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Synthesis, characterization and biological activity of diorganotin dithioate derivatives

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Reaction of dithioacid ($ArCS_2CH_2CO_2H$, Ar = phenyl, 2-furyl or 2-thienyl) with $^nBu_2SnO$ gives monomeric $(ArCS_2CH_2CO_2)_2Sn(Bu^n)_2$ in a 2:1 molar ratio, and dimeric $\{[(ArCS_2CH_2CO_2)Sn(Bu^n)_2]_2O\}_2$ in a 1:1 molar ratio, respectively, which have been characterized by IR, NMR (^1H, ^{13}C and ^{119}Sn) spectra and elemental analyses. X-ray crystal structure analyses indicate that the compound $[(C_4H_3S)CS_2CH_2CO_2]_2Sn(Bu^n)_2$ is monomeric with the tin atom occupying a skew-trapezoidal bipyramidal geometry. In addition, this compound forms a three-dimensional structure through the weak intermolecular S···S and Sn···O interactions. Compound $\{[((C_4H_3S)CS_2CH_2CO_2)Sn(Bu^n)_2]_2O\}_2$ is a centrosymmetric dimer with a cyclic Sn_2O_2 unit, in which the coordination modes of the two crystallographically unique carboxylic ligands are different. One acts as monodentate ligand by the carboxylate oxygen atom, the other bridges two tin atoms via only one carboxylate oxygen atom. Furthermore, each tin atom in this compound locates a distorted trigonal bipyramidal geometry. Biological activities of these organotin compounds show that they have hardly acaricidal activity, but display certain activities on fungi. In mononuclear tin compounds, the inhibition percentage of $[(C_4H_3S)CS_2CH_2CO_2]_2Sn(Bu^n)_2$ *in vitro* for *Alternaria solani* and *Physolospora piricola* is 57.1% and 43.9%, respectively, while in dimers $\{[((C_4H_3O)CS_2CH_2CO_2)Sn(Bu^n)_2]_2O\}_2$ shows high inhibition percentage for *Gibbereila zeae* (52.6%) and *Physolospora piricola* (50.0%), respectively. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: organotin(IV) carboxylates; dithioacids; crystal structures; biological activity

INTRODUCTION

Organotin(IV) carboxylates, especially diorganotin carboxylates, have been extensively investigated for a long time due to their wide applications in many fields, for example as pesticidal, bactericidal and antitumor agents, etc.[1–4] Many such compounds have been synthesized by the most common dehydration reaction of diorganotin oxides with carboxylic acids and tested for their biological activity.[5–12] Depending on the stoichiometry of the reactants, mononuclear tin compounds $R_2Sn(O_2CR')_2$ (acid: $R_2SnO = 2:1$) or tetranuclear compounds $\{[R_2Sn(O_2CR')_2]_2O\}$ (acid: $R_2SnO = 1:1$) can be obtained. The coordination mode of the carboxylate group in these compounds is usually monodentate, bridging bidentate or chelating bidentate. The tridentate coordination mode of the carboxylate group has also been observed in diorganotin carboxylate compound.[13] We recently also became interested in studying the reactions of diorganotin oxides with functionalized carboxylic acids with additional O, S or N donor groups.[14–21] Owing to the presence of additional coordinating atoms, some organotin carboxylates with fascinating structures, such as hexameric cyclic diorganotin carboxylate,[18,19] have been isolated. Heteroaromatic dithioacid ($ArCS_2CH_2CO_2H$) belongs to a bifunctional *S,O*-ligand, and some transition metal complexes of its derivatives have been reported to display significant biological properties such as antitumor, antibacterical and antifungal activities.[22–25] As a continuation of our studies of biological organotin

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compounds, we report here the reaction of dithioacid ($ArCS_2CH_2CO_2H$, Ar = phenyl, 2-furyl or 2-thienyl) with $^nBu_2SnO$ to yield mononuclear diorganotin dicarboxylate compounds $(ArCS_2CH_2CO_2)_2Sn(Bu^n)_2$ and tetranuclear compounds $\{[(ArCS_2CH_2CO_2)Sn(Bu^n)_2]_2O\}_2$. These organotin carboxylates display certain activities on fungi *in vitro*.

EXPERIMENTAL

Materials and measurements

Di-*n*-butyltin oxide ($^nBu_2SnO$)[26] was prepared by the published method. Multinuclear NMR spectra were obtained with a Bruker AV300 or Mercury 300BB spectrometer using $CDCl_3$ as solvent unless otherwise noted, and the chemical shifts were reported in ppm with respect to reference standards (internal $SiMe_4$ for ^1H NMR and ^{13}C NMR spectra, external $SnMe_4$ for ^{119}Sn NMR). IR spectra were obtained from a Bio-Rad FTS 6000 spectrometer using KBr discs. Elemental analyses were carried out on a Perkin-Elmer 2400C analyzer. Melting points were measured using a PHMK melting-point apparatus and were uncorrected.

Synthesis

Preparation of $ArCS_2CH_2CO_2H$

These acids were prepared using methods available in the literature.[27] The data for $PhCS_2CH_2CO_2H$ are: yield, 81%; m.p. 122–124 °C (lit: 126–127 °C). ^1H NMR: $\delta = 9.40$ (br, 1H, CO_2H), 7.94, 7.49, 7.33 (d, t, t, 2H, 1H, 2H, C_6H_5), 4.21 (s, 2H, CH_2) ppm. ^{13}C NMR: $\delta = 173.3$ (C=S), 162.4 (CO_2H), 144.4, 133.0, 128.5, 127.1 (C_6H_5), 38.9 (CH_2) ppm. IR (cm^{-1}): ν(OH) 2590–3245 (br, s), ν(C=O) 1701 vs. The data for $(C_4H_3O)CS_2CH_2CO_2H$ (C_4H_3O = 2-furyl) are: yield, 20%; m.p. 119–121 °C (lit: 123–124 °C). ^1H NMR: $\delta = 8.69$ (br, 1H, CO_2H), 7.60, 7.37, 6.49 (d, d, t, 1H, 1H, 1H, C_4H_3O), 4.18 (s, 2H, CH_2) ppm. ^{13}C NMR: $\delta = 204.1$ (C=S), 173.1 (CO_2H), 162.3, 147.0, 116.8, 113.7 (C_4H_3O), 36.1 (CH_2) ppm. IR (cm^{-1}): ν(OH) 2450–3258 (br, s), ν(C=O) 1713 vs. The data for $(C_4H_3S)CS_2CH_2CO_2H$ (C_4H_3S = 2-thienyl) are: yield, 18%; m.p. 131–132 °C (lit: 132–133 °C). ^1H NMR: $\delta = 9.08$ (br, 1H, CO_2H), 7.79, 7.60, 7.07 (d, d, t, 1H, 1H, 1H, C_4H_3S), 4.16 (s, 2H, CH_2) ppm. ^{13}C NMR: $\delta = 211.0$ (C=S), 173.1 (CO_2H), 162.3, 135.8, 128.7, 127.6 (C_4H_3S), 37.7 (CH_2) ppm. IR (cm^{-1}): ν(OH) 2563–3236 (br, s), ν(C=O) 1698 vs.

*Preparation of $(PhCS_2CH_2CO_2)_2Sn(Bu^n)_2$ (**1**)*

The mixture of $PhCS_2CH_2CO_2H$ (0.42 g, 2 mmol) and $^nBu_2SnO$ (0.249 g, 1 mmol) in anhydrous benzene (30 ml) was stirred and heated at reflux for 6 h to yield a clear red solution. After removing the benzene *in vacuo*, the crude product was recrystallized from benzene–hexane to afford red crystals of **1** (0.52 g, 80%); m.p. 127–128 °C. ^1H NMR: $\delta = 7.96$, 7.47, 7.31 (d, t, t, 2H, 1H, 2H, C_6H_5), 4.18 (s, 2H, CH_2), 1.78–1.58, 1.34–1.27 (m, m, 4H, 2H, $SnCH_2CH_2CH_2$), 0.83 (t, 3H, CH_3) ppm. ^{13}C NMR: $\delta = 176.9$ (C=S), 163.2 (COO), 144.2, 132.8, 128.4, 127.0 (C_6H_5), 39.1 (CH_2), 26.6, 26.4, 25.9, 13.6 (butyl carbons) ppm. ^{119}Sn NMR: $\delta = -105.1$ ppm. IR (cm^{-1}): ν_{as} (COO) 1619, ν_s (COO) 1372. Anal. found: C, 47.59; H, 4.64; calcd for $C_{26}H_{32}O_4S_4Sn$ C, 47.63; H, 4.89%.

*Preparation of $(ArCS_2CH_2CO_2)_2Sn(Bu^n)_2$ (**2**) (Ar = 2-furyl)*

This compound was obtained similarly using carboxymethyl 2-furandithioate (2 mmol) reacted with $^nBu_2SnO$ (1 mmol) as described above for **1**. The reaction time was 4 h. After removing the benzene *in vacuo*, the crude product was recrystallized from benzene–hexane to afford red powder of **2**. Yield: 90% (0.61 g); m.p. 116–118 °C. ^1H NMR: $\delta = 7.58$, 7.33, 6.47 (d, d, m, 1H, 1H, 1H, C_4H_3O), 4.15 (s, 2H, CH_2), 1.68–1.56, 1.36–1.24 (m, m, 4H, 2H, $SnCH_2CH_2CH_2$), 0.84 (t, 3H, CH_3) ppm. ^{13}C NMR: $\delta = 204.9$ (C=S), 177.1 (COO), 162.3, 146.8, 116.3, 113.5 (C_4H_3O), 36.7 (CH_2), 26.6, 26.4, 25.8, 13.6 (butyl carbons) ppm. ^{119}Sn NMR: $\delta = -130.8$ ppm. IR (cm^{-1}): ν_{as} (COO) 1618, ν_s (COO) 1377. Anal. found: C, 40.93; H, 4.00; calcd for $C_{22}H_{28}O_6S_4Sn$ C, 41.57; H, 4.41%.

*Preparation of $(ArCS_2CH_2CO_2)_2Sn(Bu^n)_2$ (**3**) (Ar = 2-thienyl)*

This compound was obtained similarly using carboxymethyl 2-thiephendithioate (2 mmol) reacted with $^nBu_2SnO$ (1 mmol) as described above for **1**. The reaction time was 4 h. After removing the benzene *in vacuo*, the crude product was recrystallized from CH_2Cl_2–hexane to afford orange-red crystals of **3**. Yield: 54% (0.36 g); m.p. 132–134 °C. ^1H NMR: $\delta = 7.80$, 7.59, 7.06 (d, d, t, 1H, 1H, 1H, C_4H_3S), 4.17 (s, 2H, CH_2), 1.70–1.57, 1.36–1.24 (m, m, 4H, 2H, $SnCH_2CH_2CH_2$), 0.84 (t, 3H, CH_3) ppm. ^{13}C NMR: $\delta = 211.8$ (C=S), 176.9 (COO), 162.5, 135.4, 128.6, 127.3 (C_4H_3S), 38.1 (CH_2), 26.6, 26.4, 25.8, 13.6 (butyl carbons) ppm. ^{119}Sn NMR: $\delta = -129.3$ ppm. IR (cm^{-1}): ν_{as} (COO) 1604, ν_s (COO) 1373. Anal. found: C, 39.75; H, 3.87; calcd for $C_{22}H_{28}O_4S_6Sn$ C, 39.58; H, 4.20%.

*Preparation of $\{[(PhCS_2CH_2CO_2)Sn(Bu^n)_2]_2O\}_2$ (**4**)*

This compound was obtained similarly using $PhCS_2CH_2CO_2H$ (0.21 g, 1 mmol) reacted with $^nBu_2SnO$ (0.249 g, 1 mmol) as described above for **1**. After removing the benzene in vacuo, the crude product was recrystallized from benzene–hexane to afford 0.30 g of red crystals of **4**. Yield: 68%; m.p. 114–115 °C. ^1H NMR: $\delta = 8.03$, 7.53, 7.38 (d, t, t, 2H, 1H, 2H, C_6H_5), 4.08 (s, 2H, CH_2), 1.63–1.26 (m, 12H, $SnCH_2CH_2CH_2$), 0.93, 0.83 (t, t, 3H, 3H, CH_3) ppm. ^{13}C NMR: $\delta = 172.2$ (C=S), 162.2 (COO), 144.4, 132.6, 128.4, 127.0 (C_6H_5), 41.2 (CH_2), 28.5, 27.8, 27.6, 27.3, 26.9, 26.8, 13.7 and 13.6 (butyl carbons) ppm. ^{119}Sn NMR: $\delta = -175.1$, -182.9 ppm. IR (cm^{-1}): ν_{as} (COO) 1667, 1609, ν_s (COO) 1449, 1367. Anal. found: C, 44.87; H, 5.12; calcd for $C_{34}H_{50}O_5S_4Sn_2$ C, 45.13; H, 5.53%.

*Preparation of $\{[(ArCS_2CH_2CO_2)Sn(Bu^n)_2]_2O\}_2$ (**5**) (Ar = 2-furyl)*

This compound was obtained similarly using carboxymethyl 2-furandithioate (1 mmol) reacted with $^nBu_2SnO$ (1 mmol) as described above for **1**. The reaction time was 4 h. After

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removing the benzene *in vacuo*, the crude product was recrystallized from benzene–hexane to afford orange-red solids of **5**. Yield: 58% (0.25 g); m.p. 130–132 °C. ^{1}H NMR: $\delta = 7.58$, 7.33, 6.46 (d, d, m, 1H, 1H, 1H, C_4H_3O), 4.00 (s, 2H, CH_2), 1.60–1.21 (m, 12H, $SnCH_2CH_2CH_2$), 0.87, 0.79 (t, t, 3H, 3H, CH_3) ppm. ^{13}C NMR: $\delta = 204.9$ (C=S), 171.3 (COO), 161.5, 145.7, 114.9, 112.5 (C_4H_3O), 37.6 (CH_2), 28.6, 26.9, 26.7, 26.3, 25.9, 25.8, 13.7, 13.6 (butyl carbons) ppm. ^{119}Sn NMR: $\delta = -200.0$, -206.2 ppm. IR (cm^{-1}): ν_{as} (COO) 1652 (s, br), ν_s (COO) 1451 (s, br). Anal. found: C, 40.89; H, 5.08; calcd for $C_{30}H_{46}O_7S_4Sn_2$ C, 40.72; H, 5.20%.

*Preparation of {[(ArCS$_2$CH$_2$CO$_2$)Sn(Bu^n)$_2$]$_2$O}$_2$ (**6**) (Ar = 2-thienyl)*

This compound was obtained similarly using carboxymethyl 2-thiephendithioate (1 mmol) reacted with ^{n}Bu$_2$SnO (1 mmol) as described above for **1**. The reaction time was 4 h. After removing the benzene *in vacuo*, the crude product was recrystallized from hot benzene to afford red crystals of **6**. Yield: 37% (0.17 g); m.p. 129–131 °C. ^{1}H NMR: $\delta = 7.80$, 7.57, 7.04 (d, d, t, 1H, 1H, 1H, C_4H_3S), 4.01 (s, 2H, CH_2), 1.53–1.26 (m, 12H, $SnCH_2CH_2CH_2$), 0.85, 0.79 (t, t, 3H, 3H, CH_3) ppm. ^{13}C NMR: $\delta = 212.4$ (C=S), 172.4 (COO), 162.7, 135.2, 128.9, 127.3 (C_4H_3S), 40.3 (CH_2), 27.9, 27.6, 27.5, 27.2, 26.8, 26.4, 13.7, 13.6 (butyl carbons) ppm. ^{119}Sn NMR: $\delta = -200.3$, -207.0 ppm. IR (cm^{-1}): ν_{as} (COO) 1669, 1614, ν_s (COO) 1406, 1372. Anal. found: C, 39.55; H, 5.18; calcd for $C_{30}H_{46}O_5S_6Sn_2$ C, 39.30; H, 5.02%.

X-ray crystallography

Red crystals of **3** and **6** suitable for X-ray analyses were obtained by slow evaporation of their CH_2Cl_2–hexane solutions at room temperature. Intensity data were collected at 293 K on a Bruker Apex II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω scan mode. All data were corrected by a semi-empirical method using an SADADS[28] program. The program SAINT[29] was used for integration of the diffraction profiles. The structures were solved by direct-methods using the SHELXS program of the SHELXTL-97 package and refined with SHELXL.[30] All non-hydrogen atoms were refined with anisotropic displacement parameters. The methyl carbon (C26) of one butyl group (C23–C26) and the propyl carbons (C28, C29, C30) of one butyl group (C27–C30) in **6** were disordered. The site occupation factors of these disordered atoms were adjusted (0.5 for each atom) to give reasonable thermal parameters. Crystallographic data for **3** and **6** are listed in Table 1.

Table 1. Crystal data and refinement parameters for **3** and **6**

Compound	**3**	**6**
Formula	$C_{22}H_{28}O_4S_6Sn$	$C_{30}H_{46}O_5S_6Sn_2$
Formula weight	667.49	916.41
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	9.181(4)	12.136(5)
b (Å)	19.269(8)	12.150(5)
c (Å)	15.996(6)	13.668(6)
α (deg)	90	73.800(5)
β (deg)	96.579(5)	80.711(6)
γ (deg)	90	84.736(5)
V (Å)^3	2811.0(19)	1907.8(13)
Z	4	2
D_c (g cm^{-3})	1.577	1.595
F(000)	1352	924
μ (mm^{-1})	1.381	1.672
No. of unique reflections	6449	6667
No. of observed reflections [$I > 2\sigma(I)$]	4373	5068
No. of parameters	300	426
Residuals R, Rw	0.041, 0.123	0.033, 0.093

RESULTS AND DISCUSSION

(ArCS$_2$CH$_2$CO$_2$)$_2$Sn(Bu^n)$_2$

The reaction of ArCS$_2$CH$_2$CO$_2$H with ^{n}Bu$_2$SnO in a 2:1 molar ratio in anhydrous benzene yields the monomeric tin derivatives (**1**)–(**3**), which are soluble in chlorinated solvents at room temperature. These compounds have been characterized by elemental analyses, IR and NMR spectra. A remarkable difference between the IR spectra of the free acids and those of the corresponding complexes is that the stretching vibration bands of the hydroxyl group disappear from the spectra of the complexes. In addition, the absorption frequency of carbonyl significantly decreases in complexes. The characteristic frequency of the ν_{as}(COO) and ν_s(COO) stretching vibrations is observed in the region 1619–1604 and 1377–1372 cm^{-1}, respectively. The corresponding differences ([ν_{as}(COO) − ν_s(COO]) are between 247 and 231 cm^{-1}, comparable with those values observed in weak six-coordinate $R_2Sn(O_2CR')_2$ derivatives,[31] implying the weak bidentate chelated coordination mode of the carboxylate group in these three compounds, which is consistent with the results of the X-ray crystallography analyses of **3**. In addition, the ^{119}Sn spectra of **1** (−105.1 ppm), **2** (−129.3 ppm) and **3** (−130.8 ppm) are consistent with those reported for diorganotin dicarboxylates.[6,31–33]

In order to confirm the role of these heteroatoms in the carboxylate ligands, the structure of **3** is determined by single crystal X-ray crystallography. The molecular structure is presented in Fig. 1 and selected bond distances and angles are listed in Table 2. The tin atom adopts a common skew-trapezoidal bipyramidal geometry, with four oxygen atoms of two chelating carboxylate ligands occupying the equatorial plane and two butyl groups lying in axial positions, as found in other diorganotin dicarboxylate derivatives.[31–33] The distances of Sn1–O2 [2.124(3) Å] and Sn1–O4 [2.134(3)

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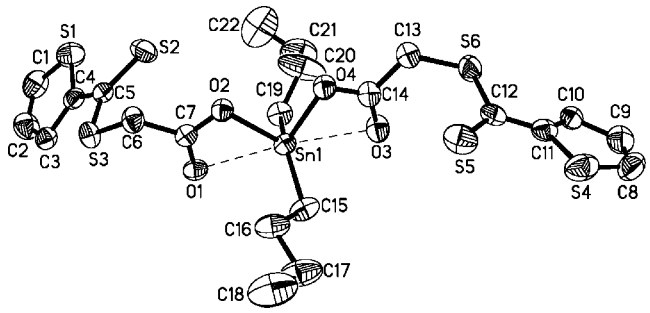

Figure 1. Molecular structure of **3** with the thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond distances and bond angles for **3**

	Bond distances (Å)		
Sn1···O1	2.561(7)	S5–C12	1.641(5)
Sn1–O2	2.124(3)	S6–C12	1.730(5)
Sn1···O3	2.565(5)	S6–C13	1.786(5)
Sn1–O4	2.134(3)	O1–C7	1.220(5)
S2–C5	1.632(4)	O2–C7	1.295(5)
S3–C5	1.734(4)	O3–C14	1.233(5)
S3–C6	1.797(4)	O4–C14	1.290(5)
	Bond angles (deg)		
Sn1–O2–C7	101.6(2)	O1–C7–O2	120.6(4)
Sn1–O4–C14	101.3(2)	O1–C7–C6	122.7(4)
S2–C5–C4	122.4(3)	O2–C7–C6	116.6(4)
S2–C5–S3	125.0(3)	O2–Sn1–O4	81.5(1)
S3–C5–C4	112.7(3)	O2–Sn1–C15	107.8(1)
S5–C12–S6	123.8(3)	O2–Sn1–C19	100.7(1)
S5–C12–C11	123.5(3)	O3–C14–O4	121.1(4)
S6–C12–C11	112.7(3)	O4–Sn1–C19	101.9(1)
C15–Sn1–C19	145.5(2)	O4–C14–C13	115.3(4)

Å] are significantly shorter than those of Sn1–O1 [2.561(7) Å] and Sn1–O3 [2.565(5) Å], in accordance with the stronger coordinative ability of the carboxylate oxygen atom than the carbonyl oxygen atom. In addition, the Sn1···O1 distance in adjacent molecules is 3.115(1) Å, shorter than the sum of the van der Waals radii of the Sn and O atoms, exhibiting the presence of intermolecular Sn···O interactions. It is also noted that these heteroatoms in the carboxylate ligands do not participate in the coordination to the tin atom, but some intermolecular weak S···S interactions extensively exist.[34] This compound extends a three-dimensional structure through the intermolecular weak Sn···O and S···S interactions [S2···S4^{i} 3.619(1) Å and S3···S3^{ii} 3.506(1) Å; symmetric code: i, $1.5-x$, $0.5+y$, $0.5-z$; and ii, $-x$, $-y$, $-z$].

$\{[(ArCS_2CH_2CO_2)Sn(Bu^n)_2]_2O\}_2$

Upon treatment of $ArCS_2CH_2CO_2H$ with $^nBu_2SnO$ in a 1:1 molar ratio under analogous conditions, dimeric compounds

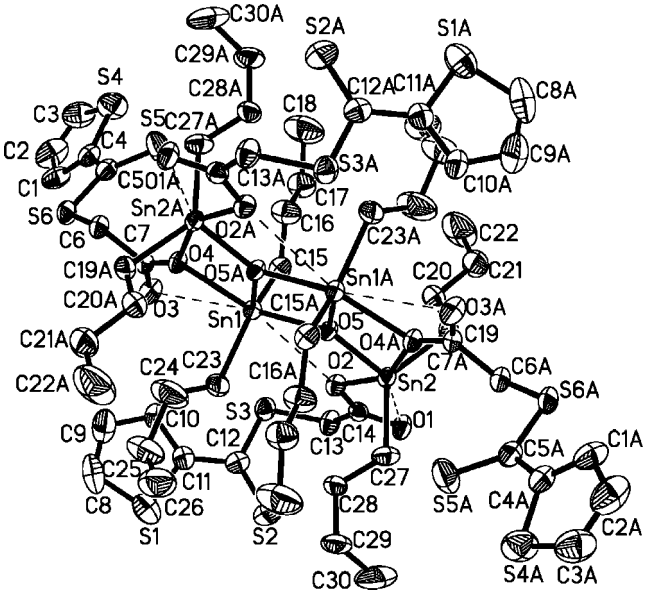

Figure 2. Molecular structure of **6** with the thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetric operations of 'A' are $2-x$, $-y$, $-z$.

(**4**)–(**6**) are obtained, which have been characterized by elemental analyses, IR as well as NMR spectra. The NMR spectra of these three complexes are consistent with their structures of dimeric distannoxanes. For instance, the ^{119}Sn spectra of these compounds display the presence of *endo*- and *exo*-cyclic tin atoms. A pair of resonances of equal intensities is observed at −175.1 and −182.9 ppm for **4**, −200.0 and −206.2 ppm for **5**, as well as −200.3 and −207.0 ppm for **6**, respectively. These values are comparable with those reported for other centrosymmetric dimers with cyclic Sn_2O_2 units.[13,31,35] Two sets of butyl signals of ^{1}H and ^{13}C NMR spectra in these three compounds also reflect them being attached to different tin atoms.

The structure of **6** has been confirmed further by X-ray crystallography. Its molecular structure is presented in Fig. 2 and selected bond distances and angles are given in Table 3. As seen in Fig. 2, the core geometry of the molecule comprises a ladder-type centrosymmetric dimer with four-membered Sn_2O_2 ring. The crystallographically unique carboxylic ligands display different coordination modes: one coordinated to Sn2 is monodentate, via the carboxylate O2 atom, while the other bridges two tin atoms only via the carboxylate O4 atom. Such coordination modes have also been observed in other $\{[R_2Sn(O_2CR')_2]_2O\}_2$ compounds.[17,35] Each tin atom adopts, to a first approximation, a five-coordinate distorted trigonal bipyramidal geometry with two butyl carbon atoms and one oxygen atom (O5 for Sn2 and O5A for Sn1) occupying the equatorial positions as well as the O2 and O4A for Sn2 and O4 and O5 for Sn1 occupying the axial positions. The axial O–Sn–O

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Table 3. Selected bond distances and bond angles for **6**

	Bond distances (Å)		
Sn1–O5A	2.044(3)	S3–C13	1.797(5)
Sn1–O5	2.168(3)	S5–C5	1.636(5)
Sn1–O4	2.248(3)	S6–C5	1.743(6)
Sn2–O5	2.011(3)	S6–C6	1.787(5)
Sn2–O2	2.124(3)	O1–C14	1.225(5)
Sn2–O4A	2.509(3)	O2–C14	1.293(5)
S2–C12	1.631(5)	O3–C7	1.199(5)
S3–C12	1.728(6)	O4–C7	1.313(5)
	Bond angles (deg)		
Sn1–O4–C7	120.6(2)	O2–Sn2–O4A	152.6(1)
Sn1–O4–Sn2A	95.8(1)	O2–Sn2–O5	83.7(1)
Sn1–O5–Sn1A	106.4(1)	O4–Sn1–O5	147.6(1)
Sn1–O5–Sn2	132.4(1)	O4–Sn1–O5A	74.1(1)
Sn2–O2–C14	108.9(3)	O4A–Sn2–O5	69.0(1)
Sn2–O5–Sn1A	121.2(1)	O5–Sn1–O5A	73.6(1)
Sn2A–O4–C7	143.6(3)	C4–C5–S6	114.1(4)
S2–C12–S3	124.5(3)	C5–S6–C6	104.1(2)
O1–C14–O2	123.1(4)	C12–S3–C13	104.0(3)

Symmetry operations of 'A' are $2-x, -y, -z$.

angles [O2–Sn2–O4A 152.6(1)° and O4–Sn1–O5 147.6(1)°] significantly derivate from 180°. In addition, the bridging carboxylate ligand shows markedly asymmetric Sn–O distances [Sn1–O4 2.248(3) Å and Sn2–O4A 2.509(3) Å], as found in other analogous $\{[R_2Sn(O_2CR')_2]_2O\}_2$ compounds with three coordinative oxygens.[17,35] The above results indicate that the geometry is highly distorted. Some weak intramolecular Sn···O interactions have also been observed. Thus, the Sn···O distances [Sn1···O2 3.279(6) Å, Sn1···O3 3.264(9) Å and Sn2···O1 2.828(7) Å] are significantly shorter than the sum of the van der Waal's radii for the Sn and O atom of 3.74 Å.[36]

Biological activity

Bioassay screening for fungicide[37] indicates that these compounds have certain fungicidal activities (Table 4). In these mononuclear tin compounds, **3** displays good activity for *Alternaria solani* and *Physolospora piricola*, the inhibition percentage *in vitro* being 57.1 and 43.9%, respectively, while in centrosymmetric dimers, **5** shows high inhibition percentage for *Gibbereila zeae* (52.6%) and *Physolospora piricola* (50.0%), respectively. These compounds have little acaricidal activity for *Tetranychus cinnabarinus*.[38,39]

Supplementary materials

CCDC numbers 601932 for **3** and 601931 for **6** contain the supplementary crystallographic data for this paper. Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or web site: www.ccdc.cam.ac.uk).

Table 4. The fungicidal activities of compounds **1**–**6**

	Inhibition ratio (%) (50 ppm)					
Compound	**1**	**2**	**3**	**4**	**5**	**6**
Gibbereila zeae	28.9	21.1	34.2	21.1	52.6	21.1
Alternaria solani	28.6	31.4	57.1	28.6	25.7	22.9
Cercospora arachidicola	18.2	13.6	18.2	9.0	22.7	9.0
Physolospora piricola	31.8	31.8	43.9	34.8	50.0	27.3
Fusarium oxysporum	17.5	37.5	15.0	5.0	7.5	10.0

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