 d (8.0) | 7.15 d (8.0) | 7.23 d (7.7) | 7.31 d (8.1) | 7.33 d (8.1) |
| *$CH_2$ | - | - | - | - | 2.91 s [60.4] | - | - | - | - | - | - | - | 2.94s [73.9] |
| R | - | 0.8 s [57.1] | 1.2 t [59,63] 1.38 m [54.6] | 7.40-7.70 m | 7.30-7.60 m | 0.75 s [71.1] | 0.8 t [69.7] 7.45-7.6 m | 7.31 d [69.7] 7.45-7.6 m | 0.91 s [73.2] | 1.3 t [71.1] 1.45 m | 0.85-1.85 m | 7.7 d [63.0] 7.45 m [18.4] 7.78 m | 7.25-7.66 m |

[a] In $CDCl_3$ at 298K (40%) [b] Chemical shift (δ) in ppm. $^nJ(^1H,^1H)$ in Hz, $^nJ(^{119}Sn,^1H)$ in Hz.
[c] Multiplicity is given by s, singlet; d, doblet; t, triplet; and m, multiplet.
[d] For numbering scheme, see Figure 1. [e] octyl, phenyl and benzyl ring protons were difficult to assign.

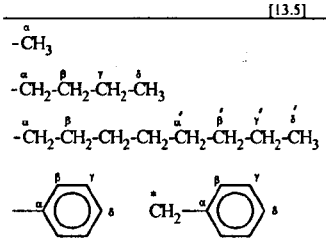
intensities which indicates that fragmentation through these species is not favourable [24].

### *$^1$H NMR Spectroscopy*

$^1$H NMR data for tri-, di-, and chloro-diorganotin(IV) 2-(4-isobutylphenyl) propanoate are given in Table 5. The signals were assigned on the basis of the chemical shifts, peaks multiplicity, intensity pattern and their coupling constants. In all investigated organotin(IV) derivatives signals of the ligand protons were observed with in the expected range. Methyl groups at C-3 gave doublet whereas H(3) gave multiplet and H(4) doublet at lower field. Although aromatic protons of the ligand 9,9' and 10,10' have rather identical environment, 10,10' shifted slightly to downfield probably due to carboxylate group. Protons of methyl, H(5) appeared

Table 6: $^{13}C$ NMR Data of Organotin(IV) 2-(4-isobutylphenyl) propanoate

| Carbon | LH | I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,2 | 22.4 | 22.4 | 22.7 | 22.3 | 22.4 | 21.8 | 22.9 | 22.3 | 21.2 | 23.2 | 22.4 | 22.3 | 22.4 |
| 3 | 44.9 | 45.0 | 45.1 | 45.0 | 45.1 | 44.6 | 44.5 | 45.8 | 44.5 | 44.1 | 45.1 | 45.0 | 45.0 |
| 4 | 30.2 | 30.1 | 30.1 | 30.1 | 30.2 | 30.0 | 30.1 | 30.1 | 30.2 | 30.0 | 30.2 | 30.1 | 30.2 |
| 5 | 18.1 | 18.4 | 20.4 | 19.3 | 18.5 | 18.6 | 18.6 | 19.3 | 18.3 | 18.5 | 18.8 | 18.9 | 18.5 |
| 6 | 45.0 | 45.1 | 45.8 | 45.9 | 45.8 | 44.8 | 45.2 | 46.0 | 44.7 | 44.9 | 45.0 | 45.6 | 45.6 |
| 7 | 180.4 | 180.7 | 180.0 | 181.3 | 182.4 | 183.9 | 185.2 | 178.5 | 181.3 | 185.3 | 185.0 | 180.0 | 174.5 |
| 8 | 137.3 | 137.4 | 137.9 | 138.6 | 134.5 | 140.6 | 137.4 | 136.5 | 137.6 | 137.2 | 137.9 | 137.4 | 134.7 |
| 9,9′ | 127.3 | 127.0 | 127.0 | 128.2 | 127.4 | 127.0 | 127.1 | 128.9 | 127.1 | 127.0 | 127.1 | 127.0 | 127.7 |
| 10,10′ | 129.4 | 129.2 | 129.9 | 129.2 | 129.2 | 129.3 | 129.2 | 130.1 | 129.2 | 129.2 | 129.2 | 129.0 | 128.6 |
| 11 | 140.9 | 140.5 | 141.5 | 139.3 | 140.4 | 140.6 | 140.3 | 140.5 | 140.7 | 140.5 | 140.3 | 141.5 | 140.8 |
| *$CH_2$ | - | - | - | - | 24.5 [352] | - | - | - | - | - | - | - | 32.4 [560] |
| α | - | - | -2.5 [401] | 15.8 [319, 351] | 138.5 620, 649] | 138.7 | 5.9 [517.8] | 7.6 [525] | 139.6 [765] | 18.7 [521] | 33.1 α′ | 25.2 138.4 [630] | 135.7 |
| β | - | - | 29.1 [21.3] | 136.6 [47.5] | 127.9 | - | 26.5 | 136.6 | - | 21.4 [37] | 31.8 β′ | 24.3 134.5 [43.8] | 128.3 |
| γ | - | - | 28.5 [65.0] | 128.7 [62.4] | 128.6 | - | 27.0 | 128.7 | - | 24.1 | 29.7 γ′ | 22.3 126.7 | 128.1 |
| δ | - | - | 14.2 | 129.9 [13.5] | 124.5 | - | 14.0 | 129.9 | - | 13.9 | 29.1 δ′ | 14.1 129.0 | 125.3 |



more downfield as doublet because of $COO^-$ while H(6) gave the typical quartet signal. The peculiarity of these peaks were critically observed in the synthesized organotin(IV) derivatives. Much complexities were observed in case of the phenyltin(IV) and benzyltin(IV) derivatives due to partial overlap of the signals from the ligand and phenyl rings. The magnitude of the indirect tin-proton coupling, $^2J$ [$^{119}$Sn,$^1$H] are more often exploited for the structure elucidation of the compounds. For example, $^2J$ values for tetrahedral compounds are lower than those for pentacoordinate complexes [25-28].

### *$^{13}C$ NMR Spectroscopy*

$^{13}C$ NMR data of organotin(IV) derivatives of 2-(4-isobutylphenyl) propanoic acid are given in Table 6. There is no appearent change for the carbon signals of the ligand and complexes. However, $^1J$ [$^{119}$Sn,$^{13}$C] couplings were observed in almost all cases. Applying various equations, C-Sn-C bond angles were calculated and are reported in Table 7. Triorganotin(IV) derivatives, compounds I-III and $Ph_2SnL_2$, compound VIII have their C-Sn-C angle values near to tetrahedral environment while the remaining $R_2SnL_2$ and $R_2SnClL$ have C-Sn-C angles in range of 122-127$^0$ which propose anisobidentate nature of carboxylic group in these complexes in non-coordinating solvent [29], which further confirmed from $^2J$ values of these complexes.

Table-7:C-Sn-C Bond angle (degrees) based on $^{13}C$ NMR Data.

| No. | Compound | $^1J$[$^{119}$Sn, $^{13}$C] | Angle(°) |
|---|---|---|---|
| I | $Me_3SnL$ | 401 | 112 |
| II | $Bu_3SnL$ | 351 | 112 |
| III | $Ph_3SnL$ | 649 | 110 |
| V | $Me_2SnClL$ | 517 | 122 |
| VI | $Bu_2SnClL$ | 525 | 127 |
| VII | $Ph_2SnClL$ | 865 | 126 |
| VIII | $Me_2SnL_2$ | 580 | 122 |
| IX | $Bu_2SnL_2$ | 521 | 127 |
| XI | $Ph_2SnL_2$ | 630 | 115 |

### *$^{119}Sn$ NMR Spectroscopy*

$^{119}$Sn Chemical shift δ ($^{119}$Sn) of organotin compounds cover a range of over 600 ppm and are quoted relative to tetramethytin with downfield shifts from reference compound having a positive sign. As the electron releasing power of alkyl group increases, the tin atom becomes progressively more shielded and δ ($^{119}$Sn) value moves to higher field. These values are also dependent upon the nature of the X in $R_{4-n}SnX_n$ and generally move to low field as the electronegativity of the latter increases. A very important property of $^{119}$Sn chemical shift is that an increase in coordination number of the tin atom from four to five, six or seven usually produces a large upfield shift of δ ($^{119}$Sn) [29]. $^{119}$Sn NMR data for the investigated compounds (Table 8) fall in different coordination range, i.e., four, five and nearly six [30]. $R_3SnL$, compounds **I, II** and **III** are clearly in four coordination range while $R_2SnClL$, compounds **V-**

Table 8: $^{119}$Sn NMR Data of Organotin(IV) 2-(4-isobutylphenyl) propanoate.

| No. | Compound | Chemical Shift | No. | Compound | Chemical Shift |
|---|---|---|---|---|---|
| I | $Me_3SnL$ | 140.0 | VII | $Ph_2SnClL$ | – |
| II | $Bu_3SnL$ | 114.0 | VIII | $Me_2SnL_2$ | – |
| III | $Ph_3SnL$ | 103.0 | IX | $Bu_2SnL_2$ | -221.4 |
| IV | $Bz_3SnL$ | -30.0 | X | $Oct_2SnL_2$ | -201.7 |
| V | $Me_2SnClL$ | -190.7 | XI | $Ph_2SnL_2$ | -143.7 |
| VI | $Bu_2SnClL$ | -152.0 | XII | $Bz_2SnL_2$ | -235.1 |

Table 9: Mössbauer Data of Organotin(IV) 2-(4-isobutylphenyl)propanoate.

| No. | Compound | IS | QS | QS/IS |
|---|---|---|---|---|
| I | $Me_3SnL$ | 1.8 | 3.53 | 1.96 |
| III | $Ph_3SnL$ | 1.43 | 1.7 | 1.19 |
| VI | $Bu_2SnClL$ | 1.8 | 3.9 | 2.16 |
| VII | $Ph_2SnClL$ | 1.78 | 3.2 | 1.80 |
| VIII | $Me_2SnL_2$ | 1.15 | 3.34 | 2.90 |
| IX | $Bu_2SnL_2$ | 1.35 | 3.36 | 2.49 |
| XI | $Ph_2SnL_2$ | 1.38 | 3.67 | 2.65 |

**VII** and $Ph_2SnL_2$, compound **XI** are in five coordinating environment. $R_2SnL_2$, compounds **IX, X** and **XII** are more towards six coordination range than five.

*Mössbauer Spectroscopy*

The Mössbauer data for the compounds are given in Table 9. Various reports [28,30,31] show that quadrupole splitting parameters fall in the range of 2.30-2.55 mm $s^{-1}$ for monomeric triorganotin carboxylate having trigonal bipyramidal geometry, whereas those of five coordinate structure formed by bridging carboxylate groups have 3.59-3.70 mm $s^{-1}$ QS values. Hence in present work QS values fall in 3.41-3.55 mm $s^{-1}$ are consistant with a five coordinate *trans*-$O_2CSnR_3$ geometry having bridged chain polymeric structures [32].

There is a distortion from perfect octahedral geometry in diorganotin(IV) derivatives due to high electronegativity of oxygen atoms which gives closer values to trigonal bipyramidal [29-32]. However, the QS/IS(ρ) ratio is greater than 2.1 suggests the *trans*-octahedral geometry [33]. Hence ρ values of 2.90, 2.49 and 2.65 for compounds VIII, IX and XI strongly recommend the *trans*- structures. Chlorodinganotin(IV) derivatives have closer values to the trigonal bipyramidal. The IR data also coinside the Mössbauer results.

*Thermogravimetric Analysis*

The thermal decomposition of the synthesized complexes was studied to investigate their thermal satability, fragmentation pattern and some kinetic parameters.The data in terms of evolved and remained species, based on the coincidence between the calculated and the found values (± 3% acceptable error) are given in Table 10. It is observed that all the compounds are decomposed in a single step eliminating ligand and other R groups leaving $SnO_2$ as a residue. The enegy of activation for the decomposition step is calculated according to Coats' method [34] as well as Horowitz's method [35] and compared. The data for order of reaction and energy of activation are reported in Table 11. From the thermal data it is concluded that R groups have pronounced effect on the enegy of activation, i.e., energy of activation is less for the phenyl derivatives compared to methyl and butyl derivatives.

*Biological Activity*

Biological screening test for the investigated complexes were carried out against various bacteria

Table 10:Proposed Thermal Decomposition Pattern of Organotin(IV) 2-(4-isobutylphenyl)propanoate

| No. | Compound | $T_s$ (K) | Evolved Species (mole) | Remained Species (mole) | Weight loss(%) | |
|---|---|---|---|---|---|---|
| | | | | | Calculated | Observed |
| I | $Me_3SnL$ | 613 | $C_{16}H_{26}$ ($0.7SnO_2$) | $0.3SnO_2$ | 87.7 | 86.5 |
| II | $Bu_3SnL$ | 593 | $C_{25}H_{44}O_2$ ($0.4SnO_2$) | $0.6SnO_2$ | 81.5 | 78.5 |
| III | $Ph_3SnL$ | 603 | $C_{31}H_{32}O_2$ ($0.1SnO_2$) | $0.9SnO_2$ | 75.4 | 73.9 |
| V | $Me_2SnClL$ | 563 | $C_{15}H_{33}O_2Cl$ ($0.8SnO_2$) | $0.2SnO_2$ | 92.1 | 89.5 |
| VI | $Bu_2SnClL$ | 543 | $C_{21}H_{35}O_2Cl$ ($0.7SnO_2$) | $0.3SnO_2$ | 90.4 | 88.2 |
| VII | $Ph_2SnClL$ | 583 | $C_{31}H_{32}O_2Cl$ ($0.6SnO_2$) | $0.4SnO_2$ | 89.1 | 87.6 |
| VIII | $Me_2SnL_2$ | 613 | $C_{28}H_{40}O_4$ ($0.6SnO_2$) | $0.4SnO_2$ | 89.1 | 88.2 |
| IX | $Bu_2SnL_2$ | 633 | $C_{34}H_{52}O_4$ ($0.5SnO_2$) | $0.5SnO_2$ | 88.9 | 86.5 |
| XI | $Ph_2SnL_2$ | 603 | $C_{38}H_{44}O_4$ ($0.4SnO_2$) | $0.6SnO_2$ | 86.7 | 85.2 |

Table 11:Kinetic Parameters of Tri- and Diorganotin (IV) 2-(4-isobutylphenyl) propanoate.

| No. | Compounds | $T_s$ (K) | Order (n) | Activation Energy (kcal mol$^{-1}$) Coats | Horowitz |
|---|---|---|---|---|---|
| I | $Me_3SnL$ | 613 | 1.25 | 15.43 | 14.58 |
| II | $Bu_3SnL$ | 603 | 1.25 | 14.58 | 15.45 |
| III | $Ph_3SnL$ | 623 | 1.25 | 11.94 | 12.78 |
| V | $Me_2SnClL$ | 563 | 1.25 | 12.82 | 12.77 |
| VI | $Bu_2SnClL$ | 543 | 1.25 | 14.82 | 15.73 |
| VII | $Ph_2SnClL$ | 593 | 0.75 | 10.71 | 11.67 |
| VIII | $Me_2SnL_2$ | 613 | 0.75 | 11.85 | 12.83 |
| IX | $Bu_2SnL_2$ | 633 | 1.25 | 12.79 | 12.78 |
| XI | $Ph_2SnL_2$ | 613 | 1.0 | 10.41 | 11.57 |

and fungi. The Gram positive and negative antibacterial activities results are given in Tables 12 and 13. Various compounds showed different levels of activities against almost all the tested bacteria. From the data it is revealed that triorganotin derivatives have more activity as compared to di- and chlorodiorganotins. It is well established that tributyltin compounds are significantly more biocidally active than other classes of alkyltin species [36]. Amongst present series butyl derivatives have the highest activity for all the types of bacteria. It is also observed that ligand itself has low activity as compared to organotin derivatives.

Molloy [4] reported that within a given series triorganotin(IV) derivatives are more active against fungi. Our results are quite consistent with the early reports. Within the $R_{4-n}SnL_n$ system, the nature of R determines the specificity of the activity. Apparently, the function of the ligand is to support the transport of the active organotin moiety to the site of action where it is released by hydrolysis [36]. The anionic ligand also play an important role in determining the degree of activity.

From the prsent studies it is observed that triorganotin(IV) derivatives are highly active against Gram positive and negative bacteria and have good activity against various fungi.

## Experimental

### *Chemicals*

All the solvents used were purchased from Merck Chemicals and dried before use according to the standard methods [37]. Di- and triorganotin chlorides were purchased from Aldrich Chemicals except di- and tribenzyltin(IV) chlorides which were synthesized according to reported method [38]. All

Table-12:Antibacterial Activity (Gram positive) of Organotin(IV) 2-(4-isobutylphenyl) propanoate.

| Bacterium | Compounds | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | LH | I | II | III | V | VI | VII | IX | X | XI |
| Staphylococcus aureus | ++ | + | +++ | +++ | 0 | +++ | + | +++ | 7 | + |
| Staphylococcus epidermiedis | + | + | +++ | +++ | + | ++ | 0 | +++ | 0 | ++ |
| Strepotococous pyogenes | + | ++ | +++ | +++ | + | 0 | ++ | ++ | 0 | ++ |
| Bacillus anthracis | 0 | + | +++ | 0 | + | ++ | ++ | +++ | 0 | 0 |
| Corynebacterium species | + | ++ | +++ | ++ | ++ | +++ | + | ++ | 0 | + |
| Clostridium species | ++ | ++ | ++ | 0 | + | ++ | ++ | 0 | 0 | + |
| Peptococcus species | + | + | +++ | +++ | + | +++ | + | +++ | 0 | + |
| Streptococcus pneumonial | + | + | ++ | +++ | ++ | +++ | 0 | 0 | 0 | + |
| Streptofaecates | 0 | - | +++ | +++ | ++ | +++ | + | ++ | 0 | + |
| Listeris monocytogenes | + | + | ++ | ++ | + | ++ | - | 0 | 0 | - |
| Micrococci | ++ | + | +++ | +++ | - | 0 | + | ++ | 0 | + |

+++ = High activity, ++ = moderate activity, + = low activity, 0 = not tested, - = no activity.
LH = 2-(4-isobutylphenyl) propanoic acid.

Table-13:Antibacterial Activity (Gram negative) of Organotin(IV) 2-(4-isobutylphenyl) propanoate.

| Bacterium | Compounds | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | LH | I | II | III | V | VI | VII | IX | X | XI |
| Escherichia coli | + | + | +++ | ++ | 0 | + | 0 | + | 14 | - |
| Proteus mirablis | + | + | +++ | +++ | + | ++ | - | ++ | 0 | + |
| Proteus vulgeris | + | + | ++ | +++ | ++ | + | - | ++ | 0 | + |
| Sallmonella typhi | 0 | + | +++ | +++ | + | + | + | ++ | - | + |
| C. diptherial | ++ | + | +++ | +++ | + | ++ | 0 | + | 0 | ++ |
| P. aeruginosa | 0 | - | 0 | ++ | ++ | + | + | + | 19 | + |
| Aeromans sobrial | + | + | ++ | +++ | + | - | + | - | 0 | + |
| Shigella boydie | + | + | +++ | 0 | - | + | ++ | 0 | 0 | + |
| Vibrio cholera | ++ | + | +++ | +++ | + | 0 | + | + | 0 | - |
| Brucella species | + | 0 | +++ | +++ | + | + | + | + | 0 | 0 |

+++ = High activity, ++ = moderate activity, + = low activity, 0 = not tested, - = no activity.
LH = 2-(4-isobutylphenyl) propanoic acid.

Table 14:Antifungal Activity of Organotin(IV) 2-(4-isobutylphenyl) propanoate.

| Fungus | Compounds | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | LH | I | II | III | V | VI | VII | IX | X | XI |
| Candida albican | - | + | ++- | +++ | ++ | ++ | ++ | + | - | ++ |
| Pencillium notatum | + | ++ | ++- | ++ | + | + | ++ | ++ | 0 | + |
| Dutarium notatum | 0 | + | ++ | ++ | ++ | ++ | + | + | 0 | + |
| Gurvularia lunata | ++ | ++ | +++ | ++ | ++ | + | + | 0 | 0 | + |
| Alternaria solani | 0 | + | 0 | +++ | ++ | +++ | + | ++ | 0 | ++ |
| Fusarium solani | - | ++ | +++ | +++ | ++ | + | ++ | + | - | + |
| E. flocosum | +++ | + | ++ | +++ | ++ | ++ | + | 0 | 0 | ++ |
| Candida tropicalis | + | + | +++ | ++ | + | + | ++ | ++ | 0 | + |
| Aspergillus nigar | + | + | +++ | +++ | + | ++ | + | + | - | ++ |
| Ascomycetes | 0 | + | +++ | ++ | ++ | + | ++ | + | 0 | + |
| Microsponum canis | +++ | + | +++ | +++ | +++ | + | + | - | - | + |

+++ = High activity, ++ = moderate activity, + = low activity, 0 = not tested, - = no activity.
L$^2$H = 2-(4-isobutylphenyl) propanoic acid.

chemicals were of analytical reagent grade and used without further purification. The 2-(4-isobutylphenyl) propanoic acid, was kindly provided by Ferozsons Laboratories, Nowshehra, Pakistan.

*Instrumentation*

Melting points were determined in capillary tube using electrothermal melting point apparatus model MP-D Mitamura Riken Kogyo (Japan) and are uncorrected. Infrared spectra were recorded within the range 4000-250 $cm^{-1}$ as KBr or CsI pellets on a Perkin Elmer 3300 Spectrometer (USA). The $^{1}H$, $^{13}C$ and $^{119}Sn$ NMR spectra were recorded on Bruker ARX 250 Spectrophotometer (Germany), using $CDCl_3$ as an internal reference for $^{1}H$ and $^{13}C$ [$\delta$ $^{1}H(CDCl_3) = 7.24$ : $\delta$ $^{13}C(CDCl_3) = 77.0$] and $Me_4Sn$ as external reference for $^{119}Sn$ [$\Xi$ (Sn) = 37.296665]. Thermal analysis were carried out by Netzsch Simultaneous Thermal Analyzer STA-429 while mass data were recorded on a 70 eV Mass spectrometer model MAT 8500 Finnigan (Germany).

*General Synthesis*

The ligand, 2-(4-isobutylphenyl)propanoic acid, 10 mmole (2.06 g) was dissolved in dry chloroform (50 mL) in 250 mL two necked flask equipped with water condenser and magnetic stirrer. Equimolar organotin(IV) chlorides (10 mmole $R_3SnCl$ or 5 mmole $R_2SnCl_2$) and triethylamin (10 mmole or 5 mmole) were added in cloroform solution dropwise with constant stirring at room temperature. The reaction mixture was refluxed for 6 h and filtered after cooling to room temperature. The filtrate was treated with activated charcoal for 15 minutes and fitered. The solvent was removed by rotary evaporator and the solid obtained was recrystallized in dichloromethane at low temperature, 5-10 $^{0}C$ (Yield 70-85%). $R_2SnClL$ were synthesized as reported earlier [39]. Physical data for the synthesized compounds are reported in Table 1.

**Acknowledgements**

One of us (S. A) is thankful to the Quaid-i-Azam University for financial support as URF and the Alexander von Humboldt Foundation for awarding Georg Forster Research Fellowship. Prof. Dr. B. Wrackmeyer, University of Bayreuth, Germany, is acknowledged for providing spectral facilities.

**References**

1. Z. Solel, *Phytopathology* **61**, 738 (1971).
2. G. Davies and P. J. Smith, *Adv. Inorg. Chem. Radiochem.*, **23**, 1 (1980).
3. M. Moriya, T. Ohta, K. Watanabe, T. Miyazawa, K. Kato and Y. Shirasu, *Mutat. Res.*, **116**, 185 (1983).
4. K. C. Molloy, in F. R. Hartley (ed.), *The Chemistry of Metal-Carbon Bond, Bioorganotin Compounds*, **Vol. 5**, John Wiley, New York, (1989).
5. N. F. Cardarelli, *Tin as a Vital Nutrient: Implications in Cancer Prophylaxis and Other Physiological Processes*, CRC, Boca Raton, Florida, (1986).
6. A. J. Crowe, P. J. Smith and G. Atassi, *Chem. Biol. Interact.*, **32**, 171 (1980).
7. S. M. Budd, *Thin Solid Films*, **77**, 13 (1981).
8. L. W. Hall and A. E. Pinkney, *Crit. Rev. Toxicol.*, **14**, 159 (1985).
9. E. R. T. Tiekink, *J. Organomet. Chem.*, **408**, 323 (1991).
10. C. J. Evans and S. Karpel, *Organotin Compounds in Modern Technology, J.*

*Organomet. Chem. Libr.* **vol. 16**, Elsevier, Amsterdam, (1985).
11. I. Omae, *Organotin Chemistry, J. Organomet. Chem. Libr.* **vol. 21**, Elsevier, Amsterdam, (1989).
12. M. Danish, S. Ali, M. Mazhar and A. Badshah, *Main Group Met. Chem.*, **19**, 121 (1996).
13. A. Badshah, M. Danish, S. Ali, M. Mazhar, S. Mahmood and M. I. Chaudhry, *Synth. React. Inorg. Met. –Org. Chem.*, **24**, 1155 (1994).
14. M. Danish, S. Ali, M. Mazhar, A. Badshah, T. Masood and E. R. T. Tiekink, *Main Group Met. Chem.*, **18**, 697 (1995).
15. M. Danish, S. Ali and M. Mazhar, *Heteroatom Chem.*, **7**, 233 (1996).
16. M. Danish, S. Ali, A. Badshah, M. Mazhar, M. I. Chouhdary, H.G. Alt and G. Kehr, *Polyhedron*, **14**, 3115 (1995).
17. *The Merck Index*, Merck & Co. Inc. Rahway, N.J., USA (1989).
18. M. Parvez, S. Ali, T. M. Masood, M. Mazhar and M. Danish, *Acta Cryst.*, **C53**, 1211 (1997).
19. B. Wrackmeyer, *Ann. Rep. NMR Spectrosc.*, **38**, 203 (1999).
20. A. Lycka, D. Micak, J. Holecek, M. Biesemans, J. C. Martins and R. Willem, *Organometallics*, **19**, 703 (2000).
21. T. Lebl, J. Holecek and A. Lycka, *Sci. Pap. Univ. Pardubice Ser.* **A2**, 5 (1996).
22. G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, **33**, 227 (1980).
23. C. Picard, P. Tisnes and L. Cazaux, *J. Organomet. Chem.*, **315**, 277 (1986).
24. M. Danish, S. Ali, M. Mazhar, A. Badshah, M. I. Chauhdary, H.G. Alt and G. Kehr, *Polyhedron*, **14**, 1315 (1995).
25. C. Vatsa, V. K. Jain, T. Kesavadas and E. R. T. Tiekink, *J. Organomet. Chem.*, **410**, 135 (1991).
26. G. K. Sandhu and G. Kaur, *Main Group Met. Chem.*, **13**, 149 (1990).
27. G. K. Sandhu and N. S. Boparoy, *Synth. React. Inorg. Met. –Org. Chem.*, **20**, 975 (1990).
28. A. G. Davies and P. J. Smith, *Tin in Comprehensive Organomettalic Chemistry* eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Oxford **vol. 2**, pp.519 (1982).
29. A. Fiaz, M. Parvez, S. Ali, M. Mazhar and A. Munir, *Synth. React. Inorg. Met. -Org. Chem.*, **32**, 665 (2002).
30. J. Holecek, M. Nadvornik, K. Handlir and A. Lycka, *J. Organomet. Chem.*, **315**, 299 (1986).
31. (a) S. Ali, A. Badshah, M. Danish and M. Mazhar, *Chem. Environ. Res.*, **3**, 135 (1994); (b) S. Ali, M. Danish, M. H. Bhatti, M. Mazhar and S. Mahmood, *Pak. J. Sci. Ind. Res.*, **44**, 194 (2001).
32. J. Holecek, A. Lycka, D. Micak, L. Nagy, G. Vanko, J. Brus, S. S. S. Raj, H. K. Fun and S. W. Ng, *Collect. Czech. Chem. Commun.*, **64**, 1028 (1999).
33. M. Nadvornik, J. Holecek and A. Lycka, *J. Organomet. Chem.*, **275**, 43 (1984).
34. A. W. Coats and J. P. Redfern, *Nature*, **21**, 68 (1964).
35. H. H. Horowitz and G. A. Metzger, *Anal. Chem.*, **35**, 1464 (1963).
36. S. Shahzadi, M. H. Bhatti, K. Shahid, S. Ali, S. R. Tariq, M. Mazhar and K. M. Khan, *Monat. Chem.*, **133**, 1089 (2002).
37. D. D. Perrin and W. L. F. Armengo, *Purification of Laboratory Chemicals*. 3rd Edn., Pergamon, Oxford (1988).
38. K. Sisido, Y. Takeda and Y. Kingawa, *J. Am. Chem. Soc.*, **83**, 538 (1961).
39. S. Ali, M. Danish and M. Mazhar, *Heteroatom Chem.*, **8**, 273 (1997).