Full Paper

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Organotin(IV) carboxylates of cyclopropane carboxylic acid and 3-cyclohexylpropanoic acid: synthesis, characterization and biological activity. The crystal structure of bis(cyclopropanecarboxylato) tetramethyldistannoxane

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A series of tri- and di-organotin(IV) derivatives of the types R_3SnL, R_2SnL_2 and $[(R_2SnL)_2O]_2$ have been synthesized by the reaction of tri- and di-organotin(IV) chloride(s) with sodium cyclopropane carboxylate and sodium 3-cyclohexylpropanoate. Based on spectroscopic evidence (IR and NMR), all the triorganotin carboxylates were found to be penta-coordinated in the solid state (except the tricyclohexyltin derivative, which was found to be four-coordinated) and four-coordinated in the solution state. Attempted reaction of Me_2SnCl_2 with sodium cyclopropane carboxylate in 1 : 2 stoichiometry afforded a bis(dicarboxylato tetraorganodistannoxane) complex, $\{[Me_2Sn(cyclo\text{-}CH_2)_2CHCOO]_2O\}_2$. The X-ray diffraction of this 'dimethyltin(IV) complex' shows that the compound possesses a tetranuclear aggregate with one bridging bidentate and other free organic ester type monodentate carboxylate groups in which each Sn atom has a five-coordinated geometry. These complexes were also screened for their antifungal activities.

Keywords: tin; organotin(IV); carboxylates; distannoxanes; crystal structure; biological activity

Introduction

Organotin compounds have been the subject of study due to their diverse biological[1,2] and other[3,4] applications along with their interesting structural diversities. The structure of the molecule, coordination number, extent of alkylation and nature of organic groups attached to the tin atom are the main factors deciding the biological activity of the organotin compounds.[5–7] These compounds having suitable ligands exhibit a number of interesting structural features because of the tendency of the ligands to coordinate inter- or intra-molecularly to tin. Two comprehensive reviews on the structural aspects of organotin carboxylates have been published.[8,9] Organotin carboxylates adopt structures, which are dependent on both the nature of the alkyl (or aryl) substituent bound to the tin atom and on the type of the carboxylate ligand. Crystallographic studies of the dicarboxylato tetraorganostannoxanes, of formula $\{[R_2Sn(O_2CR')]_2O\}_2$, have shown that there are at least five distinct types of structure known for them.[8] Organotin carboxylates are known to exhibit significant biocidal properties.[10] As a continuation of our previous studies of biological organotin chemistry[11–13] we wish to report here the two series of carboxylic acid derivatives, namely cyclopropane carboxylic acid and 3-cyclohexylpropanoic acid. During the preparation of the manuscript we have come across a report on the synthesis and larvicidal activity of a tetramethyl derivative of cyclopropane carboxylic acid incorporating triorganotin moiety.[14] The crystal structures of trimethyltin[15] and tricyclohexyltin[16] derivative of 2,2,3,3-tetramethyl cyclopropane carboxylate have also been reported in literature.

Experimental

General comments

Cyclopropane carboxylic acid (Lancaster, USA) and 3-cyclohexylpropanoic acid (Lancaster, USA) were used as received from commercial sources. Ph_3SnCl (Fluka, Germany), $(c\text{-}Hex)_3SnCl$ (Aldrich, USA), $n\text{-}Bu_3SnCl$ (Merck, Germany), Me_3SnCl (Merck, Germany), Me_2SnCl_2 (Fluka, Germany) and $n\text{-}Bu_2SnCl_2$ (Merck, Germany) were used after purification wherever necessary. Triphenyltin hydroxide was prepared by alkaline hydrolysis of the triphenyltin chloride in ether–water mixture. All the solvents used in the reactions were of AR grade and obtained from commercial sources (Merck, India). The solvents were dried before use, using standard literature procedures. All experiments were carried out under a dry nitrogen atmosphere.

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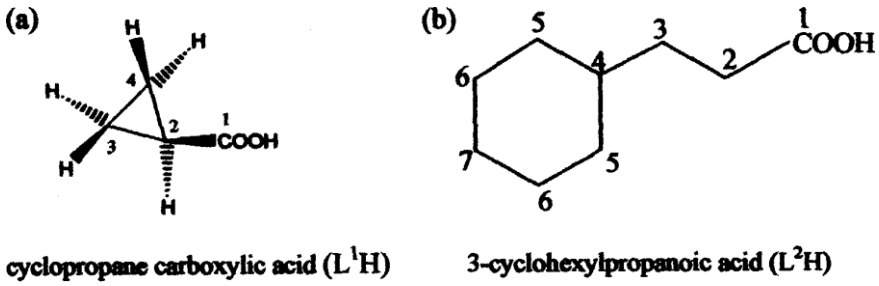

Figure 1. Numbering scheme of the ligands. (a) Cyclopropane carboxylic acid (L^1H); (b) 3-cyclohexylproponoic acid (L^2H).

Table 1. The physical and analytical data for **1–12**[a,b]

Complex	Crystallization solvent	Yield (%)	Melting point (°C)	Elemental composition[a] (%)		
				C	H	Sn
1 $C_{16}H_{32}O_2Sn$ n-Bu_3SnL^1	Petrol[d]	92	93–94	51.19 (51.23)	8.50 (8.60)	31.58 (31.64)
2 $C_{22}H_{20}O_2SnPh_3SnL^1$	Benzene	85	136	60.64 (60.73)	4.84 (4.63)	27.28 (27.28)
3 $C_{22}H_{38}O_2Sn$(c-Hex)$_3SnL^1$	Petrol[d]	80	139–142	58.29 (58.30)	8.44 (8.45)	26.14 (26.19)
4 $C_7H_{14}O_2SnMe_3SnL^1$	Petrol[d]	84	124–126	33.60 (33.78)	5.60 (5.67)	47.34 (47.69)
5 $C_{24}H_{44}O_{10}Sn_4[(Me_2SnL^1)_2O]_2$	Methanol	72	216–217	29.75 (29.80)	4.59 (4.58)	49.05 (49.08)
6 $C_{48}H_{92}O_{10}Sn_4[(n\text{-}Bu_2SnL^1)_2O]_2$	Petrol[d]	77	130–132	44.19 (44.21)	7.05 (7.11)	36.40 (36.41)
7 $C_{21}H_{42}O_2Sn$ n-Bu_3SnL^2	Petrol[d]	88	96	56.14 (56.65)	9.30 (9.51)	26.61 (26.67)
8 $C_{27}H_{30}O_2SnPh_3SnL^2$	Benzene	73	111–112	63.46 (64.19)	5.35 (5.99)	23.42 (23.49)
9 $C_{27}H_{48}O_2Sn$(c-Hex)$_3SnL^2$	Petrol[d]	67	168–170	61.72 (61.96)	9.10 (9.24)	22.59 (22.68)
10 $C_{12}H_{24}O_2SnMe_3SnL^2$	Petrol[d]	79	130–131	45.35 (45.18)	6.61 (7.58)	37.47 (37.21)
11 $C_{44}H_{84}O_{10}Sn_4[(Me_2SnL^2)_2O]_2$	Petrol[d]	72	102–104	42.19 (42.35)	6.72 (6.78)	37.98 (38.04)
12[c] $C_{26}H_{48}O_4Sn$ n-$Bu_2Sn(L^2)_2$	–	65	–	57.45 (57.47)	8.82 (8.90)	21.84 (21.84)

[a] Calculated values in parentheses.
[b] Reaction time was 5–6 h. All compounds are white.
[c] viscous liquid.
[d] b.p.60–80 °C

Physical measurements

The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using TMS as an internal standard on a Bruker DPX 300 spectrophotometer. The solution ^{119}Sn NMR spectra were measured in $CDCl_3$ solution at 149.05 MHz using a Jeol Eclipse Plus 400 spectrometer and were referenced against $SnMe_4$. IR spectra in the range 4000–400 cm^{-1} were recorded on a FTIR-8300 Shimadzu spectrophotometer with samples investigated as KBr discs. Microanalyses were performed at RSIC, NEHU, Shillong, India and at IACS, Jadavpur, Kolkata. Tin was estimated gravimetrically as SnO_2 using standard procedure in our laboratory.

Synthesis

Preparation of sodium cyclopropane carboxylate (L^1Na) and sodium 3-cyclohexylpropanoate (L^2Na).

Sodium cyclopropane carboxylate and sodium 3-cyclohexylpropanoate were prepared by titrating a methanolic solution of the ligands with 0.5 M methanolic NaOH in the presence of phenolphthalein as an indicator. The solvent was removed by distillation. The solid sodium salts obtained were then dried in an air oven at 105 °C for 48 h. The structures of the cyclopropane carboxylic acid and 3-cyclohexylpropanoic acids, their numbering schemes and the abbreviations are presented in Fig. 1.

*Synthesis of tri-n-butyltin(IV) cyclopropane carboxylate (**1**)*

A typical procedure is described below considering **1** as an example. Tri-*n*-butyltin(IV) chloride (0.500 g, 1.536 mmol) in 30 ml of methanol was added to a hot methanol solution (30 ml) containing sodium cyclopropane carboxylate (0.166 g, 1.536 mmol) under inert atmosphere. The reaction mixture was heated under reflux for 5 h and then the volatiles were removed by distillation. The dry mass was extracted thoroughly with hot petrol (60–80 °C, 45 ml). Shiny white needle-shaped crystals of the desired product was deposited upon cooling. The other triorganotin complexes (except the triphenyltin-derivative, **8** of L^2H) of the ligands were prepared analogously using appropriate triorganotin chlorides and L-Na. The characterization, analytical and spectroscopic data of these compounds are reported in Tables 1–3.

*Synthesis of triphenyltin(IV) 3-cyclohexylpropanoate (**8**)*

Triphenyltin hydroxide (0.500 g, 1.364 mmol) in 45 ml benzene was added to the solution of 3-cyclohexylpropanoic acid (0.213 g, 1.365 mmol) in benzene under inert atmosphere. The reaction was performed under reflux for 4 h with water thus produced removed azeotropically using a Dean–Stark trap. The volatiles were removed by distillation. The dry mass was extracted thoroughly with hot petrol (60–80 °C, 50 ml). The crude product obtained was deposited upon cooling, which was then recrystallized from benzene.

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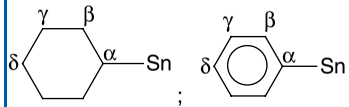
Table 2. ^{1}H NMR data (in ppm) for **1–12**[a,b,c]

	Ligand skeleton						Sn–R skeleton			
	H-2	H-3	H-3,4	H-4,5	H-6	H-7	H-α	H-β	H-γ	H-δ
1	1.59 (m,1H)	–	1.07–0.88 (m,2H) 0.79–0.76 (m,2H)	–	–	–	1.70–1.52 (m,6H)	1.25–1.08 (m,6H)	1.49–1.29 (m,6H)	0.90 (t,9H)
2	1.69 (m,1H)	–	1.06–0.97 (m,2H) 0.93–0.82 (m,2H)	–	–	–	–	7.72–7.69 (m,6H) [63 Hz][d]	7.43 (t,6H)	7.43 (t,3H)
3	1.77–1.63 (m,1H)	–	1.02–0.85 (m,2H) 0.79–0.76 (m,2H)	–	–	–	1.45–1.31 (m,3H)	1.91–1.81 (m,12H)	1.77–1.63 (m,12H)	1.45–1.31 (m,6H)
4	1.56 (m,1H)	–	0.99–0.84 (m,2H) 0.83–0.70 (m,2H)	–	–	–	0.52 (m,9H) [58.8,56.4][e]	–	–	–
5	1.45–1.36 (m,2H)	–	1.01–0.52 (m,8H)	–	–	–	exocyclic 0.74 [85.0][e] endocyclic 0.79 [89.0][e]	–	–	–
6	1.71–1.57 (m,2H)	–	0.94–0.76 (m,8H)	–	–	–	1.71–1.57 (m,8H)	1.45–1.28 (m,8H)	1.45–1.28 (m,8H)	0.92 (t,6H) 0.90 (t,6H)
7	2.30 (t,2H)	1.68–1.47 (m,2H)	–	1.68–1.47 (m,5H)	1.39–1.16 (m,4H)	0.98–0.83 (m,2H)	1.68–1.47 (m,6H)	1.39–1.16 (m,6H)	1.39–1.16 (m,6H)	0.90 (t,9H)
8	2.41 (t,2H)	1.63–1.50 (m,2H)	–	1.63–1.50 (m,5H)	1.11–1.09 (m,4H)	0.89–0.82 (m,2H)	–	7.69 (m,6H) [57Hz][d]	7.41 (t,6H)	7.41 (t,3H)
9	2.37–2.17 (m,2H)	2.37–2.17 (m,2H)	–	1.98–1.42 (m,5H)	1.42–1.19 (m,4H)	0.94–0.87 (m,2H)	1.98–1.94 (m,3H)	1.87–1.46 (m,12H)	1.87–1.46 (m,12H)	1.42–1.19 (m,6H)
10	2.29 (t,2H)	1.54–1.46 (m,2H)	–	1.71–1.57 (m,5H)	1.26–1.10 (m,4H)	0.93–0.83 (m,2H)	0.53 (t,9H) [57.0][e]	–	–	–
11	2.18 (t,4H)	1.49–1.41 (m,4H)	–	1.71–1.57 (m,10H)	1.27–1.10 (m,8H)	0.96–0.82 (m,4H)	Exocyclic 0.76 [84.0][e] Endocyclic 0.78 [90.0][e]	–	–	–
12	2.18 (t,4H)	1.41–1.32 (m,4H)	–	1.72–1.48 (m,10H)	1.25–1.10 (m,8H)	0.93–0.83 (m,4H)	1.72–1.48 (m,4H)	1.41–1.32 (m,4H)	1.41–1.32 (m,4H)	0.91 (t,6H)

[a] Spectra recorded in $CDCl_3$,multiplicity is given as t, triplet; m, multiplet.
[b] Refer to Fig. 1 for numbering scheme in the ligand skeleton.
[c] Numbering scheme for Sn–R skeleton: $^{\alpha}CH_3-Sn$; $^{\delta}CH_3-^{\gamma}CH_2-^{\beta}CH_2-^{\alpha}CH_2-Sn$:



;
[d] $^{3}J(^{119}Sn-^{1}H)$ in Hz.
[e] $^{2}J(^{119}Sn-CH_3)$ in Hz, $^{2}J(^{117}Sn-CH_3)$ in Hz.

Table 3. ^{13}C and ^{119}Sn NMR data[a–c] (in ppm) of **1**–**12**

	Ligand skeleton							Sn–R skeleton				
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-α	C-β	C-γ	C-δ	δ (^{119}Sn)
1	180.2	13.21	8.26	–	–	–	–	16.36 [360.0][d]	27.78 [28.3][e]	26.98 [66.7][f]	13.62	104.68
2	181.7	12.82	9.06	–	–	–	–	138.5	136.8[47][e]	128.8 [62.2][f]	130.0 [13.5][g]	−117.09
3	180.02	13.36	8.26	–	–	–	–	33.6	31.01 [14.2][e]	28.88 [63.0][f]	26.89 [59.2][g]	7.52
4	180.2	13.15	8.28	–	–	–	–	−2.43[400.0/382.8][d]	–	–	–	129.35
5	181.2	14.3	8.08	–	–	–	–	5.94 [753.0/720.0][d]	–	–	–	δ(^{119}Sn)*endo*, −190.8
								8.65 [800.0/763.0][d]				δ(^{119}Sn)*exo*, −179.1
6	180.6	14.4	7.99	–	–	–	–	28.67	27.55 [37.5][e]	26.92	13.64	δ(^{119}Sn)*endo*, −218.7
									27.30	26.77 [123.4][f]		δ(^{119}Sn)*exo*, −209.6
7	179.82	37.40	33.26	32.45	33.04	26.60	26.30	16.36 [357.7/342.1][d]	27.84 [19.5][e]	27.02 [64.5][f]	13.63	103.73
8	181.27	37.33	33.06	31.71	32.94	26.51	26.21	138.45	136.85 [47.2][e]	128.83 [62.2][f]	130.03 [15.0][g]	−115.18
9	184.40	37.37	32.56	28.52	29.45	26.55	26.30	32.99 [340.5]d	29.76 [18.7][e]	28.85 [56.25][f]	26.48 [45.0][g]	n.m.[h]
10	179.8	37.40	33.08	32.39	32.97	26.54	26.23	−2.50[398.62/381.0][d]	–	–	–	128.82
11	180.6	37.37	33.79	30.04	30.09	26.53	26.25	8.75 [807.6][d]	–	–	–	δ(^{119}Sn)*endo*, −186.9
								6.35 [750.0][d]				δ(^{119}Sn)*exo*, −176.1
12	184.5	37.28	32.88	27.19	31.71	26.57	26.23	24.81	26.45	26.16	13.45	−148.6

[a] Spectra recorded in $CDCl_3$.
[b] For numbering scheme of the ligands see Fig. 1.
[c] For numbering scheme of Sn–R skeleton see footnotes of Table 2.
[d] $^1J(^{13}C-^{119/117}Sn)$ in Hz.
[e] $^2J(^{13}C-^{119}Sn)$ in Hz.
[f] $^3J(^{13}C-^{119}Sn)$ in Hz.
[g] $^4J(^{13}C-^{119}Sn)$ in Hz.
[h] n.m. = not measured.

*Synthesis of bis(cyclopropanecarboxylato)tetramethyldistannoxane (**5**)*

The complex **5** was obtained during an attempted synthesis of dimethyltin(IV) dicyclopropanecarboxylates. Me_2SnCl_2 (0.700 g, 3.186 mmol) in 40 ml of methanol was added to a hot methanol solution (45 ml) containing L^1Na (0.688 g, 6.366 mmol). The reaction mixture was heated under reflux for 6 h and then the solvent was removed by distillation. The dry mass was extracted thoroughly with hot petrol (60–80 °C, 25 ml). The crude product was deposited upon cooling. The product was recrystallized from methanol to yield crystals of **5**. The compounds **6** and **11** were prepared analogously using appropriate diorganotin chlorides and L^1/L^2Na.

*Synthesis of di-n-butyltin(IV) di-3-cyclohexylpropanoate (**12**)*

n-Bu_2SnCl_2 (0.700 g, 2.303 mmol) in 45 ml of methanol was added to a hot methanolic solution (30 ml) containing L^2Na (0.820 g, 4.607 mmol). The reaction mixture was heated under reflux for 6 h and then the solvents were removed by distillation. The dry mass was extracted thoroughly with hot petroleum ether (60–80 °C; 40 ml). The viscous product was obtained after slow evaporation of the petroleum ether solution.

X-ray crystallography

Colourless X-ray quality crystals of **5** were obtained by the slow evaporation of the methanolic solution of **5**. A suitable single crystal of the compound **5** was selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed with a Siemens smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoKα radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature at 1321 frames with ω scans (width of 0.300 and exposure time 20 s per frame) in the 2θ range 2.5–46.50. The structure was solved by direct methods using SHELXS-86,[17] which readily established the heavy atom positions (Sn) and facilitated the identification of the light atoms (O, C) from different Fourier maps. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS program.[18] All the hydrogen positions were initially observed in the Fourier maps, but for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycle refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Seven carbon atoms [C(5), C(7), C(15), C(16), C(19), C(20) and C(23)] were refined only isotropically because of their poor thermal parameters. Full-matrix-least-squares structure refinement against F^2 was carried out using SHELXTL-PLUS program.[19] The details of final refinements of **5** are given in Table 4.

Biological studies

The biological activity of di- and tri-organotin complexes of cyclopropane carboxylic acid and 3-cyclohexylpropanoic acid against four fungal pathogens (*Curvularia eragrostidis, Macrophomina phaseolina, Dreschlerea oryzae, Alternaria porri)* of four different crops (*Camellia sineusis, Solanum melongena, Oryzae sativa* and *Guizotia abyssinica* respectively) were investigated. The fungal strains used in the study were gifts from the Plant Pathology Laboratory, Department of Botany, North Bengal University. Fungi were

Table 4. Crystal data and structure refinement for the compound $\{[Me_2Sn(cyclo CH_2)_2CHCOO]_2O\}_2$ (**5**)

Identification code	sad	
Empirical formula	C24 H44 O10 Sn4	
Formula weight	967.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P-1$	
Unit cell dimensions	$a = 10.1806(1)$ Å	$\alpha = 84.454(1)^\circ$
	$b = 11.3774(2)$ Å	$\beta = 83.6480(10)^\circ$
	$c = 15.9447(3)$ Å	$\gamma = 74.2260(1)^\circ$
Volume	1762.11(5) $Å^3$	
Z	2	
Density (calculated)	1.823 mg m^{-3}	
Absorption coefficient	2.845 mm^{-1}	
$F(000)$	936	
Crystal size	$0.28 \times 0.08 \times 0.08$ mm^3	
Theta range for data collection	1.29–23.25°	
Index ranges	$-11 \le h \le 10, -12 \le k \le 12, -14 \le l \le 17$	
Reflections collected	7328	
Independent reflections	4923 [R(int) = 0.0245]	
Absorption correction	SADABS	
Max. and min. transmission	1.000000 and 0.437669	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4923/0/310	
Goodness-of-fit on F^2	1.036	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0391, wR_2 = 0.1017$	
R indices (all data)	$R_1 = 0.0562, wR_2 = 0.1112$	
Extinction coefficient	0.0009(2)	
Largest difference peak and hole	0.888 and −0.754 e $Å^{-3}$	

grown on potato–dextrose–agar (PDA) medium at 28 ± 1 °C. The fungicidal activities were determined following spore germination bioassay as described by Rouxel *et al*.[20] Purified eluents (10 µl) were placed on two spots 3 cm apart on a clean, grease-free slide and the solvent was allowed to evaporate. One drop of spore suspension (0.02 ml per drop) prepared from 15-day-old cultures of the fungi was added to the treated spots. In this way, sets for various concentrations of the compounds were prepared. The slides were incubated at 27 ± 1 °C for 24 h under humid conditions in Petri plates. Finally, after proper incubation period, one drop of a Cotton Blue–lactophenol mixture was added to each spot to fix the germinated spores. The number of spores germinated compared with the germinated spores of control (where no chemicals were used) was calculated using an average of 300 spores per treatment. The minimum inhibitory concentration required for complete inhibition was recorded in units of microgram/millilitre (µg ml^{-1}).

Phytotoxicities[21] of these new organotin compounds were determined on healthy wheat seeds (variety Sonalika) purchased from Anup Seed Company, Bidhan Market, Siliguri, West Bengal. These healthy seeds were dipped in acetone–water suspensions of the compounds of different concentrations (25, 50, 100 µg ml^{-1}) for 1, 4 and 8 h. The treated seeds were allowed to germinate sown over a mat of moist filter papers arranged in covered Petri plates. One hundred seeds were treated for each experiment. After two days, the germinated seeds (treated with compounds) were counted against the germinated seeds of the control (where no compounds were used) and those seeds, which had produced coleoptiles, were considered to have germinated. Each experiment was repeated in triplicate. All apparatus and materials used were sterilized where necessary using standard procedures.

Results and Discussion

Synthetic aspects

The triorganotin complexes were obtained in moderate to good yields by the reaction between the respective R_3SnCl and the sodium salt of the acids (L^1Na and L^2Na) in stoichiometric amounts in methanol. Complex **8** was obtained by heating at reflux the stoichiometric amount of L^2H and Ph_3SnOH in benzene:

$$R_3SnCl + LNa \longrightarrow R_3SnL + NaCl \quad (1)$$

$$Ph_3SnOH + L^2H \longrightarrow Ph_3SnL^2 + H_2O \quad (2)$$

whereas dimeric distannoxanes **5, 6** and **11** were obtained by heating at reflux the 2:1 stoichiometric amount of ligands or their sodium salts with corresponding diorganotin oxides in benzene or diorganotin chlorides in methanol solution. Dicarboxylatotetraorganostannoxanes are the hydrolysis products of diorganotin dicarboxylates[22,23] and the references of these compounds are available in the literature.[9] This made the authors presume that the traces of moisture or alkali present as impurities might have caused the hydrolysis of the initially formed dicarboxylates, as these compounds are very susceptible

to hydrolysis.[9,22–24]

$$R_2SnCl_2 + 2\,LNa \longrightarrow R_2SnL_2 + 2NaCl \quad (3)$$

$$R_2SnO + 2\,LH \longrightarrow R_2SnL_2 + H_2O \quad (4)$$

$$R_2SnL_2 \xrightarrow{\text{hydrolysis}} [(R_2SnL)_2O]_2 \quad (5)$$

for R = (**6**); L = L^1(**5**, **6**)/L^2(**11**)Me (**5,11**); *n*-Bu (**6**);

$$R_2SnCl_2 + 2\,L^2Na \longrightarrow R_2Sn(L^2)_2 + 2NaCl \quad (6)$$

for R = *n*-Bu(**12**).

However, **12** isolated as a dicarboxylate is a viscous liquid. The physical data is summarized in Table 1.

Crystal structure

Complex **5** adopts the most common structural types found for compounds of the general formula $[(R_2SnL)_2O]_2$.[25,26] The X-ray diffraction analysis of **5** reveals that the complex has a one-dimensional chain motif constructed from a secondary building unit of approximately rectangular Sn_2O_2 rings (Fig. 2). The rings are made up of a central planar $(Me_2Sn)_2O_2$ four-membered aggregate and two other peripheral (*exo*-cyclic) Me_2Sn units attached to two μ_3-oxygen atoms. The penta-coordinated Sn atoms have a bent C_2Sn skeleton, C(2)–Sn(1)–C(1) = 147.9(3) *exo*-cyclic and C(7)–Sn(4)–C(8) = 144.8(4) *endo*-cyclic, respectively. All the Sn atoms in the dimer are in five-coordinated environment. It is interesting to note that there are two different carboxylate ligands in the structure. One is bidentate bridging linking *endo*- and *exo*-cyclic Sn centres invoking two different Sn–O bond distances, e.g. Sn(4)–O(8) = 2.317(6) and Sn(1)–O(3) = 2.224(6). The second carboxylate group binds the *exo*-cyclic Sn atom in a monodentate mode (free organic ester type).[25,26] The pendant O atom, O(9), is far removed from the Sn(1) atom, which is reflected by the C(9)–O(9) bond distance of 1.254(7), indicative of the presence of substantial multiple bond character in it and not significantly different from O(2)–C(9) bond distance of 1.270(8). The Sn(1)–O(3) and Sn(4)–O(8) bond distances involving the bridging carboxylate ligand, 2.224(6) and 2.317(6) Å, respectively differ by 0.093 Å, indicating a nearly symmetrical bridge; this is supported by both distances being longer than the Sn(1)–O(2) bond distance, 2.202(5) Å, formed by the monodentate carboxylato ligand. The monodentate carboxylato ligand has a difference of 0.016 Å between its C–O bonds {C(9)–O(9) = 1.254(7) and C(9)–O(2) = 1.270(8) Å} while for the bidentate carboxylato this difference {C(13)–O(3) = 1.173(10) and C(13)–O(8) = 1.168(9) Å} is only 0.005 Å. The different modes of bonding of the cyclopropane carboxylates, i.e. bridging or hanging, are thus easily differentiated by the relevant bond lengths. Slightly distorted axial angles of the trigonal bipyramidal geometry – O(2)–Sn(1)–O(3) (*exo*-cyclic Sn) and O(4)–Sn(4)–O(8) (*endo*-cyclic Sn) are 168.9(2) and 166.6(2), respectively. The distance between the two Sn atoms in the four-membered ring is Sn(3)–Sn(4) = 3.2761(7), which is smaller than the sum of the van der Waals radii of Sn (II) (3.40 Å). This suggests that there possibly exists a weak metal–metal interaction in the ring. Moreover, the non-covalent weak interactions via Sn(1)–O(10), Sn(2)–O(9), etc., allow the linear polymeric chain (Fig. 3) to propagate. To summarize, interest in this structure arises not from the point of view of its chemistry, since it is a well-characterized species,[25,26] but rather because this work brings out the use of a carboxylic acid containing a

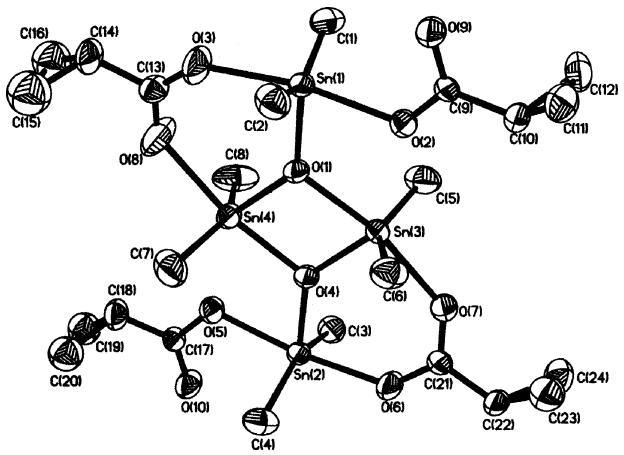


Figure 2. ORTEP plot with atom labelling scheme of the molecular structure of $\{[Me_2Sn(cycloCH_2)_2CHCOO]_2O\}_2$ (**5**).

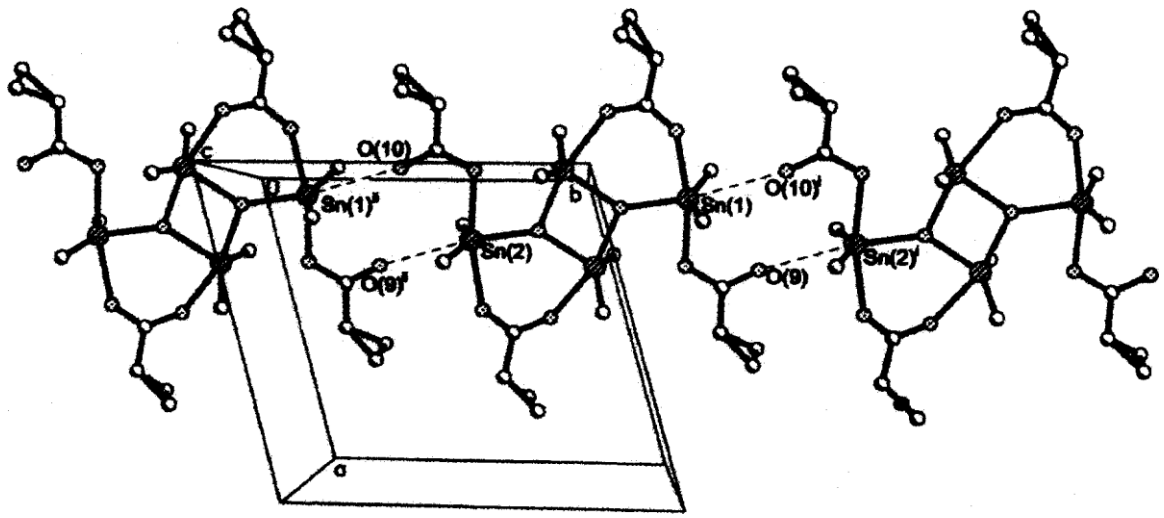


Figure 3. Crystal packing in $\{[Me_2Sn(cycloCH_2)_2CHCOO]_2O\}_2$ (**5**). Symmetry codes: (i) = x, $1+y$, x; (ii) = x, $-1+y$, z.

strained ring as ligand for the synthesis of distannoxane not demonstrated earlier.

IR spectra

The assignments of IR bands for all the complexes were done by comparing the IR spectra of the free acids, their sodium salts, and similar organotin compounds.[27] The cyclopropane carboxylic acid and 3-cyclohexylpropanoic acid ligands display bands at 1695 and 1708 cm^{-1} which are assigned to the $\nu(OCO)_{asym}$ stretching vibration. The considerable shift of this vibration in the organotin(IV) complexes is owing to the coordination through the carbonyl oxygen atom.[28] The observed Δ, [$\nu(OCO)_{asym} - \nu(OCO)_{sym}$] values, which are in the range 123–158 cm^{-1}, indicate a bidentate bonding mode for the carboxylate moiety.[29] This suggests a penta-coordination[30] around the tin atom in the synthesized triorganotin(IV) carboxylates, probably through intermolecular coordination.[31] In complexes **3** and **9**, the observed value of $\Delta\nu$ (231 and 230 cm^{-1} respectively) indicates that the carboxylate moiety is behaving as a free organic ester type, in these cases probably due to the bulky nature of the c-Hex groups around the tin atom.[32] The ν (Sn–C) stretching frequencies appear in the range 440–560 cm^{-1}, which is consistent with the literature data.[29]

In complexes **5, 6** and **11**, two types of carboxylate stretching bands are identified in the same compound. In compound **5**, the difference Δ, [$\nu(OCO)_{asym} - \nu(OCO)_{sym}$] between these frequencies is close to that found for (free ester type) monodentate (307 cm^{-1}) and bridging bidentate/chelated carboxylato groups (154 cm^{-1}).[33] Similar types of carboxylate stretching frequencies in the range 301–310 cm^{-1} for monodentate and 141–146 cm^{-1} for bridging bidentate groups are also observed for **6** and **11**. A strong band in the region 626–634 cm^{-1} can be assigned to the $\Delta\nu$ (Sn–O–Sn) mode.[34] In **12**, $\Delta\nu = 145$ cm^{-1} indicates that the carboxylate moiety is functioning as a bidentate group.[34]

NMR spectra

The ^1H and ^{13}C NMR data of complexes **1–12** are given in Tables 2 and 3, respectively. The observed resonances have been assigned on the basis of their integration, multiplicity pattern and coupling constants. The different R groups (Me, Ph, *n*-Bu, c-Hex) attached to the tin atom gave signals in the expected region.[29,35,36]

In complexes **1, 3, 7** and **9** the ligand protons overlap with the signal of the organic groups (*n*-Bu and c-Hex) attached to the tin atom, which makes the identification of the individual protons of the ligand moieties difficult. As expected, the four hydrogens on the cyclopropane ring were observed as two singlets.[14] In **4** and **10**, the Sn–Me protons appear as a sharp singlet at δ 0.52 and δ 0.53 ppm, respectively. The $^2J(^{119}Sn-^1H)$ coupling constant of 58.80 and 57.00 Hz and $^1J(^{119}Sn-^{13}C)$ values = 400.00 Hz and 398.60 Hz in **4** and **10**, respectively, falls in the range of tetrahedral geometry in solution.[14] The $^1J(^{119}Sn-^{13}C)$ values of tri-*n*-butyltin and triphenyltin derivatives confirm the tetrahedral structure in non-coordinating solvents. In addition, the calculated C–Sn–C angles of 111° for **4** and 112° for **1**, using the Lockhart equation[37] and Holecek and Lycka equation,[38] respectively, also suggest that these complexes are four-coordinated in solution. To sum up, these observations indicate that all the triorganotin carboxylates have tetrahedral geometry in solution.

In the case of triorganotin carboxylates the ^{119}Sn spectrum of each of the complexes showed only a sharp singlet. In general, ^{119}Sn chemical shifts move to lower frequencies with increasing coordination. Although the shift ranges are somewhat dependent on the nature of the substituent at the tin atom, an approximate range between +200 and −60 ppm has been proposed for the four-coordinated alkyltin compounds.[14] On the basis of ^{119}Sn NMR data (Table 3), it appears reasonable to assume that in all the triorganotin carboxylates the effective coordination number is four in solution,[14–16] as is consistent with previous literature reports of similar compounds.[14–16]

The ^1H and ^{13}C NMR spectra of **5, 6** and **11** (Tables 2 and 3, respectively) displayed two sets of R–Sn resonances, as expected for dimeric dicarboxylatotetraorganodistannoxanes, with high-field resonances for *exo*-cyclic and low-field resonances for the *endo*-cyclic R_2Sn moieties.[25,26,39,40] Consistent with the spectroscopic studies, the X-ray crystal structure determination of **5** showed that **5** adopted the dicarboxylatotetraorganodistannoxane structure in the solid state. Furthermore, two signals observed in the ^{119}Sn NMR spectra of **5, 6** and **11** (Table 3) also reflect different environment around the tin atoms in the same molecule, and support the presence of dimeric structure in solution.[39,40]

The ^1H and ^{13}C NMR spectral data of **12** exhibited only one set of Sn–Bu resonances, indicating that it is a dicarboxylate,[36] not a bis(dicarboxylatotetraorganodistannoxane). Diorganotin dicarboxylates having a five-coordinate tin center show tin chemical shifts in the range of −110 to −161 ppm.[41] The ^{119}Sn NMR spectra of **12** show a sharp singlet at −148.63 ppm, which can thus be assigned to a five-coordinated tin atom.

Biocidal activity

Study of the antifungal activity of the organotin(IV) carboxylates

The newly synthesized tri- and diorganotin(IV) complexes of cyclopropane carboxylic acid and 3-cyclohexylpropanoic acid were tested for their antifungal activity by spore germination method as described by Rouxel *et al*.[20] The data are given in Table 5. Among the triorganotin carboxylates, the nature of the R group was found to play an important role for the fungicidal activity of the complex. In this case, the tri-*n*-butyltin carboxylates were found to be more active (over the range of fungi tested) than the triphenyltin derivative, which in turn was more active than the tricyclohexyltin complex.[27,42] Apparently, the function of the ligand is to support the transfer of the active organotin moiety to the site of action where it was released by hydrolysis. The findings are in agreement with the literature report,[4] which indicates that anionic groups in the organotin complexes play a secondary role in determining the degree of activity of R_3SnL compounds. It was noticed that fairly high concentrations of diorganotin derivatives of L^1H and L^2H were required to inhibit the fungal growth when compared with the R_3SnL analogs. The di-*n*-butyltin derivative of L^1H is found to be the least effective among the compounds against the tested fungal strains. The biocidal activity of the triorganotin carboxylates relates to their structure by the fact that the species generating tetrahedral structure in solution are more active.[42] As explained before, while discussing the NMR spectra of these complexes, all the triorganotin complexes adopted tetrahedral structure in solution.

Phytotoxicity studies

Wheat seed (variety Sonalika) germination studies (Table 6) showed that the compounds have practically insignificant phytotoxicity at the concentrations levels tested. A comparison of

Table 5. Effect of organotin(IV) carboxylates on spore germination

Spore	Complex	MIC[a]
Curvularia eragrostidis	**1**	2.08
	2	22.40
	3	49.80
	5	50.00
	6	570.00
	7	3.15
	11	62.5
Alternaria porri	**1**	1.95
	2	2.24
	3	50.50
	5	60.00
	6	57.00
	7	2.95
	11	64
Dreschlerea oryzae	**1**	1.64
	2	2.29
	3	49.80
	5	56.00
	6	570.00
	7	3.00
	11	62.5
Macrophomina phaseolina	**1**	2.00
	2	2.45
	3	4.58
	5	52.00
	7	59.00
	9	3.15
	11	70.5

[a] Minimum Inhibitory Concentration in μg/ml.

Table 6. Effect of organotin(IV) carboxylates on wheat seed germination

Complex	Concentration (μg ml^{-1})	Percentage of germinated seeds[a] after treatment: Duration of treatment 1 h	4 h	8 h
1	100	90	90	85
	50	93	93	92
	25	95	95	94
2	100	97	97	97
	50	98	98	98
	25	99	98	98
3	100	97	96	96
	50	99	98	98
	25	99	99	99
5	100	97	97	97
	50	98	98	98
	25	98	98	98
6	100	97	97	97
	50	97	97	97
	25	98	98	98
7	100	91	91	87
	50	94	94	92
	25	95	95	94
11	100	92	92	95
	50	95	95	98
	25	96	96	98
Control	100	100	99	99
	50	99	99	99
	25	99	99	99

[a] With respect to the control.

the levels of phytotoxicity among these compounds reveals that the tri-*n*-butyltin compounds are more phytotoxic than the triphenyltin compounds followed by the other organotin derivatives of L^1H and L^2H. The difference may, however, be attributable to the triphenyltin moiety in **2** and tri-*n*-butyltin moiety in **1**, and is consistent with literature observation that triphenyltin derivatives are tolerated by plants to a greater degree compared with the tri-*n*-butyltin compounds.[43]

Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 211490 for compound $\{[Me_2Sn(CH_2)_2CHCOO]_2O\}_2$. Copies of this information may be obtained free of charge from: The Director, CCDC 12 Union Road, Cambridge, CB2 1EZ UK, Fax. +44(1223)336-033 or email: deposit@ccdc.cam.ac.uk or www : http : //www.ccdc.cam.ac.uk

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