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Synthesis and structural characterization of several tris(2-methyl-2-phenylpropyl)tin carboxylates containing germanium

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Abstract

Thirteen tris(2-methyl-2-phenylpropyl)tin germylpropionates have been synthesized and their structures characterized by elemental analysis, IR, multinuclear NMR (^{1}H, ^{13}C, ^{119}Sn) and MS spectroscopies. The structure of $(PhC(CH_3)_2CH_2)_3SnO_2CCH_2CH(o\text{-}C_6H_4Cl)GePh_3$ has been determined by X-ray diffraction study, which indicated that the tin in the compound possess a tetrahedral geometry. Bioassay results have shown that some of the compounds have good acaricidal activity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Organotin; Organogermanium; Synthesis; IR; Multinuclear NMR; X-ray diffraction; Acaricial activity

1. Introduction

Organotin compounds have been extensively studied of their biological activity [1,2]. In general, the in vitro fungicidal and antibacterial properties of organotins have indicated that the order of activity is related to the number of R groups attached to the tin atom. The order of activity has been observed to be: $RSnX_3 < R_2SnX_2 < R_3SnX$. The nature of the X group has relatively little influence on the fungicidal activity of an organotin compound [3]. However, studies have continued on the structures of various triorganotin compounds, especially those containing X groups that themselves have some biological activity [4–8]. In addition, these compounds show an interesting range of structural variations leading to activity–structure relationships [9]. These latter studies have shown that triorganotin carboxylates that have either isolated tetrahedral tin centers or *trans* R_3SnO_2 tin atom geometries (arising from bridging carboxylate ligands) possess significantly greater biocidal activity than the compounds with the monomeric *cis*-C_3SnO_2 structural type, i.e. compounds with chelating carboxylate ligand spanning both equatorial and axial sites.

To link the biological active properties of organotin and organogermanium compounds, we have previously reported the biological activity of trialkyltin germylpropionates [10] and the anticancer activity of dibutyl digermylpropionates [11]. In the continuation of our previous work [10,11], we now introduce a very bulky R (2-methyl-2-phenylpropyl) group into the R_3Sn moiety, and have synthesized a series of triorganotin carboxylates containing the biologically active germyl groups in the carboxylate ligands. The synthetic procedures and their structural characterization using various spectroscopic methods are reported herein.

2. Experimental

2.1. Materials

Torque (tris(2-methyl-2-phenylpropyl)tin oxide) was used as received since the melting point agreed with the literature value [12]. Solvents were dried with Na metal

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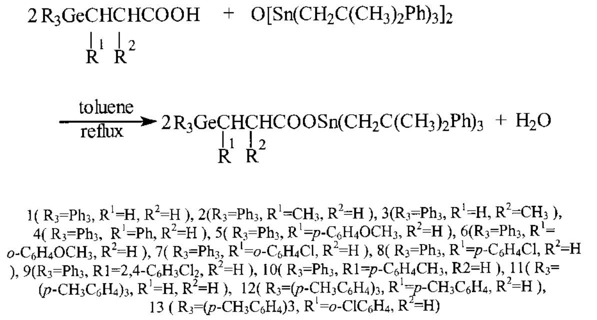


$$2\,R_3Ge\underset{R^1}{CH}\underset{R^2}{CH}COOH + O[Sn(CH_2C(CH_3)_2Ph)_3]_2 \xrightarrow[\text{reflux}]{\text{toluene}} 2\,R_3Ge\underset{R^1}{CH}\underset{R^2}{CH}COOSn(CH_2C(CH_3)_2Ph)_3 + H_2O$$

Scheme 1. **1** ($R_3 = Ph_3$, $R^1 = H$, $R^2 = H$), **2** ($R_3 = Ph_3$, $R^1 = CH_3$, $R^2 = H$), **3** ($R_3 = Ph_3$, $R^1 = H$, $R^2 = CH_3$), **4** ($R_3 = Ph_3$, $R^1 = Ph$, $R^2 = H$), **5** ($R_3 = Ph_3$, $R^1 = p\text{-}C_6H_4OCH_3$, $R^2 = H$), **6** ($R_3 = Ph_3$, $R^1 = o\text{-}C_6H_4OCH_3$, $R^2 = H$), **7** ($R_3 = Ph_3$, $R^1 = o\text{-}C_6H_4Cl$, $R^2 = H$), **8** ($R_3 = Ph_3$, $R^1 = p\text{-}C_6H_4Cl$, $R^2 = H$), **9** ($R_3 = Ph_3$, $R^1 = 2,4\text{-}C_6H_3Cl_2$, $R^2 = H$), **10** ($R_3 = Ph_3$, $R^1 = p\text{-}C_6H_4CH_3$, $R^2 = H$), **11** ($R_3 = (p\text{-}CH_3C_6H_4)_3$, $R^1 = H$, $R^2 = H$), **12** ($R_3 = (p\text{-}CH_3C_6H_4)_3$, $R^1 = p\text{-}CH_3C_6H_4$, $R^2 = H$), **13** ($R_3 = (p\text{-}CH_3C_6H_4)_3$, $R^1 = o\text{-}ClC_6H_4$, $R^2 = H$).

before use. All the substituted germylpropanoic acids were prepared according to known literature methods [10,11].

The NMR data were recorded on a Bruker AC-P 200, using $CDCl_3$ as the solvent, and the references were TMS or Me_4Sn (for ^{119}Sn-NMR). The IR spectra were recorded on a SHIMADZU IR-435 Spectrometer using KBr disc. The elemental analyses were determined using a YANACO MT-3 analyzer. The MS data were recorded on an HP-5988A mass spectrometer (EI source at 200°C, 70 eV).

Crystals of compound **7** suitable for X-ray diffraction experiments were obtained from solutions of chloroform–petroleum ether mixtures over a prolonged period at room temperature (r.t.). The reflection data were collected on a Brucker Smart 1000 diffractometer.

2.2. Synthesis of the products

All the compounds were synthesized using similar procedures. The synthetic procedure is shown in Scheme 1.

Typically, a mixture of Torque (1.0 mmol), substituted germylpropanoic acid (2.0 mmol) and toluene (50 ml) was refluxed for 6 h. The water liberated in the reaction was removed azeotropically by a Dean–Stark apparatus. Then the mixture was cooled down and the toluene was removed using a rotary evaporator. The sticky residue obtained was dried in vacuum to give a white solid. Recrystallization of the white solid from a mixture of chloroform and petroleum yielded fine crystals. The analytical and physical data of the products are given in Table 1.

2.3. Crystallography

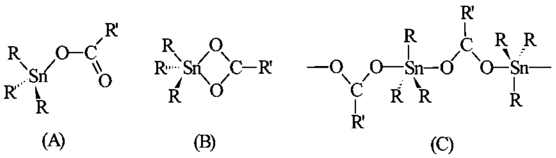
Intensity data for a colorless crystal 0.72 × 0.50 × 0.26 mm were measured at r.t. on a Bruker SMART 1000 diffractometer fitted with graphite monochromatized Mo–K_α radiation, $\lambda = 0.71073$, in the range of $2° < \theta < 23°$ employing the ω–2θ scan techniques. The data were corrected for Lorentz and polarization effects, and of 10032 unique data, 7970 satisfied the $I \geq 2\delta\ (I)$ criterion of observability and were used in the subsequent analysis.

Crystal data for $C_{57}H_{61}ClGeO_2Sn$: $M_r = 1004.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.666(1)$, $b = 15.354(1)$, $c = 16.006(1)$ Å, $\alpha = 117.437(1)°$, $\beta = 94.38(3)°$, $\gamma = 90.407(1)°$, $V = 2540.4(3)$ Å^3, $Z = 2$, $D_{calc} = 1.314$ mg m^{-3}, $F(000) = 1.36$, $\mu = 1.175$ mm^{-1}.

The structure was solved by direct methods, and refined by a full-matrix least-squares procedure based on F. Nonhydrogen atoms were refined with anisotropic thermal parameters. The analysis of variance

Table 1
The analytical and physical data of tris(2-methyl-2phenylpropyl)tin germylpropionates

No.	Formula	State	M.p. (°C)	Yield (%)	Elemental analysis (%)	
					C	H
1	$C_{51}H_{58}GeO_2Sn$	White crystal	90–93	91	68.40(68.50)	6.70(6.54)
2	$C_{52}H_{60}GeO_2Sn$	White crystal	104–105	86	68.85(68.76)	6.61(6.66)
3	$C_{52}H_{60}GeO_2Sn$	White crystal	83–85	87	68.79(68.76)	6.88(6.66)
4	$C_{57}H_{62}GeO_2Sn$	White crystal	102–104	85	70.60(70.55)	6.64(6.44)
5	$C_{58}H_{64}GeO_3Sn$	White crystal	116–118	83	69.97(69.63)	6.72(6.45)
6	$C_{58}H_{64}GeO_3Sn$	White crystal	112–124	75	70.00(69.63)	6.52(6.45)
7	$C_{57}H_{61}ClGeO_2Sn$	White crystal	134–136	87	68.21(68.13)	6.41(6.12)
8	$C_{57}H_{61}ClGeO_2Sn$	White crystal	117–119	94	68.35(68.13)	6.30(612)
9	$C_{57}H_{60}Cl_2GeO_2Sn$	White crystal	102–104	79	65.75(65.87)	5.74(5.82)
10	$C_{58}H_{64}GeO_2Sn$	White crystal	110–112	83	70.52(70.77)	6.74(6.66)
11	$C_{55}H_{66}GeO_2Sn$	White crystal	137–139	86	69.60(69.27)	7.07(6.89)
12	$C_{62}H_{73}GeO_2Sn$	White crystal	100–102	98	71.30(71.38)	7.02(6.87)
13	$C_{61}H_{69}ClGeO_2Sn$	White crystal	134–136	60	69.06(68.84)	6.64(6.45)



Scheme 2.

showed no special feature and the maximum residual in the final difference map was 0.52 e Å^{-3}.

3. Results and discussion

3.1. Spectroscopy

It is well established that triorganotin carboxylates adopt three structural types in the solid state [13] as shown in Scheme 2.

The monomeric structure (**A**) is four-coordinated, whereas the polymeric structure (**C**) generally contains five-coordinate tin atoms. A second five-coordinate structure can exist as structural type (**B**). This inevitably occurs when the carboxylates group acts as a chelating ligand. The different structures can be inferred by the analysis of the IR, NMR and MS data of the compounds.

The main IR spectral data are listed in Table 2. The assignments of ν_{as}(Sn–C) and ν_{as}(Sn–O) are consistent with the values reported in the literature [14]. The bonding of the carboxylate groups can be deduced by IR spectroscopy.

The coordination number of tin affects the absorption vibration frequency of carbonyl group. The $\Delta\nu$ ($\Delta\nu = \nu$(COO)as $- \nu$(COO)s) value, which is useful in drawing structural influences in the case of metal carboxylate, is used to determine the nature of bonding of carboxylate to tin(IV) [15] compounds. It is generally believed that the difference in $\Delta\nu$ between asymmetric (ν(COO)as) and symmetric (ν(COO)s) absorption frequencies is below 200 cm^{-1} for the five-coordinated structure of triorganotin carboxylates, but greater than 200 cm^{-1} for the four-coordinated one. As shown in Table 2, all the values of $\Delta\nu$ are between 252 and 282 cm^{-1}, and strongly indicate that all the title compounds are four-coordinated. The preference to forming a five-coordinated structure is probably due to the steric effect of the 2-methyl-2-phenylpropyl group.

The ^{1}H-, ^{13}C- and ^{119}Sn-NMR data of the title compounds are given in Table 3. All the ^{1}H-NMR data are in good agreement with the expected structures.

To confirm the structure of the title compounds, ^{13}C- and ^{119}Sn-NMR data were also recorded for four of these compounds. These parameters are very useful for the determination of the coordination number of tin, its molecular geometry and stereochemistry. It is reported [16] that in the alkyltin carboxylates, four-coordinate tin has δ (^{119}Sn) values range from about $+200$ to -60 ppm, five-coordinate tin from -90 to -190 ppm, and six-coordinate tin from -200 to -400 ppm. A single resonance in the range of $83 \sim 89$ ppm, compatible with the tetrahedral geometry proposed for the solution structure, is observed for the selected four compounds. Substitution of a chloride for a carboxylate induces only slight upfield shift of the ^{119}Sn resonance, which is unlikely to arise from a significant additional coordination by the oxygen atom of the carbonyl group (the δ value of a tetra-coordinated tin compound R_3SnCl is 118.5 ppm).

Holecek et al. [17–20] reported that the ^1J (^{13}C, ^{119}Sn) coupling constant can be a function of the coordination number of triorganotin compounds, ranging between 327 and 387 Hz for tetra-coordinated compounds, and between 442 and 509 Hz for penta-coordinated ones. The triorganotin germylpropionates exhibit ^1J coupling constants ranging from 349.6 to 353.9 Hz indicating tetra-coordination in chloroform solution, in agreement with our IR spectroscopic study and the ^{119}Sn-NMR data.

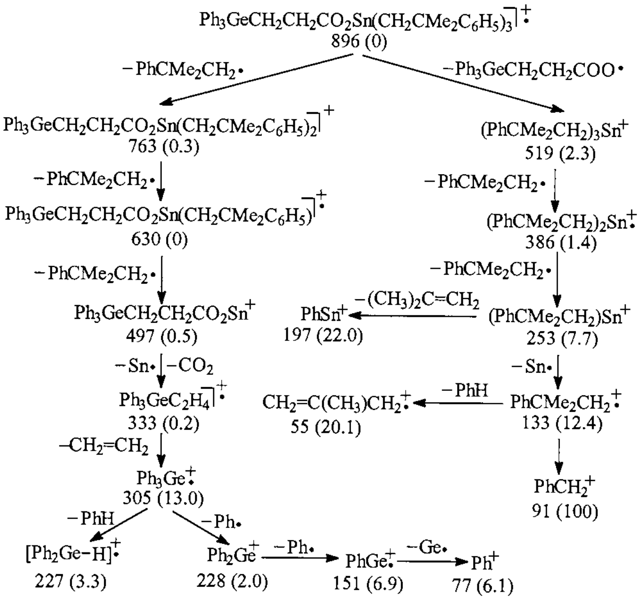
Table 2
The IR data of the title compounds (cm^{-1})

Compound	ν(COO)as	ν(COO)s	$\Delta\nu$	ν_{as}(Sn–O)	ν_{as}(Sn–C)
1	1649	1356	293	457	555
2	1650	1361	289	465	557
3	1650	1359	291	468	556
4	1653	1360	293	462	555
5	1647	1358	289	465	554
6	1652	1358	294	460	553
7	1665	1359	306	467	552
8	1658	1358	300	461	552
9	1649	1377	272	461	567
10	1659	1361	298	465	556
11	1652	1380	272	463	563
12	1658	1376	282	462	556
13	1652	1388	272	464	558

Table 3
The NMR data of the title compounds

No.	^{1}H-NMR (ppm)	^{119}Sn-NMR (ppm)	^{1}J (Hz) (^{13}C–^{119}Sn)
1	1.13, 6H[s, $3\times CH_2$]; 1.17, 18H[s, $3\times C(CH_3)_2$]; 1.80, 2H[t, $GeCH_2$]; 2.20–2.25, 2H[t, CH_2CO_2]; 7.00–7.60, 30H[m, $6\times C_6H_5$]	83.2	349.6
2	1.13, 6H[s, $3\times CH_2$]; 1.17, 18H[s, $3\times C(CH_3)_2$]; 1.25, 3H[dd, $GeCH(CH_3)$]; 2.20–2.25, 2H[t, CH_2CO_2]; 2.25–2.65, 1H[dd, $J=12$, $CHCO_2$]; 7.00–7.60, 30H[m, $6\times C_6H_5$]		
3	1.09, 6H[s, $3\times CH_2$]; 1.17, 18H[s, $3\times C(CH_3)_2$]; 1.50–1.70, 1H[dd, $GeCH$]; 2.00–2.20, 1H[d, $J=12$, $GeCH$]; 2.45–2.70, 1H[t, $CHCO_2$]; 7.00–7.60, 30H[m, $6\times C_6H_5$]	83.4	353.9
4	0.91, 6H[s, $3\times CH_2$]; 1.04, 18H[s, $3\times C(CH_3)_2$]; 2.70–2.95, 2H[m, CH_2CO_2]; 3.50–3.70, 1H[q, $GeCH$]; 6.80–7.60, 35H[m, $7\times C_6H_5$]	86.1	352.8
5	0.92, 6H[s, $3\times CH_2$]; 1.05, 18H[s, $3\times C(CH_3)_2$]; 2.87, 2H[d, $J=8$, CH_2CO_2]; 3.60, 1H[t, $GeCH$]; 3.72, 3H[s, OCH_3]; 6.55–6.73, 2H[d, $J=8$, $1/2C_6H_4OCH_3$]; 6.75–6.88, 2H[d, $J=8$, $1/2C_6H_4OCH_3$]; 6.90–7.60, 30H[m, $6\times C_6H_5$]		
6	0.90, 6H[s, $3\times CH_2$]; 1.04, 18H[s, $3\times C(CH_3)_2$]; 2.70–2.95, 2H[m, CH_2CO_2]; 3.17, 3H[s, OCH_3]; 4.06–4.25, 1H[m, $GeCH$]; 6.40–7.60, 34H[m, $6\times C_6H_5+C_6H_4$]		
7	0.96, 6H[s, $3\times CH_2$]; 1.03, 18H[s, $3\times C(CH_3)_2$]; 2.70–2.95, 2H[m, CH_2CO_2]; 4.20–4.45, 1H[m, $GeCH$]; 6.80–7.60, 34H[m, $6\times C_6H_5+C_6H_4$]	89.0	352.0
8	0.91, 6H[s, $3\times CH_2$]; 1.04, 18H[s, $3\times C(CH_3)_2$]; 2.70–2.95, 2H[d, $J=8$, CH_2CO_2]; 3.40–3.80, 1H[t, $J=8$, $GeCH$]; 6.80–7.60, 34H[m, $6\times C_6H_5+C_6H_4$]		
9	0.92, 6H[s, $3\times CH_2$]; 1.04, 18H[s, $3\times C(CH_3)_2$]; 2.70–2.95, 2H[d, $J=8$, CH_2CO_2]; 4.10–4.35, 1H[t, $J=8$, $GeCH$]; 6.80–7.60, 33H[m, $6\times C_6H_5+C_6H_3$]		
10	0.91, 6H[s, $3\times CH_2$]; 1.04, 18H[s, $3\times C(CH_3)_2$]; 2.25, 3H[s, $C_6H_4CH_3$]; 2.70–2.95, 2H[m, CH_2CO_2]; 3.50–3.80, 1H[m, $GeCH$]; 6.60–7.60, 33H[m,$6\times C_6H_5+C_6H_4$]		
11	0.92, 6H[s, $3\times CH_2$]; 1.03, 18H[s, $3\times C(CH_3)_2$]; 2.34, 9H[s, $3\times C_6H_4CH_3$]; 2.75–2.92, 2H[m, CH_2CO_2]; 4.25–4.35, 1H[m, $GeCH$]; 6.90–7.25, 31H[m, $3\times C_6H_5+4\times C_6H_4$]		
12	1.04–1040, 26H[m, $CH_2CO_2+3\times SnCH_2C(CH_3)_2$]; 2.29–2.45, 11H[m, $3\times C_6H_4CH_3+GeCH_2$]; 7.00–7.30, 27H[m, $3\times(C_6H_5+C_6H_4)$]		
13	0.90, 6H[s, $3\times CH_2$]; 1.04, 18H[s, $3\times C(CH_3)_2$]; 2.25, 3H[s, $C_6H_4CH_3$]; 2.34, 9H[s, $3\times C_6H_4CH_3$]; 2.75–2.85, 2H[m, CH_2CO_2]; 3.65–3.75, 1H[m, $GeCH$]; 6.80–7.25, 31H[m, $3\times C_6H_5+4\times C_6H_4$]		

The main mass spectra data of the title compounds are in good agreement with the expected structure, and generally they have almost the same fragmentation pattern with either Ph_3Ge^+ or $PhCH_2^+$ as the basic peak. A possible fragmentation pattern for $Ph_3GeCH_2CH_2CO_2Sn(CH_2CMe_2C_6H_5)_3$ is given in Scheme 3.



Scheme 3.

In conclusion, all the spectral data for the compounds support a tetrahedral geometry for the tin atoms. Thus, the structure of the compounds contains a four-coordinated tin as depicted in structure **A**.

3.2. Crystal structure of compound 7

In order to confirm the structure of these compounds, the solid structure of **7** was determined by

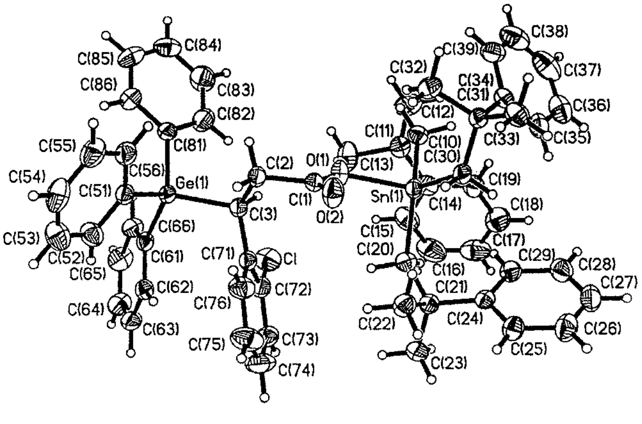


Fig. 1. X-ray molecular structure of compound **7**.

Table 4
Selected bond lengths(Å) and bond angles(°) for the compound **7**

Bond lengths			
Cl–C(72)	1.742(4)	C(26)–C(25)	1.374(6)
Sn(1)–O(1)	2.056(2)	C(26)–C(27)	1.354(7)
Sn(1)–C(10)	2.143(4)	C(28)–C(27)	1.374(7)
Sn(1)–C(20)	2.150(3)	C(28)–C(29)	1.387(6)
Sn(1)–C(30)	2.155(3)	C(30)–C(31)	1.545(5)
Ge(1)–C(51)	1.953(4)	C(32)–C(31)	1.527(5)
Ge(1)–C(81)	1.954(4)	C(34)–C(31)	1.528(5)
Ge(1)–C(61)	1.955(3)	C(33)–C(31)	1.545(5)
Ge(1)–C(3)	1.990(3)	C(37)–C(38)	1.356(9)
O(1)–C(1)	1.287(4)	C(37)–C(36)	1.384(9)
C(1)–O(2)	1.195(4)	C(34)–C(35)	1.376(6)
C(1)–C(2)	1.516(4)	C(34)–C(39)	1.396(6)
C(2)–C(3)	1.528(5)	C(36)–C(35)	1.391(7)
C(3)–C(71)	1.491(5)	C(38)–C(39)	1.374(8)
C(10)–C(11)	1.534(5)	C(51)–C(52)	1.381(5)
C(11)–C(14)	1.511(6)	C(51)–C(56)	1.390(5)
C(11)–C(13)	1.523(6)	C(53)–C(52)	1.380(6)
C(11)–C(12)	1.554(6)	C(53)–C(54)	1.358(7)
C(19)–C(14)	1.377(6)	C(55)–C(54)	1.364(7)
C(19)–C(18)	1.398(7)	C(55)–C(56)	1.375(6)
C(18)–C(17)	1.367(9)	C(61)–C(66)	1.387(5)
C(14)–C(15)	1.383(6)	C(61)–C(62)	1.393(5)
C(17)–C(16)	1.355(9)	C(63)–C(62)	1.382(5)
C(15)–C(16)	1.358(8)	C(63)–C(64)	1.363(7)
C(20)–C(21)	1.544(5)	C(65)–C(64)	1.369(7)
C(24)–C(21)	1.527(5)	C(65)–C(66)	1.398(6)
C(23)–C(21)	1.528(5)	C(71)–C(72)	1.388(5)
C(22)–C(21)	1.526(5)	C(71)–C(76)	1.388(6)
C(24)–C(29)	1.379(5)	C(73)–C(72)	1.390(6)
C(24)–C(25)	1.396(5)	C(73)–C(74)	1.350(7)
Bond angles			
O(1)–Sn(1)–C(10)	93.22(13)	C(24)–C(21)–C(22)	111.8(3)
O(1)–Sn(1)–C(20)	98.57(14)	C(24)–C(21)–C(20)	112.1(3)
C(10)–Sn(1)–C(20)	118.22(14)	C(22)–C(21)–C(20)	108.3(3)
O(1)–Sn(1)–C(30)	111.24(12)	C(24)–C(21)–C(23)	107.6(3)
C(10)–Sn(1)–C(30)	113.90(14)	C(22)–C(21)–C(23)	109.3(3)
C(30)–Sn(1)–C(20)	117.15(13)	C(20)–C(21)–C(23)	107.5(3)
C(51)–Ge(1)–C(81)	110.65(15)	C(29)–C(24)–C(21)	123.7(3)
C(51)–Ge(1)–C(61)	110.13(14)	C(25)–C(24)–C(21)	120.2(3)
C(81)–Ge(1)–C(61)	109.71(15)	C(31)–C(30)–Sn(1)	117.2(2)
C(81)–Ge(1)–C(3)	110.34(14)	C(32)–C(31)–C(34)	112.7(3)
C(61)–Ge(1)–C(3)	105.94(14)	C(32)–C(31)–C(33)	108.2(3)
C(51)–Ge(1)–C(3)	109.99(13)	C(34)–C(31)–C(33)	108.6(3)
C(1)–O(1)–Sn(1)	126.4(2)	C(32)–C(31)–C(30)	107.1(3)
O(2)–C(1)–O(1)	124.6(3)	C(34)–C(31)–C(30)	111.7(3)
O(2)–C(1)–C(2)	122.7(3)	C(33)–C(31)–C(30)	108.4(3)
O(1)–C(1)–C(2)	112.6(3)	C(35)–C(34)–C(31)	120.2(4)
C(1)–C(2)–C(3)	113.2(3)	C(39)–C(34)–C(31)	121.7(4)
C(71)–C(3)–C(2)	114.8(3)	C(38)–C(39)–C(34)	120.4(5)
C(71)–C(3)–Ge(1)	110.7(2)	C(52)–C(51)–Ge(1)	121.3(3)
C(2)–C(3)–Ge(1)	110.8(2)	C(56)–C(51)–Ge(1)	121.2(3)
C(11)–C(10)–Sn(1)	119.9(3)	C(66)–C(61)–Ge(1)	120.4(3)
C(14)–C(11)–C(13)	112.9(4)	C(62)–C(61)–Ge(1)	121.5(3)
C(14)–C(11)–C(10)	111.0(3)	C(72)–C(71)–C(3)	123.4(3)
C(13)–C(11)–C(10)	109.2(3)	C(76)–C(71)–C(3)	121.4(3)
C(14)–C(11)–C(12)	108.2(3)	C(71)–C(72)–Cl	119.8(3)
C(13)–C(11)–C(12)	108.6(4)	C(73)–C(72)–Cl	117.0(3)
C(10)–C(11)–C(12)	106.7(4)	C(82)–C(81)–C(86)	117.8(4)
C(19)–C(14)–C(11)	120.4(4)	C(82)–C(81)–Ge(1)	120.4(3)
C(11)–C(14)–C(15)	122.8(4)	C(86)–C(81)–Ge(1)	121.8(3)
C(21)–C(20)–Sn(1)	117.9(2)		

Table 5
Some comparable structural parameters of R_3SnO_2CCR'

R	R′	Sn–O(1) (Å)	Sn–O(2) (Å)	Ref.
c-Hexyl	CF_3	2.08(4)	3.11(4)	[21]
Ph	C_6H_4OH-*o*	2.083(2)	3.071(2)	[22]
c-Hexyl	CH_3	2.12(3)	2.95(4)	[23]
c-Hexyl	$CH_2(C_8H_5N)$ [a]	2.086(3)	2.929(4)	[6]
Ph	C_6H_4Cl-*p*	2.048(4)	2.861(4)	[24]
Ph	$C_6H_4NH_2$-*o*	2.043(3)	2.823(3)	[25]
Ph	$C_6H_4SCH_3$-*p*	2.060(2)	2.783(3)	[22]
Ph	$C_6H_4OCH_3$-*o*	2.054(3)	2.781(3)	[22]
c-Hexyl	$CH_2(C_8H_6NCH_3)$ [b]	2.05(1)	2.78(1)	[26]
Neophyl	Germyl carboxylate [c]	2.056(2)	3.269(3)	This paper

[a] Indole-3-acetic acid.

[b] *N*-methylindole-3-acetic acid.

[c] See Scheme 1.

Table 6
The insecticidal and acaricidal activity of some compounds

Compound	Average percentage inhibition after 24 h (%)	
	Tetraanychus Urticae koch (200 ppm)	*Culicidae* (10 ppm)
1	93.7	100
2	17.7	0
3	15.1	0
4	93.4	100
7	11.8	0
8	11.3	0
9	8.3	0
10	96.3	100

X-ray structure determination. The crystal structure with numbering scheme is shown in Fig. 1. Selected bond lengths and bond angles were listed in Table 4.

In the structure, the two atoms Sn and Ge are both occupying essentially tetrahedral geometries, the average bond angles around each metal being 110.2° and 101.0°, respectively. The bond length of Sn–O(1) is 2.056(2) Å, and for Sn–O(2) the bond length is 3.269(3) Å, which is far from the sum of their Van der Waal's radii, and suggests that there is no interaction between the carbonyl group and the Sn(1) atom. The carbonyl group, C(1)–O(2), is sterically encumbered by the three neophyl groups attached to the tin atom, as well as by the germyl substitution on the carboxylate group, all of which act as a barrier preventing the carbonyl oxygen from approaching to the tin in the neighbouring molecule, to form associated polymeric structure. The bond lengths of the two C–O bonds in the COO fragment are 1.20 and 1.29 Å, which are consistent with the general single and the double bond lengths, respectively. Some important comparable structural parameters for this type of structure reported in the literature were listed in Table 5, the structure of the title compound is mostly like that of (*cyclo*-$C_6H_{11})_3SnO_2CCF_3$.

3.3. Biological test

The preliminary insecticidal and acaricidal activities of compounds **1**–**10** are given in Table 6. The biological tests showed that the compounds **1**, **4** and **10** have good acaricidal activity against *Tetraanychus Urticae koch* (200 ppm) and *Culicidae* (10 ppm), and the results of bioassay have shown that all these compounds have poor fungicidal activity on the *Aphis craccivora* (not listed).

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