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Synthesis, coordination and biological aspects of organotin(IV) derivatives of 4-[(2,4-dinitrophenyl)amino)]-4-oxo-2-butenoic acid and 2-{[(2,4-dinitrophenyl)amino]carbonyl}benzoic acid

KHADIJA SHAHID[1], SAIRA SHAHZADI[2] and SAQIB ALI[1*]

[1]*Department of Chemistry, Quaid-i-Azam University, Islamabad – 45320 and*
[2]*Department of Chemistry, GC University, Faisalabad, Pakistan*

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Abstract: New series of organotin(IV) complexes of aniline derivatives, R_2SnL_2 and R_3SnL [where R = Me, *n*-Bu, Ph, *n*-Oct] have been synthesized by the reaction of HL^1 and HL^2 with respective organotin halides or oxides. Experimental details for the preparation and characterization (including elemental analysis, IR and multinuclear NMR (^{1}H-, ^{13}C- and ^{119}Sn-) spectra in $CDCl_3$ and EI mass spectra of both series are provided. The binding sites of the ligands were identified by means of FTIR spectroscopic measurements. It was found that in all cases the organotin(IV) moiety reacts with the oxygen of COO^- group to form new complexes. In the diorganotin complexes, the COO^- group is coordinated to the organotin(IV) centres in a bidentate manner in the solid state. The ^{119}Sn NMR data and the $^nJ(^{13}C–^{119/117}Sn)$ coupling constant support the tetrahedral coordination geometry of the organotin complexes in non-coordinating solvents. Biological activities (antibacterial, antifungal, cytotoxicity, antileishmanial and insecticidal) of these compounds are also reported.

Keywords: organotin(IV) carboxylates; IR; multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn); mass spectrometry; biological activity.

INTRODUCTION

The chemistry of organotin(IV) complexes has developed considerably during the last 30 years, highlighting the syntheses of a number of complexes with interesting properties.[1–3] Organotin carboxylates are widely used owing to their potential biocidal activity[4] and cytotoxicity,[5] as well as to their industrial and agricultural applications.[6–10] In general, the biocidal activity of organotin complexes is greatly influenced by the molecular structures and coordination number of the tin atom.[11]

* Corresponding author. E-mail: drsa54@yahoo.com
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The environmental and biological chemistry of organotin(IV) carboxylates have been the subject of interest for some time, due to their increasingly widespread use in industry and agriculture.[12–16] Our current interest focuses on the synthesis, characterization and biological studies of different aniline derivatives of carboxylic acids.

EXPERIMENTAL

Physical measurements

Melting points were determined in capillary tubes using a MP-D Mitamura Riken Kogyo (Japan) electrothermal melting point apparatus and are uncorrected. Infrared absorption spectra (4000–400 cm^{-1}) were recorded as KBr pellets on a Bio-rad FTIR spectrophotometer.

^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded on a Bruker AM 250 spectrometer (Germany), using $CDCl_3$ as an internal reference ($\delta\,^{1}H(CDCl_3) = 7.25$ and $\delta\,^{13}C(CDCl_3) = 77.0$). Coupling constants (in H_2) are given in brackets. ^{119}Sn-NMR spectra were obtained with Me_4Sn as the external reference (δ(Sn) = 37.290665). The numbering schemes for the organotin(IV) derivatives of HL^1 and HL^2 are given in Schemes 1 and 2, respectively.

Mass spectral data were measured on a MAT 8500 Finnigan 70 eV mass spectrometer (Germany).

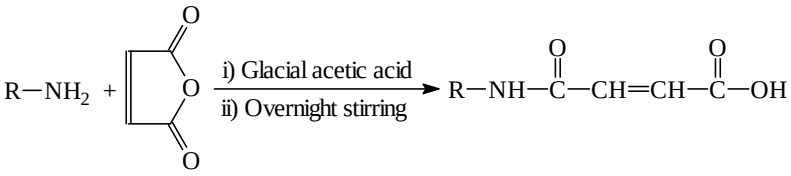
Materials and chemicals

Organotin compounds are moisture and air sensitive; hence, the reactions were performed under an inert atmosphere. All the glass apparatus with standard quick fit joints used throughout the work were cleaned and dried at 120 °C. Di- and tri-organotin(IV) salts were purchased from Aldrich. All other reagents were of the purest grade available. Solvents were purified as in previously published methods.[17] The anhydrides and 2,4-dinitroaniline were commercial products and used without further purification.

General procedure for the synthesis of the ligands (HL^1, HL^2)

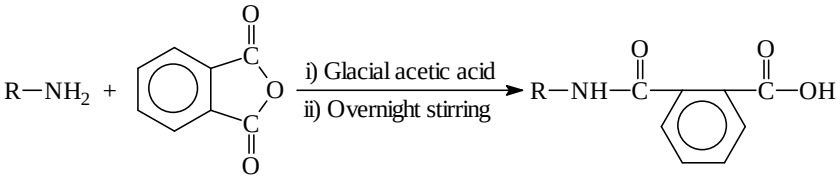
A solution of anhydride (1 mmol) in acetic acid (300 ml) was added to a solution of 2,4--dinitroaniline (1 mmol) in acetic acid (150 ml) and the mixture was stirred at room temperature overnight. The coloured precipitates formed were filtered off, washed with cold distilled H_2O (200 ml) and air-dried. The general chemical reaction is given by Eqs. (1) and (2).

For HL^1:



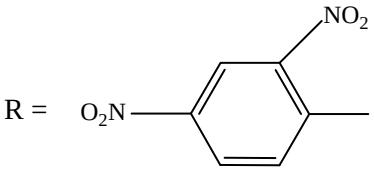
1)

For HL^2:



2)

where



General procedure for the synthesis of the di/tri-organotin(IV) complexes

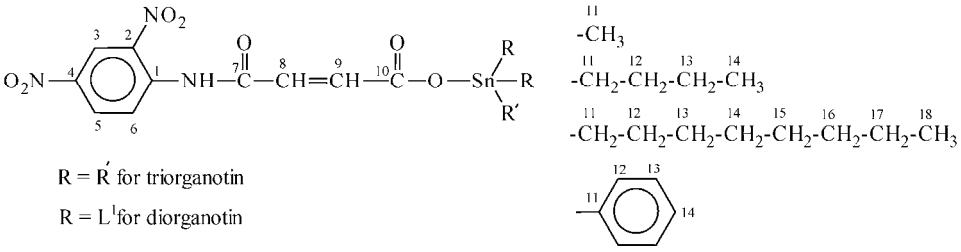
The ligand (5 mmol) was suspended in dry toluene (100 ml) and treated with triethylamine (0.59 ml, 5 mmol). The mixture was refluxed for 2–4 h. To a reaction mixture, diorganotin dichloride or triorganotin chloride (2.5 mmol/5 mmol) was added as a solid to the reaction flask under constant stirring and then refluxed for 8–10 h. The reaction mixture containing Et_3NHCl was filtered off such that the filtrate contained the organotin(IV) derivative. The solvent was removed under reduced pressure using a rotary evaporation (Eqs. (3) and (4)). However, for $Oct_2Sn(L^1/L^2)_2$, 5 mmol of the ligand HL^1/HL^2 was suspended in dry toluene (100 ml), solid Oct_2SnO (2.5 mmol) was added under constant stirring and refluxed for 8–10 h. The formed water was removed *via* a Dean-Stark trap. After cooling to room temperature, the solvent was removed under reduced pressure using a rotary evaporator (Eq. (5)).

The general chemical reactions for the synthesis of the di/triorganotin compounds are given by Eqs. (3)–(5).

$$R_2SnCl_2 + 2HL \xrightarrow{2Et_3N} R_2SnL_2 + 2Et_3NHCl \quad (3)$$

$$R_3SnCl + HL \xrightarrow{Et_3N} R_3SnL + Et_3NHCl \quad (4)$$

$$R_2SnO + 2HL \rightarrow R_2SnL_2 + H_2O \quad (5)$$



Scheme 1. NMR numbering scheme for the organotin(IV) derivatives of 4-[(2,4-dinitrophenyl)amino]-4-oxo-2-butenoic acid (HL^1).

Biological activity

Antibacterial activities. The antibacterial activities were determined using the agar well diffusion method.[18] Wells (diameter, 25 mm) were made in the media with a sterile borer and an eight-hour-old bacterial inoculum containing *ca.* 10^4–10^6 colony forming units (CFU)/mL was spread on the surface of the nutrient agar using a sterile cotton swab. The recommended concentration of the test sample (2 mg/mL in DMSO) was introduced into the respective wells. Other wells containing DMSO and the reference antibacterial drug served as negative and positive controls, respectively. The plates were incubated immediately at 37 °C for 20 h. The activity was determined by measuring the diameter (in mm) of the inhibition zone

showing complete inhibition. Growth inhibition was calculated with reference to the positive control.

LD_{50} data of the compounds were determined by the brine-shrimp assay method.[18]

Insecticidal activity. The insects were exposed to the test compounds by the contact method[18] using filter paper. Different concentrations of every compound (1 ml) were applied by micropipette to 90 mm diameter filter papers, which were then placed in petri dishes. Subsequently, four adult insects of the same size and age of each batch were transferred to the petri dishes. A control batch was treated with solvent for the determination of the environmental effects. Another batch was supplemented with reference insecticides, *i.e.*, Coopex and Decis (synthetic pyrethroids). All batches were kept without food throughout the 24 h exposure period, after which the mortality counts were determined.

Antileishmanial activity. Leishmania promastigotes were grown in bulk early in a liquid medium RPMI-1640 supplemented with 10 % foetal calf serum. At the log phase, the parasites were centrifuged at 2000 rpm for 10 min and the old medium was discarded. The parasites were diluted with fresh culture medium to a final density of 106 cells ml^{-1}. 100 µl of the culture was added in all the wells, except the first column, which received 180 µl. The last two rows of the microtiter plate were control containing varying concentrations of standard antileishmanial compounds, *e.g.*, amphotericin B or pentmidine.

The samples were prepared by dissolving 1.0 mg of the experimental compounds/crude extract (test sample) in 50 µl of DMSO and diluted up to 1.0 ml with complete medium containing antibiotics.

The method of addition and serial dilution of the samples was applied. Thus, 20 µl of a solubilised compound was added in to the first well (duplicate or triplicate) and mixed well with the micropipette. 100 µl of sample was removed and added into the next well, mixed well, 100 µl removed and added into the next well until the 8^{th} well was reached. The remaining 100 µl was discarded. In this manner, the first well received a final concentration of 100 µg ml^{-1}, and the last 0.78 µg ml^{-l} of the compound/crude extract to be tested. The plate was incubated in the dark at 25 °C for 3–5 days (preferably on an orbital shaker).

After 5 days exposure, the drug activity was assessed microscopically using an improved Neubauer chamber (hemocytometer). Thus, using a micropipette, 10 µl of the culture was removed and transferred to both chambers of the hemocytometer. Starting with chamber "o" of the hemocytometer, the cells were counted in the 1 mm centre square and the four 1 mm corner square at a magnification of 40×. The number of cells/ml was determined using the following formula: cells per ml = the average count per square$\times 10^4$, *e.g.*, if the average counts per large square was 45 cells, then there were 4.5×10^5 cells/ml.

The average number of parasites were counted in several negative control wells.[19] The parasites exposed to varying concentration of the test compounds were counted and the % mortality was calculated by the following formula: % survival = (no. of parasites test)×100/(no. of parasites negative control).

RESULTS AND DISCUSSION

The synthesized complexes were obtained pure in good yields and were air stable. They were characterized by elemental analysis, IR, multinuclear NMR spectroscopy and mass spectrometry and screened to check their biological activity.

Analytical and spectral characterization

Ligand (HL^1). Yield: 85 %; m.p. 127 °C. Anal. Calcd. for $C_{10}H_7N_3O_7$ (M.W. 281): C, 42.70; H, 2.48; N, 14.94 %. Found: C, 42.74; H, 2.50; N, 14.51 %. IR (KBr, cm^{-1}): 2850 (–OH), 3336 (–NH), 1769 (C=O), 1530 $(COO)_{asym}$, 1314 $(COO)_{sym}$, 216 ($\Delta\nu$). ^{1}H-NMR ($CDCl_3$, δ, ppm): 9.15 (*d*, [2.7] (N_2O_4–C_6H_3), 4.35 (*s*, –NH), 8.24 (*d*, [2.6]), 8.27 (*d*, [2.6], –CH=CH), 9.10 (*s*, –OH). ^{13}C-NMR ($CDCl_3$, δ, ppm): 142.9 (C_1), 132.4 (C_2), 118.8 (C_3), 129.8 (C_4), 123.8 (C_5), 128.6 (C_6), 163.2 (C_7), 152.6 (C_8), 160.2 (C_9), 172.0 (C_{10}). EIMS (*m*/*z*, (relative abundance, %)): 183 (100) $[C_6H_5N_3O_4]^+$, 99 (20) $[C_4H_3O_3]^+$, 72 (100) $[C_3H_4O_2]^+$, 55 (25) $[C_2HNO]^+$, 45 (62) $[CHO_2]^+$.

*$Me_2Sn(L^1)_2$ (**1**)*. Yield: 75 %; m.p. 119 °C. Anal. Calcd. for $C_{22}H_{18}N_6O_{14}Sn$ (M.W. 709): C, 37.23; H, 2.53; N, 11.84 %. Found: C, 37.27; H, 2.49; N, 11.80 %. IR (KBr, cm^{-1}): 3334 (–NH), 1765 (C=O), 1578 $(COO)_{asym}$, 1452 $(COO)_{sym}$, 126 ($\Delta\nu$), 526 (Sn–C), 408 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 9.14 (*d*, [2.4], N_2O_4–C_6H_3), 4.35 (*s*, –NH), 8.21 (*d*, [2.8]), 8.24 (*d*, [2.8], –CH=CH), 0.91 (*s* (Sn–CH_3). ^{13}C-NMR ($CDCl_3$, δ, ppm): 142.0 (C_1), 131.1 (C_2), 119.0 (C_3), 129.4 (C_4), 123.9 (C_5), 128.7 (C_6), 162.2 (C_7), 152.4 (C_8), 161.5 (C_9), 176.1 (C_{10}), 6.4 [535] (C_{11}). EIMS (*m*/*z*, (relative abundance, %)): 709 (55) $[R_2Sn(OOCR')_2]^+$ or $[M^+]$, 696 (45) $[RSn(OOCR')_2]^+$, 183 (82) $[C_6H_5N_3O_4]^+$, 149 (45) $[R_2Sn]^+$, 134 (55) $[RSn]^+$, 123 (70) $[C_6H_5NO_2]^+$, 120 (15) $[Sn]^+$, 91 (100) $[C_6H_5N]^+$, 57 (80) $[C_2H_2NO]^+$.

*$Bu_2Sn(L^1)_2$ (**2**)*. Yield: 72 %; m.p. 142 °C. Anal. Calcd. for $C_{28}H_{32}N_6O_{14}Sn$ (M.W. 795): C, 42.26; H, 4.02; N, 10.56 %. Found: C, 42.22; H, 4.06; N, 10.60 %. IR (KBr, cm^{-1}): 3341 (–NH), 1762 (C=O), 1565 $(COO)_{asym}$, 1435 $(COO)_{sym}$, 130 ($\Delta\nu$), 538 (Sn–C), 420 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 9.08 (*d*, [2.5], N_2O_4–C_6H_3), 4.35 (*s*, –NH), 8.18 (*d*, [2.6]), 8.48 (*d*, [2.6], –CH=CH), 0.92 (*t*) 1.26–1.36 (*m*), 1.39 (*t*, Sn–C_4H_9). ^{13}C-NMR ($CDCl_3$, δ, ppm): 142.6 (C_1), 131.2 (C_2), 119.4 (C_3), 129.5 (C_4), 123.8 (C_5), 128.2 (C_6), 169.5 (C_7), 152.1 (C_8), 161.6 (C_9), 175.0 (C_{10}), 13.5 (C_{11}), 26.3 (C_{12}), 26.9 (C_{13}), 29.6 (C_{14}). ^{119}Sn-NMR (δ, ppm): –138.5. EIMS (*m*/*z*, (relative abundance, %)): 711 (55) $[R_2Sn(OOCR')_2]^+$, 696 (45) $[RSn(OOCR')_2]^+$, 149 (45) $[R_2Sn]^+$, 134 (55) $[RSn]^+$, 120 (15) $[Sn]^+$, 86 (100) $[C_4H_6O_2]^+$, 57 (90) $[C_4H_9]^+$.

*$Oct_2Sn(L^1)_2$ (**3**)*. Yield: 68 %; m.p. 185 °C. Anal. Calcd. for $C_{36}H_{48}N_6O_{14}Sn$ (M.W. 907): C, 47.62; H, 5.29; N, 9.26 %. Found: C, 47.66; H, 5.34; N, 9.30 %. IR (KBr, cm^{-1}): 3342 (–NH), 1763 (C=O), 1591 $(COO)_{asym}$, 1442 $(COO)_{sym}$, 149 ($\Delta\nu$), 536 (Sn–C), 422 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 9.11 (*d*, [2.6], N_2O_4–C_6H_3), 4.35 (*s*, –NH), 8.19 (*d*, [2.6]), 8.52 (*d*, [2.6], –CH=CH), 0.89 (*t*), 1.75–1.80 (*m*, Sn–C_8H_{13}). ^{13}C-NMR ($CDCl_3$, δ, ppm): 142.7 (C_1), 131.1 (C_2), 119.0 (C_3), 129.7 (C_4), 123.5 (C_5), 128.4 (C_6), 165.6 (C_7), 152.5 (C_8), 161.7 (C_9), 177.9 (C_{10}), 14.0 (C_{11}), 24.8 (C_{12}), 26.3 (C_{13}), 27.0 (C_{14}), 29.1 (C_{15}), 29.6 (C_{16}), 31.8 (C_{17}), 37.0 (C_{18}). ^{119}Sn-NMR (δ, ppm): –127.4. EIMS (*m*/*z*, (relative abundance,

%)): 907 (45) $[R_2Sn(OOCR')_2]^+$, 794 (35) $[R_2Sn(OOCR')_2]^+$, 345 (40) $[R_2Sn]^+$, 232 (25) $[RSn]^+$, 183 (78) $[C_6H_5N_3O_4]^+$, 120 (12) $[Sn]^+$, 86 (60) $[C_4H_6O_2]^+$, 57 (100) $[C_2H_2NO]^+$, 43 (70) $[C_2H_3O]^+$.

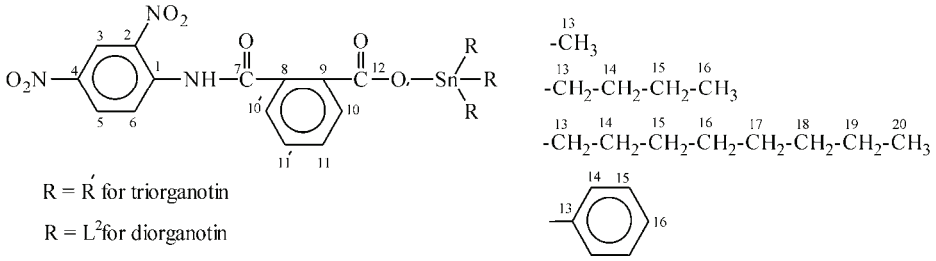
Me_3SnL^1 ***(4)***. Yield: 78 %; m.p. 101 °C. Anal. Calcd. for $C_{13}H_{16}N_3O_7Sn$ (M.W. 445): C, 35.05; H, 3.59; N, 9.43 %. Found: C, 35.01; H, 3.63; N, 9.39 %. IR (KBr, cm^{-1}): 3332 (–NH), 1774 (C=O), 1589 $(COO)_{asym}$, 1462 $(COO)_{sym}$, 127 ($\Delta\nu$), 532 (Sn–C), 418 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 9.12 (*d*, [2.6], N_2O_4–C_6H_3), 4.35 (*s*, –NH), 8.18 (*d*, [2.5], 8.94 (*d*, [2.5], –CH=CH), 0.65 (*s*, [57, 60], (Sn–CH_3). ^{13}C-NMR ($CDCl_3$, δ, ppm): 148.6 (C_1), 131.8 (C_2), 119.1 (C_3), 129.7 (C_4), 123.7 (C_5), 128.9 (C_6), 169.5 (C_7), 152.6 (C_8), 161.4 (C_9), 178.2 (C_{10}), –1.4 [382,394] (C_{11}). ^{119}Sn-NMR (δ, ppm): 144.7. EIMS (*m*/*z*, (relative abundance, %)): 445 (50) $[R_3SnOOCR']^+$, 430 (40) $[R_2SnOOCR']^+$, 415 (60) $[RSnOOCR']^+$, 183 (75) $[C_6H_5N_3O_4]^+$, 164 (35) $[R_3Sn]^+$, 149 (38) $[R_2Sn]^+$, 120 (10) $[Sn]^+$, 154 (80) $[C_8H_{10}O_3]^+$, 57 (100) $[C_2H_2NO]^+$, 43 (76) $[C_2H_3O]^+$.

Bu_3SnL^1 ***(5)***. Yield: 70 %; m.p. = 165 °C. Anal. Calcd. for $C_{22}H_{34}N_3O_7Sn$ (M.W. 571): C, 46.23; H, 5.95; N, 7.35 %. Found: C, 46.27; H, 5.90; N, 7.39 %. IR (KBr, cm^{-1}): 3330 (–NH), 1760 (C=O), 1545 $(COO)_{asym}$, 1416 $(COO)_{sym}$, 129 ($\Delta\nu$), 540 (Sn–C), 426 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 9.11 (*d*, [2.5], N_2O_4–C_6H_3), 4.35 (s, –NH), 8.19 (*d*, [2.6]), 8.46 (*d*, [2.6], –CH=CH), 0.93 (*t*), 1.27–1.36 (*m*), 1.63 (*t*, Sn-C_4H_9). ^{13}C-NMR ($CDCl_3$, δ, ppm): 142.2 (C_1), 132.3 (C_2), 119.2 (C_3), 129.7 (C_4), 123.9 (C_5), 128.3 (C_6), 169.3 (C_7), 152.3 (C_8), 161.2 (C_9), 175.6 (C_{10}), 17.4 [325, 341] (C_{11}), 26.8 [22.4] (C_{12}), 27.8 [62.6, 65.2] (C_{13}), 29.6 (C_{14}). ^{119}Sn-NMR (δ, ppm): 152.2. EIMS (*m*/*z*, (relative abundance, %)): 571 (20) $[R_3SnOOCR']^+$, 514 (40) $[R_2SnOOCR']^+$, 290 (35) $[R_3Sn]^+$, 233 (45) $[R_2Sn]^+$, 183 (75) $[C_6H_5N_3O_4]^+$, 120 (25) $[Sn]^+$, 86 (55) $[C_4H_6O_2]^+$, 57 (100) $[C_2H_2NO]^+$, 43 (76) $[C_2H_3O]^+$.

Ph_3SnL^1 ***(6)***. Yield: 72 %; m.p. 95 °C. Anal. Calcd. for $C_{28}H_{22}N_3O_7Sn$ (M.W. 779): C, 43.13; H, 2.82; N, 5.39. Found: C, 43.17; H, 2.78; N, 5.34. IR (KBr, cm^{-1}): 3339 (–NH), 1772 (C=O), 1555 $(COO)_{asym}$, 1420 $(COO)_{sym}$, 135 ($\Delta\nu$), 411 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 9.12 (*d*, [2.6], N_2O_4–C_6H_3), 4.35 (*s*, –NH), 8.15 (*d*, [2.5]), 8.38 (*d*, [2.6], –CH=CH), 7.48–7.75 (*m*, Sn–C_6H_5); ^{13}C-NMR ($CDCl_3$, δ, ppm): 142.2 (C_1), 130.3 (C_2), 119.1 (C_3), 129.5 (C_4), 124.0 (C_5), 128.5 (C_6), 169.5 (C_7), 152.4 (C_8), 161.3 (C_9), 176.4 (C_{10}), 137.4 (C_{11}), 136.1 (C_{12}), 129.0 (C_{13}), 128.7 (C_{14}). ^{119}Sn-NMR (δ, ppm): –52.4. EIMS (*m*/*z*, (relative abundance, %)): 631 (30) $[R_3SnOOCR']^+$, 554 (20) $[R_2SnOOCR']^+$, 350 (45) $[R_3Sn]^+$, 273 (50) $[R_2Sn]^+$, 196 (45) $[RSn]^+$, 120 (15) $[Sn]^+$, 154 (80) $[C_8H_{10}O_3]^+$, 57 (100) $[C_2H_3NO]^+$.

Ligand (HL^2). Yield: 84 %; m.p. 138 °C. Anal. Calcd. for $C_{14}H_9N_3O_7$ (M.W. 331): C, 50.75; H, 2.71; N, 12.68 %. Found: C, 51.71; H, 2.67; N, 12.64 %. IR (KBr, cm^{-1}): 3189 (–OH), 3325 (–NH), 1790 (C=O), 1584 $(COO)_{asym}$, 1328 $(COO)_{sym}$, 256 ($\Delta\nu$). ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.94 (*m*, N_2O_4–C_6H_3), 4.12 (*s*, –NH), 8.04 (*m*, –CO–C_6H_4–CO), 8.26 (*s*, –OH). ^{13}C-NMR ($CDCl_3$, δ,

ppm): 162.7 (C_1), 118.9 (C_2), 129.9 (C_3), 123.9 (C_4), 128.5 (C_5), 131.3 (C_6), 142.0 (C_7), 129.1 (C_8), 152.5 (C_9), 136.0 ($C_{10,10`}$), 129.7 ($C_{11,11`}$), 170.5 (C_{12}). EIMS (*m*/*z*, (relative abundance, %)): 183 (100) $[C_6H_3N_3O_4]^+$, 153 (24) $[C_6H_5NO_4]^+$, 107 (16) $[C_7H_7O]^+$, 91 (25) $[C_6H_5N]^+$.



Scheme 2. NMR numbering scheme for organotin(IV) derivatives of 2-{[(2,4-dinitrophenyl)amino)]carbonyl}benzoic acid (HL^2).

*$Me_2Sn(L^2)_2$ (**7**)*. Yield: 65 %; m.p. 148 °C. Anal. Calcd. for $C_{30}H_{24}N_6O_{14}Sn$ (M.W. 811): C, 44.38; H, 2.95; N, 10.35 %. Found: C, 44.42; H, 2.91; N, 10.31 %. IR (KBr, cm^{-1}): 3318 (–NH), 1791 (C=O), 1581 $(COO)_{asym}$, 1422 $(COO)_{sym}$, 159 ($\Delta\nu$), 522 (Sn–C), 416 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.74 (*m*, N_2O_4–C_6H_3), 4.11 (*s*, –NH), 8.33 (*m*, –CO–C_6H_4–CO), 1.26 (*s*, Sn–CH_3). ^{13}C-NMR ($CDCl_3$, δ, ppm): 142.5 (C_1), 119.7 (C_2), 129.2 (C_3), 123.7 (C_4), 128.4 (C_5), 131.5 (C_6), 165.0 (C_7), 128.4 (C_8), 152.6 (C_9), 137.3 ($C_{10,10'}$), 127.2 ($C_{11,11'}$), 172.7 (C_{12}), 8.4 [532] (C_{13}). ^{119}Sn-NMR (δ, ppm): –185.6. EIMS (*m*/*z*, (relative abundance, %)): 167 (52) $[C_6H_3N_2O_9]^+$, 149 (6) $[SnR_2]^+$, 121 (8) $[SnH]^+$, 91 (84) $[C_6H_5N]^+$, 86 (90) $[C_4H_6O_2]^+$, 84 (100) $[C_4H_4O_2]^+$, 77 (8) $[C_6H_5]^+$.

*$Bu_2Sn(L^2)_2$ (**8**)*. Yield: 79 %; m.p. 179 °C. Anal. Calcd. for $C_{36}H_{36}N_6O_{14}Sn$ (M.W. 895): C, 48.26; H, 4.02; N, 9.38 %. Found: C, 48.22; H, 4.06; N, 9.42. IR (KBr, cm^{-1}): 3323 (–NH), 1783 (C=O), 1578 $(COO)_{asym}$, 1430 $(COO)_{sym}$, 148 ($\Delta\nu$), 528 (Sn–C), 412 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.91 (*m*, N_2O_4–C_6H_3), 4.10 (*s*, –NH), 8.03 (*m*, –CO–C_6H_4–CO), 1.35 – 1.38 (*m*), 1.93 (*t*, Sn–C_4H_9); ^{13}C-NMR ($CDCl_3$, δ, ppm): 142.6 (C_1), 121.3 (C_2), 129.5 (C_3), 123.9 (C_4), 128.2 (C_5), 131.1 (C_6), 167.2 (C_7), 128.2 (C_8), 152.4 (C_9), 136.2 ($C_{10,10`}$), 124.5 ($C_{11,11`}$), 176.2 (C_{12}), 14.0 (C_{13}), 22.6 (C_{14}), 29.3 (C_{15}), 31.8 (C_{16}). ^{119}Sn-NMR (δ, ppm): –137.5. EIMS (*m*/*z*, (relative abundance, %)): 267 (100) $[C_6H_3N_2O_9]^+$, 233 (8) $[SnR_2]^+$, 176 (9) $[SnR]^+$, 77 (67) $[C_6H_5]^+$, 57 (84) $[C_4H_9]^+$.

*$Oct_2Sn(L^2)_2$ (**9**)*. Yield: 66 %; m.p.135 °C. Anal. Calcd. for $C_{44}H_{52}N_6O_{14}Sn$ (M.W. 1007): C, 52.43; H, 5.16; N, 8.34 %. Found: C, 52.47; H, 5.12; N, 8.38 %. IR (KBr, cm^{-1}): 3320 (–NH), 1793 (C=O), 1569 $(COO)_{asym}$, 1428 $(COO)_{sym}$, 141 ($\Delta\nu$), 530 (Sn–C), 418 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.93 (*m*, N_2O_4–C_6H_3), 4.12 (*s*, –NH), 8.02 (*m*, –CO–C_6H_4–CO), 0.90, 1.17 – 1.28 (*m*), 1.72–1.78 (*m*, Sn–C_8H_{13}). ^{13}C-NMR ($CDCl_3$, δ, ppm): 142.2 (C_1), 118.9 (C_2), 129.1 (C_3), 123.7 (C_4), 128.4 (C_5), 131.4 (C_6), 167.4 (C_7), 128.4 (C_8), 152.9 (C_9), 136.5

($C_{10,10`}$), 124.6 ($C_{11,11`}$), 177.4 (C_{12}), 14.1 (C_{13}), 22.6 (C_{14}), 25.8 (C_{15}), 26.2 (C_{16}), 29.3 (C_{17}), 29.3 (C_{18}), 31.8 (C_{19}), 33.4 [101] (C_{20}). ^{119}Sn-NMR (δ, ppm): –139.2. EIMS (*m*/*z*, (relative abundance, %)): 345 (4) $[SnR_2]^+$, 232 (3) $[SnR]^+$, 167 (67) $[C_6H_3N_2O_4]^+$, 91 (18) $[C_6H_5N]^+$, 85 (56) $[C_4H_5O_2]^+$, 57 (100) $[C_4H_9]^+$.

Me_3SnL^2 ***(10)***. Yield; 72 %; m.p. 101 °C. Anal. Calcd. for $C_{17}H_{18}N_3O_7Sn$ (M.W. 495): C, 41.21; H, 3.63; N, 8.48 %. Found: C, 41.25; H, 3.67; N, 8.52 %. IR (KBr, cm^{-1}): 3326 (–NH), 1780 (C=O), 1593 $(COO)_{asym}$, 1415 $(COO)_{sym}$, 178 ($\Delta\nu$), 542 (Sn–C), 422 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.92 (*m*, N_2O_4–C_6H_3), 4.11 (*s*, –NH), 8.66 (*m*, –CO–C_6H_4–CO), 0.88 (*s*, [57], Sn–CH_3). ^{13}C-NMR ($CDCl_3$, δ, ppm): 142.6 (C_1), 119.6 (C_2), 129.4 (C_3), 123.6 (C_4), 128.0 (C_5), 131.5 (C_6), 165.2 (C_7), 128.0 (C_8), 152.4 (C_9), 136.2 ($C_{10,10`}$), 125.2 ($C_{11,11`}$), 171.4 (C_{12}), –1.6 [383,395] (C_{13}). ^{119}Sn-NMR (δ, ppm): 111.6. EIMS (*m*/*z*, (relative abundance, %)):166 (22) $[C_6H_2N_2O_4]^+$, 164 (16) $[SnR_3]^+$, 149 (28) $[SnR_2]^+$, 134 (6) $[SnR]^+$, 120 (7) $[Sn]^+$, 91 (11) $[C_6H_5N]^+$, 77 (37) $[C_6H_5]^+$, 57 (100) $[C_4H_9]^+$.

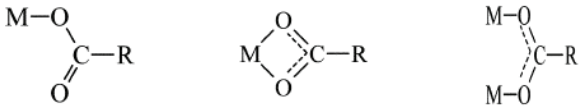
Ph_3SnL^2 ***(11)***. Yield: 55 %; m.p. 163 °C; Anal. Calcd. for $C_{32}H_{24}N_3O_7Sn$ (M.W. 681): C, 56.38; H, 3.52; N, 6.16 %. Found: C, 56.34; H, 3.48; N, 6.20 %. IR (KBr, cm^{-1}): 3324 (–NH), 1788 (C=O), 1572 $(COO)_{asym}$, 1410 $(COO)_{sym}$, 162 ($\Delta\nu$), 425 (Sn–O). ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.95 (*m*, N_2O_4–C_6H_3), 4.13 (*s*, –NH), 8.65 (*m*, –CO–C_6H_4–CO), 7.28–7.59 (*m*, Sn–C_6H_5). ^{13}C-NMR ($CDCl_3$, δ [$^{117/119}$Sn–^{13}C], ppm): 142.1 (C_1), 118.2 (C_2), 129.5 (C_3), 123.7 (C_4), 128.4 (C_5), 131.2 (C_6), 168.8 (C_7), 128.4 (C_8), 152.7 (C_9), 136.4 ($C_{10,10`}$), 125.5 ($C_{11,11`}$), 182.1 (C_{12}), 136.2 [46, 48] (C_{13}), 135.8 (C_{14}), 128.0 [62, 65] (C_{15}), 127.5 [13] (C_{16}). ^{119}Sn-NMR (δ, ppm): –109.75.; EIMS (*m*/*z*, (relative abundance, %)): 350 (4) $[SnR_3]^+$, 315 (10) $[C_{14}H_8N_3O_6]^+$, 309 (95) $[C_{20}H_{25}O_3]^+$, 273 (5) $[SnR_2]^+$, 196 (7) $[SnPh]^+$, 154 (100) $[C_8H_{10}O_3]^+$, 120 (10) $[Sn]^+$, 77 (20) $[C_6H_5]^+$.

Infrared spectra

The FTIR data are consistent with the formation of compounds with the composition R_2SnL_2 and R_3SnL. The carboxylate groups of the ligand coordinate to the metal ion in different modes as shown in Scheme 3.[20] The disappearance of a broad band in the spectra of the complexes in the region 3200––2800 cm^{-1}, which was present in the free ligands, suggests deprotonation of the free COOH group upon complexation. The bonding of the tin(IV) to the ligand was confirmed by the presence of Sn–O bands in the range of 426–408 cm^{-1}.[21] Sn–C absorption bands in the region of 542–520 cm^{-1} were observed in all complexes.

Based on the difference between $\nu(COO)_{sym}$ and $\nu(COO)_{asym}$ and the corresponding band position, it is proposed that the carboxylate group acts as bidentate in all these complexes in the solid state.[22] According to Lebl *et al.*,[23] the

values $\Delta\nu$ ($\Delta\nu = \nu(\mathrm{COO})_{asym} - \nu(\mathrm{COO})_{sym}$) can be divided into three groups: (a) when $\Delta\nu$(COO) > 350, the compounds contain, with a high probability, a monodentate carboxylate group. However, other very weak intra- and intermolecular interactions cannot be excluded; (b) when $\Delta\nu$(COO) < 200, the carboxylate groups of these compounds can be considered to be practically bidentate; (c) compounds where $\Delta\nu$(COO) is between 350 and 200 are considered as intermediate between monodentate and bidentate, which is called anisobidentate. It has also been suggested that the $\Delta\nu$(COO) value in the chelating mode is less than $\Delta\nu$(COO) in the bridging mode.[20] Some characteristic vibrational frequencies of different groups fall within the range ν(C=O) 1793–1762 cm^{-1} and ν(N–H) 3342–3320 cm^{-1}.



1 2 3

Scheme 3. Possible coordination modes of the carboxylate group to the metal.

^{1}H-NMR spectra

The ^{1}H-NMR spectra for the investigated compounds were recorded in deuterated chloroform at room temperature. Different protons were assigned based on their multiplicity and intensity patterns. The integration of the spectra was in accordance with the number of protons proposed for each molecular fragment. The ^{1}H-NMR spectra of the complexes exhibited useful features.

In the studied complexes, the COOH resonance of the ligands was absent, which suggests the replacement of the carboxylic proton by the organotin(IV) moiety. Charge donation from the COO^- donor to the tin atom decreased the electron density and resulted in a deshielding of the ligand protons. Singlets and multiplets were observed in the case of the methyl and phenyl groups, respectively. Simultaneously, the signals of the aromatic protons were shifted downfield because of the ring current effect. The aromatic protons of the phenyl group and the benzoate group were assigned with difficulty due to the narrow range on the NMR scale, hence the phenyl group gave a multiplet due to a complex pattern. The alkyl groups bonded to tin were assigned in their characteristic range. The $^nJ(^{119}Sn,^1H)$ for the dimethyl and trimethyltin(IV) derivatives had approximately the same value, confirming a tetrahedral environment in solution, *i.e.*, the carboxylate groups act as monodentate in solution. The $^nJ(^1H,^1H)$ values for the different compounds suggest that the protons of the ethylene group (HC=HC) were in the *cis*-position.[24] In all diorganotin(IV) and triorganotin(IV) derivatives, the –NH resonance was observed as a broad or a sharp weak signal. The aromatic proton resonances were assigned by comparing the experimental chemical shifts with those calculated by the incremental method.[25] In triorganotin carboxylates,

the $^{2}J[^{119}Sn,^{1}H]$ values for the triorganotin compounds suggest tetrahedral geometry (Fig. 1(a)) of the tin atom.

Unlike the triorganotin carboxylates in solution, the geometry of diorganotin dicarboxylates cannot be defined with certainty because of dynamic processes involving different modes of coordination of the carboxylate oxygens to the tin atom.[26] However, in the solid state, the tin atom is mostly hexa-coordinated in such systems (Fig.1(b)).[27]

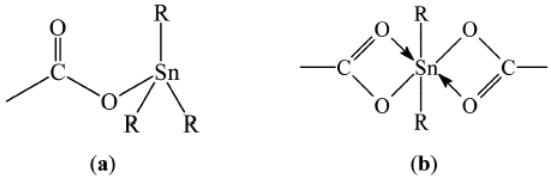


Fig. 1. Suggested structures of the complexes.

^{13}C-NMR spectra

The ^{13}C-NMR spectra of the organotin(IV) derivatives are consistent with the following observations:

According to ^{13}C-NMR data, the involvement of the carboxylate group in the bonding to Sn was confirmed by the resonance of the carboxylic carbon in all the compounds, which exhibited a lower shift after coordination as compared with the ligands, suggesting the coordination of the ligand through a carboxylic oxygen to the organotin(IV) moiety. The remaining carbons did not shift significantly after complexation.

The carbon of the phenyl and alkyl groups attached to tin were observed at almost similar positions as calculated by the incremental method[24] and reported in the literature.[28–32] Two resonances were observed in the expected range for the carboxyl and amide groups.

The tributyltin and trimethyltin complexes of the present investigation exhibit $^{1}J(^{13}C,^{117/119}Sn)$ coupling satellites in the range 325–363 Hz in $CDCl_3$ solution, suggesting that the tin atom is four-coordinated in solution.[33–36]

^{119}Sn-NMR spectra

The ^{119}Sn chemical shifts of the organotin compounds covered a range $\delta\pm600$. As the electron releasing power of the alkyl group bonded to tin increases, the tin atom becomes progressively more shielded and the $\delta(^{119}Sn)$ value moves to a higher field.[37] It was reported earlier that ^{119}Sn-NMR is also a powerful technique and the value of $\delta(^{119}Sn)$ is directly linked to the coordination number of the central tin atom.[38]

In all the complexes, the ^{119}Sn spectra show only a sharp singlet, indicating the formation of single species. In general, the ^{119}Sn chemical shifts move to lower frequency with increasing coordination number, although the shift ranges

are somewhat dependent on the nature of the substituents at the tin atom. In all the complexes, the ^{119}Sn chemical shift values for the triorganotin complexes agree well with a tetrahedral environment around the tin atom in non-coordinated solvents, whereas those of the diorganotin complexes indicate penta coordina-tion, *i.e.*, the tendency towards increased coordination number decreases as the number of R groups increases. However, in solution, such structures appear four-coordinate, the additional coordination from the carbonyl oxygen to tin being lost.[39]

Mass spectrometry

Mass spectra for the investigated compounds were recorded at 70 eV for all di- and tri-organotin(IV) derivatives. Molecular ion peaks of very low intensity are observed in few complexes.[40] In the di- and tri-organotin(IV) derivatives, a rather similar pattern of fragmentation was observed. In both cases, primary fragmentation was due to the successive loss of R groups followed by the elimination of CO_2 from the ligand and then the remaining part of the ligand, which leaves Sn^+ or SnH^+ as the end product. The second route of fragmentation was the loss of CO_2 and other neutral species, which ultimately gives $[C_6H_5]^+$ in the first step. Another possible route is the disintegration of the ligand and stepwise elimination of R groups to Sn^+ or SnH^+ as the residue.

Biological activity

The results of the antibacterial activities are given in Table I. The screening tests show that the phenyltin carboxylates were the most potent candidates against the tested bacteria. The activity of the other derivatives varies according to their R groups.

TABLE I. Antibacterial activity data for $R_2Sn(L^1)_2$/$R_2Sn(L^2)_2$ and R_3SnL^1/R_3SnL^2

Bacterium	Zone of inhibition, mm										
	Compound number										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Escherichia coli	10	–	10	14	14	20	–	–	16	–	10
Bacillus subtilis	10	–	12	–	14	10	–	–	27	–	10
Shigella flexenari	10	–	14	14	–	–	–	–	18	–	–
Staphylococcus aureus	–	–	14	20	–	–	–	–	14	–	–
Pseudomonas aeruginosa	–	–	–	–	14	16	–	–	18	–	16
Salmonella typhi	10	–	14	10	–	–	–	–	20	–	18

The LD_{50} data are summarized in Table II. A previous report[41] showed that the nature of the organic group is responsible for the toxicity of organotin compounds. Compound **5** did not show any toxicity at all.

The insecticidal activity data of the compounds are given in Table III. The trimethyltin(IV) carboxylate of HL^2 was inactive against the tested insects, while the other organotin(IV) carboxylates exhibited activity. This can be explained as

follows: as the length or number of the R group increases, the activity also increases.

TABLE II. Cytotoxicity data for $R_2Sn(L^1)_2/R_2Sn(L^2)_2$ and R_3SnL^1/R_3SnL^2 (standard drug: etoposide, LD_{50} = 7.4625 μg/ml)

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
LD_{50} / μg ml^{-1}	8.64	9.14	8.00	7.99	–	5.18	16.89	16.89	13.92	14.29	18.19

TABLE III. Insecticidal data for $R_2Sn(L^1)_2/R_2Sn(L^2)_2$ and R_3SnL^1/R_3SnL^2. Concentration of samples: 1571.2 μg/ml. Standard drug: Permethrin (235.7 μg/ml)

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
IC_{50} /μg/ml	62.12	–	65.71	64.50	64.80	–	60	65	67.8	65.5	65

Leishmaniases is a class of diseases caused by protozoan haemoflagellates of the genus *Leishmania*. The disease is transmitted by female sandflies (*Phlebotomus* or *Lutzomya*) that feed on the blood of an animal or human host. The disease occurs in most tropical and sub-tropical areas of the world. The anti-leishmanial activity data of the complexes are given in Table IV. All the compounds showed antileishmanial activity with a few exceptions.

TABLE IV. Antileishmanial activity data for $R_2Sn(L^1)_2/R_2Sn(L^2)_2$ and R_3SnL^1/R_3SnL^2. Test Organism-Leishmanial major (DESTO). Standard drug: Amphotericin B (0.19 μg/ml)

Insect	Compound										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Tribolium castaneum	25	25	25	25	25	25	40	20	25	–	20
Sitophilus oryzae	25	25	25	25	25	25	–	–	25	–	20
Rhyzoperthadominia	50	50	20	25	–	25	25	–	25	–	–
Callosbruchus analis	25	25	25	25	25	22	25	–	60	–	40

CONCLUSIONS

The synthesis of R_2SnL_2 and R_3SnL resulted in compounds with a 1:1 or 1:2 metal-to-ligand ratio in good yield. The FTIR data evidenced the formation of well-defined complexes by the appearance of the Sn–O band. The NMR data were analyzed and almost all their signals were assigned. The di- and tri-organotin complexes were proposed to have penta- and tetra-coordinated geometry around tin atom in solution, confirmed by the ^{13}C,$^{117/119}Sn$ satellites, as well as ^{1}H- and ^{119}Sn-NMR data. The results demonstrated that the effect of different alkyl groups was minor. The screening results show that the reported complexes **1**–**11** exhibited good biological activity with a few exceptions.

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ИЗВОД

СИНТЕЗА, КООРДИНАЦИЈА И БИОЛОШКИ АСПЕКТИ ОРГАНОКАЛАЈ(IV) ДЕРИВАТА 4-[(2,4-ДИНИТРОФЕНИЛ)АМИНО]-4-ОКСО-2-БУТЕНСКЕ АКРИЛНЕ КИСЕЛИНЕ И 2-{[(2,4-ДИНИТРОФЕНИЛ)АМИНО]КАРБОНИЛ} БЕНЗОЕВЕ КИСЕЛИНЕ

KHADIJA SHAHID[1], SAIRA SHAHZADI[2] и SAQIB ALI[1]

[1]Department of Chemistry, Quaid-i-Azam University, Islamabad – 45320 и [2]Department of Chemistry, GC University, Faisalabad, Pakistan

Синтетисана је нова серија органокалај(IV) комплекса анилинских деривата, R_2SnL_2 и R_3SnL [где је R = Me, *n*-Bu, Ph, *n*-Oct], реакцијом HL^1 и HL^2 са одговарајућим органокалајним халогенидима или оксидима. Дати су експериментални детаљи за добијање и карактеризацију (укључујући елементалну анализу, IR и мултинуклеарну NMR (^{1}H, ^{13}C и ^{119}Sn спектри у $CDCl_3$) и EI масене спектре) обе серије. Везујућа места лиганада су идентификована помоћу FTIR спектроскопских мерења, и нађено је да у свим случајевима органокалајни(IV) део реагује са кисеоником COO^- групе градећи нове комплексе. У диорганокалајним комплексима у чврстом стању COO^- група је координована за органокалај(IV) центре као биденстат. ^{119}Sn-NMR подаци и $^nJ(^{13}C–^{119/117}Sn)$ константа купловања у складу су са тетраедарском координационом геометријом органокалајних комплекса у растварачима који немају координациона својства. Такође је објављена биолошка активност ових једињења (антибактеријска, антифунгална, инсектицидна, цитотоксичност и против протозоа из рода *Leishmania*).

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