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The Synthesis, Structural Characterization and Biocidal Properties of Some Triorganotin(IV) Esters of *N*-arylidene-ω-Amino Acids.

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The methods of synthesis, elemental analysis, IR and NMR spectroscopic data and fungicidal activity against *Ceratocystis ulmi* are reported for a series of triorganotin esters of *N*-arylidene-ω-amino acids of general formula R_3SnO-$CO(CH_2)_nN=CHAr$ (R = Ph, n-Bu; Ar = 2-HOC_6H_4, 2-$HOC_{10}H_6$; *n* = 1, 2, 3 and 5). The crystal structures for two of the compounds, tributyltin *N*-2-hydroxynaphthalidene glycinate (1) and tributyltin *N*-2-hydroxynaphthalidene-β-alaninate (2), have been determined. Although both of these compounds have a *trans*-R_3SnO_2 structure, in compound 1 the carboxylate group is monodentate and the fifth coordination position around the tin atom is taken up by a coordinated phenolic group, whereas in 2 the carboxylate group is bridging. These two examples thus correspond to the two different structures reported for *trans*-R_3SnO_2 complexes. Both compounds were found to be active against *Ceratocystis ulmi*, but there was no significant difference in their levels of biological activity against this particular fungus. Apart from compound 1, the other tributyltin compounds reported are believed to adopt the carboxylate bridging mode shown by compound (2).

Crystal data: for 1, crystals monoclinic, space group $P2_1/c$, a = 12.9435(11) Å, b = 13.5769(10) Å, c = 15.7715(12) Å, β = 108.919(6)°, Z = 4, R_f = 0.046 and R_w = 0.058 for 1448 significant reflections; for 2, crystals monoclinic, space group $C\,2/c$, a = 24.588(14) Å, b = 9.733(3) Å, c = 27.611(12) Å, β = 113.49(4)°, Z = 8, R_f = 0.053 and R_w = 0.069 for 3822 significant reflections.

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Keywords: fungicidal activity; *Ceratocystis ulmi*; triphenyltin(IV); tributyltin(IV); phenolic bridge; carboxylate bridge; polymers; trigonal bipyramidal structures

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INTRODUCTION

Organotin carboxylates have been observed to have a variety of biocidal activities[1,2,3] and an interesting range of structural variations[4] which have led to the proposal of some structure–activity relationships.[5] The structure–activity relationship studies suggest that triorganotin carboxylates with either an isolated tetrahedral tin centre or a *trans*-R_3SnO_2 geometry about the tin atom show significantly greater biocidal activity than compounds of the monomeric *cis*-R_3SnO_2 structural type.[3,5] However, two types of bridging are known for the *trans*-R_3SnO_2 configuration of organotin carboxylates. The most commonly encountered structure is polymeric, where the carboxylate groups behave as bridging bidentate ligands and the pentacoordinated tin atoms have distorted trigonal bipyramidal geometries. Alternatives to carboxylate bridging for the *trans*-R_3SnO_2 structural moiety have been reported, however, for triorganotin carboxylates containing either donor substituent groups[6,7] or a labile phenolic group in the ester function.[8] The relative biocidal activities of these two different

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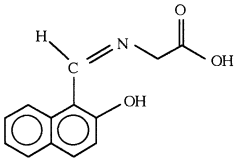
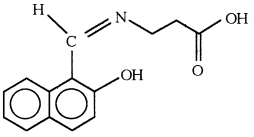


N-2-hydroxynapthalideneglycine
Ligand 1



N-2-hydroxynapthalidene-β-alanine
Ligand 2

Structures (1) and (2).

structural configurations have not previously been compared.

As a continuation of our studies on the fungicidal activities of organotin compounds against *Ceratocystis ulmi*,[9] we now report the synthesis, characterization and biocidal activity of a range of tributyltin and triphenyltin esters of some *N*-arylidene-ω-amino acids (2-$OHArCH = N(CH_2)_n$-$COOSnBu_3/Ph_3$ [Ar = $C_{10}H_6$ or C_6H_4; n = 1,2,3]). In addition, the crystal and molecular structures of the tributyltin derivatives of tributyltin *N*-2-hydroxynaphthalidene glycinate (**1**) and tributyltin *N*-2-hydroxynaphthalidene-β-alaninate (**2**) have been determined. The results of the X-ray structural investigations show that while both these compounds have a *trans*-R_3SnO_2 structure, in **1** the carboxylate group is monodentate and the fifth coordination position around the tin atom is taken up by a coordinated phenolic group, whereas in **2** the carboxylate group is bridging. These two examples thus correspond to the two different structures reported for *trans*-R_3SnO_2 complexes mentioned above. Both compounds were found to be biologically active against *Ceratocystis ulmi*, but

Table 1 Crystal data and refinement details for 2-$OHC_{10}H_6CH = N(CH_2)COOSnBu_3$ (**1**) and 2-$OHC_{10}H_6CH = N(CH_2)_2COOSnBu_3$ (**2**)

	1	**2**
Formula	$C_{25}H_{37}NO_3Sn$	$C^{26}H^{39}NO^3Sn1/4C_6H_{12}$
Formula wieght	518.25	553.33
Cell dimensions (mm^3)	$0.2 \times 0.04 \times 0.04$	$0.30 \times 0.30 \times 0.25$
Crystal system	Monoclinic	Monoclinic
Space group	$P\ 2_1/c$	$C\ 2/c$
a (Å)	12 9435(11)	24.588(14)
b (Å)	13.5769(10)	9.733(3)
c (Å)	15.7715(12)	27.611(12)
β (°)	108.919(6)	113.49(4)
Volume (Å^3)	2621.8(4)	6060(5)
Z (molecules/cell)	4	8
D_{calc} (Mg m^{-3})	1.310	1.213
μ (mm^{-1})	8.10	0.87
$F(000)$	1070 8	1151.86
$2\theta_{max}$	90	55
Index range h	−11 to 11	−31 to 39
k	0 to 11	0 to 12
l	0 to 14	0 to 35
Reflections measured	3350	7123
Unique reflections	2059	6962
Reflections with $I_{net} > 2.5\sigma$	1448	3822
R_f (significant reflections)	0 046	0.053
R_w (significant reflections)	0.058	0.069
R_f (all reflections)	0.079	0.115
R_w (all reflections)	0.064	0.072
Goodness-of-fit	1.79	2.10
Last D-map		
Deepest hole (e Å^{-3})	−0 41	−0.37
Highest peak (e Å^{-3})	0.55	0.77

Table 2 Final fractional coordinates of non-hydrogen atoms and equivalent isotropic thermal parameters (Compound **1**)

	x	*y*	*z*	B_{eq} [b]
Sn	0.64543(7)[a]	0.81433(6)	0.22902(6)	4.63(6)
O(1)	0.5401(7)	0.9068(6)	0.1213(5)	5.3(5)
O(2)	0.4586(7)	0.9810(7)	0.2090(7)	5.9(6)
O(3)	0.7527(8)	0.7020(6)	0.3403(6)	5.5(5)
N	0.3098(9)	1.0715(7)	0.0701(7)	4.1(6)
C(1)	0.4680(11)	0.9645(11)	0.1376(11)	4.4(9)
C(2)	0.3910(11)	1.0089(10)	0.0508(8)	4.8(8)
C(3)	0.7926(14)	0.5760(9)	0.4841(8)	3.9(8)
C(4)	0.8774(13)	0.6344(10)	0.4723(10)	3.6(9)
C(5)	0.9852(13)	0.6283(12)	0.5365(10)	4.1(9)
C(6)	1.0133(14)	0.5687(11)	0.6125(12)	5.6(9)
C(7)	1.1171(17)	0.5661(12)	0.6691(9)	6.4(10)
C(8)	1.2000(14)	0.6238(16)	0.6528(14)	7.4(12)
C(9)	1.1733(14)	0.6825(13)	0.5801(14)	6.4(11)
C(10)	1.0659(14)	0.6855(13)	0.5205(12)	5.4(11)
C(11)	1.0395(16)	0.7485(13)	0.4416(16)	7.1(12)
C(12)	0.9390(18)	0.7538(11)	0.3846(11)	6.4(11)
C(13)	0.8523(13)	0.6983(11)	0.3979(10)	4.6(9)
C(14)	0.7146(11)	0.7581(11)	0.1339(9)	6.3(9)
C(15)	0.7185(18)	0.6487(19)	0.1295(15)	13.3(7)
C(16)	0.7716(22)	0.6120(22)	0.0589(18)	16.7(8)
C(17)	0.794(3)	0.503(3)	0.0634(23)	23.6(12)
C(18)	0.5117(10)	0.7412(10)	0.2516(9)	5.3(8)
C(19)	0.4927(12)	0.7732(11)	0.3379(11)	6.9(10)
C(20)	0.3932(14)	0.7219(15)	0.3532(16)	11.3(14)
C(21)	0.3716(20)	0.7540(20)	0.4341(17)	16.6(21)
C(22)	0.7300(11)	0.9345(10)	0.3082(8)	5.4(8)
C(23)	0.7980(14)	0.9957(12)	0.2622(10)	7.3(11)
C(24)	0.8604(15)	1.0809(14)	0.3164(12)	9.5(13)
C(25)	0.9190(17)	1.1436(14)	0.2662(16)	13.4(17)

[a] E.S.Ds. (in parentheses) refer to the last digit printed.
[b] B_{eq} is the mean of the principal axes of the thermal ellipsoid except for C15, C16 and C17 where $B_{eq} = B_{iso}$.

there was no significant difference in their levels of activity.

EXPERIMENTAL

Reagents

Bis(tributyltin) oxide, bis(triphenyltin) oxide and other chemicals were purchased from the Aldrich Chemical Company, and used without further purification.

Instrumentation

IR spectra
The IR spectra of the complexes were recorded in the region 4000–300 cm^{-1} with a Beckman IR 20A spectrophotometer with samples either as Nujol mulls or KBr discs.

NMR spectra
The ^1H NMR spectra were recorded in $CDCl_3$/DMSO-d_6 on either a CFT-20 Varian or a Bruker AC-P300 spectrometer.

Elemental analysis
Tin was determined gravimetrically as SnO_2. Carbon, hydrogen and nitrogen microanalyses were performed in the Chemistry Department, National University of Singapore, Singapore.

Mössbauer spectroscopy
The Mössbauer spectra were measured at 80 K on a Ranger Scientific model MS-900 Mössbauer spectrometer in the acceleration mode with a moving-source geometry using a liquid-nitrogen cryostat (CRYO Industries of America, Salem, NH, USA).

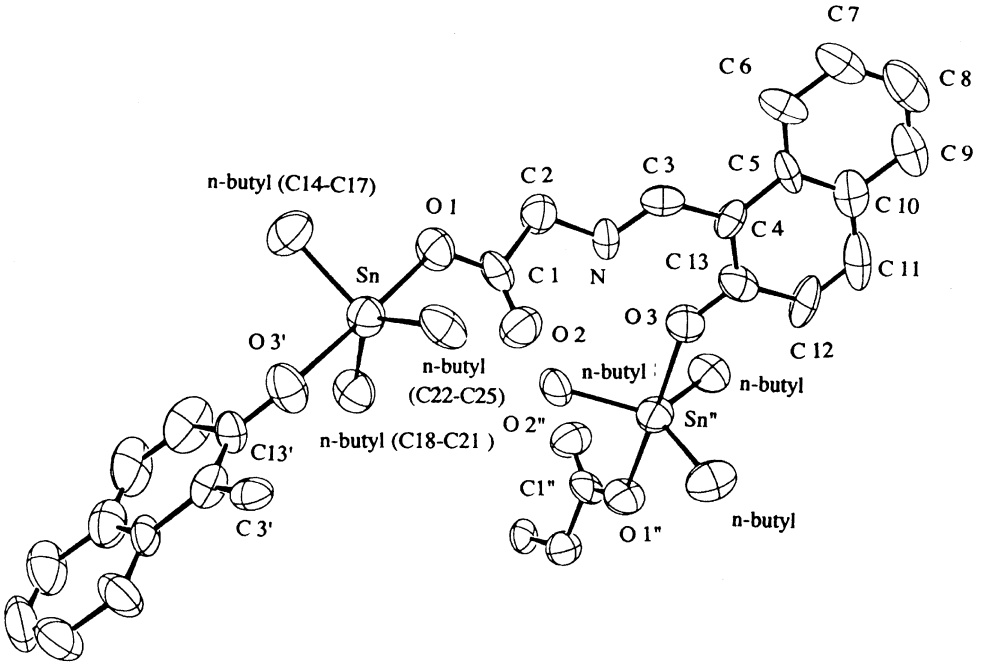


Figure 1 An ORTEP plot of compound **1**.

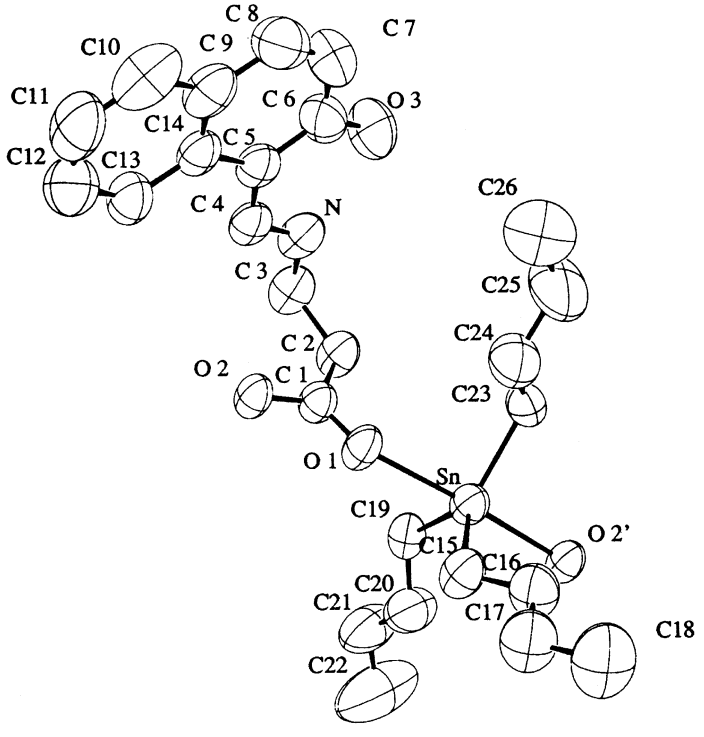


Figure 2 An ORTEP plot of compound **2**.

Table 3 Bond lengths (Å) for compound **1**[a]

Sn–O(1)	2.195(8)	C(6)–C(7)	1.35(3)
Sn–O(3)	2.399(9)	C(7)–C(8)	1.42(3)
Sn–C(14)	2.123(13)	C(8)–C(9)	1.35(3)
Sn–C(18)	2.123(13)	C(9)–C(10)	1.40(3)
Sn–C(22)	2.129(13)	C(10)–C(11)	1.46(3)
O(1)–C(1)	1.305(21)	C(11)–C(12)	1.32(3)
O(2)–C(1)	1.193(22)	C(12)–C(13)	1.422(25)
O(3)–C(13)	1.316(19)	C(14)–C(15)	1.49(3)
N–C(2)	1.459(18)	C(15)–C(16)	1.57(4)
N–C(3)a	1.325(20)	C(16)–C(17)	1.50(5)
C(1)–C(2)	1.532(19)	C(18)–C(19)	1.522(23)
C(3)–C(4)	1.415(23)	C(19)–C(20)	1.550(24)
C(4)–C(5)	1.436(22)	C(20)–C(21)	1.46(4)
C(4)–C(13)	1.411(23)	C(22)–C(23)	1.552(23)
C(5)–C(6)	1.39(3)	C(23)–C(24)	1.51(3)
C(5)–C(10)	1.39(3)	C(24)–C(25)	1.52(3)

[a] Atoms flagged 'a' are symmetry equivalents (see Table 4).

The sample was mounted in a Teflon holder. The source was 15 mCi $CaSn^{119m}O_3$, and the velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and tinfoil (splitting = 2.52 mm s^{-1}). The resultant spectra were analysed by a least-square fit to Lorenzian-shaped lines. All isomer shifts were calculated relative to $BaSnO_3$.

Preparation of tributyl- and triphenyl-tin esters of *N*-arylidene-*ω*-amino acids[8]

Tributyltin(IV) esters of *N*-arylidene-*ω*-amino acids were prepared by refluxing in absolute ethanol (*ca* 90 ml) a mixture of bis(tributyltin) oxide (10 mmol), *ω*-amino acid (20 mmol) and salicylaldehyde or 2-hydroxynaphthaldehyde (20 mmol). After refluxing for 6–8 h, the reaction mixture was cooled and the product (if there was precipitation) was isolated by filtration; otherwise the reaction mixture was concentrated under reduced pressure before either toluene or petroleum ether (60–80 °C) was added to induce precipitation. The isolated solid was recrystallized from either benzene, petroleum ether or ethanol to give the pure tributyltin carboxylates whose melting points are listed in Table 2 (below).

The triphenyltin(IV) esters were prepared in a similar manner, as described previously.[8]

A slowly evaporating solution (cyclohaxane, 30 ml) of tributyltin(IV) *N*-2-hydroxynaphthalidene glycinate (**1**) (1.6 g) yielded yellow crystals (1.2 g), m.p. 120–121 °C, from which a thin yellow plate of dimensions 0.2 mm × 0.04 mm × 0.04 mm was selected for X-ray analysis.

Tributyltin(IV)*N*-2-hydroxynaphthalidene-*β*-ala-

Table 4 Bond angles (deg) for compound **1**

O(1)–Sn–O(3)	175.4(3)	C(6)–C(5)–C(10)	118.7(15)
O(1)–Sn–C(14)	87.6(4)	C(5)–C(6)–C(7)	120.6(15)
O(1)–Sn–C(18)	93.5(4)	C(6)–C(7)–C(8)	121.0(15)
O(1)–Sn–C(22)	95.0(4)	C(7)–C(8)–C(9)	118.8(14)
O(3)–Sn–C(14)	90.7(4)	C(8)–C(9)–C(10)	120.8(16)
O(3)–Sn–C(18)	83.7(4)	C(5)–C(10)–C(9)	120.2(18)
O(3)–Sn–C(22)	89.6(4)	C(5)–C(10)–C(11)	120.2(16)
C(14)–Sn–C(18)	120.3(6)	C(9)–C(10)–C(11)	119.7(18)
C(14)–Sn–C(22)	115.8(5)	C(10)–C(11)–C(12)	121.2(15)
C(18)–Sn–C(22)	123.5(6)	C(11)–C(12)–C(13)	121.4(16)
Sn–O(1)–C(1)	119.7(9)	O(3)–C(13)–C(4)	120.5(15)
Sn–O(3)–C(13)	137.3(9)	O(3)–C(13)–C(12)	121.5(15)
C(2)–N–C(3)a	122.0(11)	C(4)–C(13)–C(12)	117.9(15)
O(1)–C(1)–O(2)	126.6(12)	Sn–C(14)–C(15)	114.9(12)
O(1)–C(1)–C(2)	111.1(14)	C(14)–C(15)–C(16)	112.3(19)
O(2)–C(1)–C(2)	122.3(14)	C(15)–C(16)–C(17)	113.5(24)
N–C(2)–C(1)	110.3(11)	Sn–C(18)–C(19)	113.2(9)
Nb–C(3)–C(4)	126.7(12)	C(18)–C(19)–C(20)	113.2(15)
C(3)–C(4)–C(5)	119.5(14)	C(19)–C(20)–C(21)	114.0(20)
C(3)–C(4)–C(13)	118.3(14)	Sn–C(22)–C(23)	113.5(9)
C(5)–C(4)–C(13)	122.1(14)	C(22)–C(23)–C(24)	115.2(13)
C(4)–C(5)–C(6)	124.3(16)	C(23)–C(24)–C(25)	113.5(15)
C(4)–C(5)–C(10)	117.1(16)		

[a] Atoms flagged 'a' are symmetry equivalents:
C(3)[a] 0.20743 1.07597 0.01589 1.000 − *x* 0.500 + *y* 0.500 − *z*.

Table 5 Final fractional coordinates of non-hydrogen atoms and equivalent isotropic thermal parameters (compound **2**)

	x	*y*	*z*	B_{eq} [b]
Sn	0.269027(25)[a]	1.09028(5)	0.230906(21)	4.79(3)
N	0.2557(4)	0.9030(7)	0.4294(3)	6.0(4)
O(1)	0.2518(3)	0.9017(5)	0.27802(21)	5.4(3)
O(2)	0.21378(24)	0.7556(5)	0.31664(20)	5.0(3)
O(3)	0.3502(3)	0.9516(6)	0.5067(3)	8.8(5)
C(1)	0.2278(4)	0.8772(7)	0.3090(3)	4.6(4)
C(2)	0.2140(4)	0.9935(7)	0.3384(3)	5.6(5)
C(3)	0.2024(4)	0.9502(8)	0.3865(4)	6.2(5)
C(4)	0.2627(4)	0.7738(8)	0.4407(3)	5.3(5)
C(5)	0.3156(4)	0.7235(9)	0.4830(3)	5.2(5)
C(6)	0.3580(5)	0.8214(11)	0.5149(4)	6.7(6)
C(7)	0.4091(5)	0.7709(13)	0.5562(5)	8.3(7)
C(8)	0.4207(5)	0.6373(14)	0.5663(4)	7.7(7)
C(9)	0.3793(5)	0.5333(11)	0.5352(4)	6.6(6)
C(10)	0.3888(5)	0.3883(13)	0.5448(5)	8.6(8)
C(11)	0.3466(7)	0.2935(11)	0.5138(6)	9.2(10)
C(12)	0.2952(6)	0.3374(12)	0.4742(5)	8.6(9)
C(13)	0.2840(5)	0.4747(10)	0.4638(4)	6.6(6)
C(14)	0.3250(4)	0.5774(9)	0.4934(3)	5.1(5)
C(15)	0.3038(4)	0.9404(8)	0.1948(4)	6.0(5)
C(16)	0.3603(4)	0.9751(10)	0.1883(4)	7.1(6)
C(17)	0.3855(5)	0.8641(10)	0.1652(5)	8.4(7)
C(18)	0.4401(6)	0.8988(12)	0.1582(6)	10.6(9)
C(19)	0.1747(4)	1.1118(8)	0.1964(3)	5.6(5)
C(20)	0.1461(5)	1.1222(13)	0.1378(4)	8.8(7)
C(21)	0.0793(5)	1.1353(16)	0.1141(5)	11.1(9)
C(22)	0.0528(6)	1.164(3)	0.0609(6)	20.9(19)
C(23)	0.3295(4)	1.1771(9)	0.3039(3)	5.7(5)
C(24)	0.3730(5)	1.0764(12)	0.3420(4)	8.3(6)
C(25)	0.4144(7)	1.1475(18)	0.3938(7)	15.3(11)
C(26)	0.4443(12)	1.068(3)	0.4347(8)	26.3(26)
CC(1)	0.5101(10)	0.2817(22)	0.2278(8)	8.5(5)
CC(2)	0.5132(10)	0.5240(23)	0.2308(9)	8.8(6)
CC(3)	0.5426(10)	0.4006(25)	0.2301(9)	8.9(6)

[a] E.S.D.s refer to the last digit printed.
[b] B_{eq} is the mean of the principal axes of the thermal ellipsoid for atoms refined anisotropically. For CC(1), CC(2) and CC(3), $B_{eq} = B_{iso}$. Note also that these three atoms have occupancies of 0.5.

ninate (**2**) (1.0 g) was recrystallized from cyclohexane (50 ml) at room temperature to yield crystals (0.7 g), m.p. 72–74 °C, from which one with dimensions 0.3 mm × 0.3 mm × 0.25 mm was selected for X-ray analysis.

X-ray crystallography of 1 and 2

The crystallographic data and refinement details from both crystal structure determinations are summarized in Table 1. For both determinations, scattering factors were taken from the literature.[10] All computation was performed using the NRCVAX system of crystal structure solving programmes.[11]

Compound 1

The intensity data were collected at 295 K on a Nonius diffractometer run by the NRCCAD diffractometer control program,[12] using the $\theta/2\theta$ scan mode and profile analysis;[13] $Cu_{K\alpha}$ radiation (λ = 1.54056 Å) was used. No absorption corrections were made since the maximum/minimum transmission ratio was found to be 1.046:1. The structure was solved by direct methods. Hydrogen atoms were calculated. The final least-squares cycle was calculated with 66 atoms, 256 parameters and 1448 out of 2059 reflections. Weights based on counting statistics were used. Figure 1 is an ORTEP plot illustrating the coordination around the tin atom. The final fractional coordinates of non-hydrogen atoms with equivalent isotropic thermal parameters are listed in Table 2 while the bond

Table 6 Bond lengths (Å) for compound **2**[a]

Sn–O(1)	2.383(5)	C(9)–C(10)	1.437(15)
Sn–O(2)a	2.221(5)	C(9)–C(14)	1.440(14)
Sn–C(15)	2.129(8)	C(10)–C(11)	1.398(21)
Sn–C(19)	2.139(8)	C(11)–C(12)	1.368(21)
Sn–C(23)	2.145(8)	C(12)–C(13)	1.372(15)
O(1)–C(1)	1.239(9)	C(13)–C(14)	1.424(13)
O(2)–Snb	2.221(5)	C(15)–C(16)	1.508(13)
O(2)–C(1)	1.273(9)	C(16)–C(17)	1.509(13)
O(3)–C(6)	1.288(12)	C(17)–C(18)	1.468(16)
N–C(3)	1.446(13)	C(19)–C(20)	1.488(13)
N–C(4)	1.291(11)	C(20)–C(21)	1.513(15)
C(1)–C(2)	1.510(11)	C(21)–C(22)	1.377(19)
C(2)–C(3)	1.525(12)	C(23)–C(24)	1.520(14)
C(4)–C(5)	1.443(13)	C(24)–C(25)	1.550(20)
C(5)–C(6)	1.428(13)	C(25)–C(26)	1.33(3)
C(5)–C(14)	1.451(12)	C(1c)–C(1c)c	1.50(4)
C(6)–C(7)	1.407(18)	C(1c)–C(3c)	1.39(3)
C(7)–C(8)	1.336(19)	C(2c)–C(2c)c	1.44(4)
C(8)–C(9)	1.449(17)	C(2c)–C(3c)	1.41(3)

[a] Atoms flagged 'a', 'b' or 'c' are symmetry equivalents (see Table 7).

lengths and bond angles for the complex are in Tables 3 and 4 respectively. Calculated and observed structure factors, calculated hydrogen-atom parameters and anisotropic thermal parameters have been deposited as Tables S-1, S-2 and S-3, respectively. The atom-numbering scheme and a stereo pair showing the packing arrangement in the unit cell have been deposited as Figs S-1 and S-2.

Compound 2

The intensity data were collected at 295 K on a Rigaku model AFC6S diffractometer run by the TEXRAY (Molecular Structure Corp., Woodlands, Tx, USA) diffractometer control program, using the ω-scan mode and $Mo_{K\alpha}$ radiation (λ = 0.70930 Å). Absorption corrections were made from four ψ-scan curves.[14] The minimum and maximum transmission factors are 0.787 and 0.821. The final least-squares cycle was calculated with 78 atoms, 292 parameters and 3822 out of 6962 reflections. Weights based on counting statistics were used. The structure was solved from a Patterson synthesis which gave the position of the tin atom. Other non-hydrogen atoms were located in difference maps. All hydrogens were given calculated positions. All other atoms, except the solvent carbons, were refined anisotropically. The crystal structure includes a solvent cyclohexane molecule, modelled at 50% occupancy, which is centred at the twofold

Table 7 Bond angles (deg) for compound **2**[a]

O(1)–Sn–O(2)a	176.07(17)	C(6)–C(7)–C(8)	123.8(10)
O(1)–Sn–C(15)	85.4(3)	C(7)–C(8)–C(9)	121.0(10)
O(1)–Sn–C(19)	85.5(3)	C(8)–C(9)–C(10)	123.5(11)
O(1)–Sn–C(23)	89.9(3)	C(8)–C(9)–C(14)	118.3(9)
O(2)a–Sn–C(15)	90.8(3)	C(10)–C(9)–C(14)	118.1(10)
O(2)a–Sn–C(19)	95.4(3)	C(9)–C(10)–C(11)	120.6(11)
O(2)a–Sn–C(23)	92.6(3)	C(10)–C(11)–C(12)	120.5(10)
C(15)–Sn–C(19)	115.2(3)	C(11)–C(12)–C(13)	121.1(11)
C(15)–Sn–C(23)	116.9(4)	C(12)–C(13)–C(14)	121.8(10)
C(19)–Sn–C(23)	127.1(3)	C(5)–C(14)–C(9)	118.4(8)
Sn–O(1)–C(1)	139.6(5)	C(5)–C(14)–C(13)	123.6(8)
Snb–O(2)–C(1)	116.5(4)	C(9)–C(14)–C(13)	118.0(8)
C(3)–N–C(4)	119.8(8)	Sn–C(15)–C(16)	117.6(6)
O(1)–C(1)–O(2)	121.9(7)	C(15)–C(16)–C(17)	116.3(8)
O(1)–C(1)–C(2)	119.8(7)	C(16)–C(17)–C(18)	116.3(9)
O(2)–C(1)–C(2)	118.2(7)	Sn–C(19)–C(20)	116.6(6)
C(1)–C(2)–C(3)	115.0(6)	C(19)–C(20)–C(21)	115.9(8)
N–C(3)–C(2)	112.3(7)	C(20)–C(21)–C(22)	116.8(10)
N–C(4)–C(5)	121.1(8)	Sn–C(23)–C(24)	115.4(6)
C(4)–C(5)–C(6)	118.3(8)	C(23)–C(24)–C(25)	111.9(10)
C(4)–C(5)–C(14)	120.9(8)	C(24)–C(25)–C(26)	117.6(16)
C(6)–C(5)–C(14)	120.8(9)	C(1c)c–C(1c)–C(3c)	109.5(18)
O(3)–C(6)–C(5)	121.8(10)	C(2c)c–C(2c)–C(3c)	113.2(19)
O(3)–C(6)–C(7)	120.6(9)	C(1c)–C(3c)–C(2c)	114.9(20)
C(5)–C(6)–C(7)	117.6(9)		

[a] Atoms flagged 'a', 'b' or 'c' are symmetry equivalents:
O(2)a 0.28622 1.25564 0.18336 1/2 − x 1/2 + y 1/2 − z
Snb 0.23097 0.59028 0.26909 1/2 − x −1/2 + y 1/2 − z
C(1c)c 0.48991 0.28169 0.27222 1 − x y 1/2 − z
C(2c)c 0.48685 0.52404 0.26917 1 − x y 1/2 − z

Table 8 Analytical data for $ArCH=N(CH_2)_nCOOSnBu_3$

Compound			Yield	M.p.	Elemental analysis: Found (Calcd) (%)		
Ar	*n*	(%)	(°C)	C	H	N	Sn
$2\text{-}OHC_{10}H_6$	1	55	117–118	57.75(57.93)	7.25(7.21)	2.62(2.70)	22.75(22.90)
$2\text{-}OHC_{10}H_6$	2	66	76–78	58.79(58.66)	7.41(7.40)	2.34(2.63)	23.00(22.39)
$2\text{-}OHC_{10}H_6$	3	82	80–81	58.90(59.36)	7.45(7.56)	2.44(2.56)	22.00(21.73)
$2\text{-}OHC_6H_4$	2	65	82–84	55.05(54.78)	7.89(7.75)	2.61(2.90)	24.16(24.61)
$2\text{-}OHC_6H_4$	3	79	48–50	55.37(55.66)	7.84(7.94)	2.92(2.82)	24.00(24.12)

axis at 1/2, *y*, 1/4). Figure 2 is an ORTEP plot illustrating the coordination around the tin atom. The final fractional coordinates of non-hydrogen atoms with equivalent isotropic thermal parameters are listed in Table 5 while the bond lengths and bond angles for the complex are in Tables 6 and 7 respectively. Calculated and observed structure factors, calculated hydrogen-atom parameters and anisotropic thermal parameters have been deposited as Tables S-4, S-5 and S-6, respectively. The atom-numbering scheme and a stereo pair showing the packing arrangement in the unit cell have been deposited as Figures S-3 and S-4.

Tests for fungicidal activity

The preparation and usage protocols of the organotin carboxylate stock solutions for the fungicidal activity studies have been described previously.[15] A stock suspension (1.0 ml) of cells of *Ceratocystis ulmi* (concentration 10^6 cells ml^{-1}), strain 32437, obtained from the American Type Culture Collection, Rockville, MD20852, USA, was added to amended potato dextrose broth and the resulting suspension was shaken for seven days in an incubator shaker (22 °C). The contents of the flask were then filtered and rinsed with distilled water. The fungal growth was dried and weighed until a constant weight was obtained. Three replicates were used for each concentration tested.

The inhibitory concentration was obtained by plotting the percentage growth of the fungus versus the concentration of organotin compound (parts per million) added. The concentration at which 50% of the fungus is inhibited is taken as the inhibitory concentration value.

RESULTS AND DISCUSSION

The tributyltin carboxylates, $2\text{-}OHC_{10}H_6CH = N(CH_2)_nCOOSnBu_3$ and $2\text{-}OHC_6H_4CH = N(CH_2)_nCOOSnBu_3$ (n = 1,2,3) can be prepared by refluxing a mixture of bis(tributyltin) oxide, an ω-amino acid and the appropriate *o*-hydoxyaromatic aldehyde in absolute ethanol.[8] The melting points and analytical data for the range of carboxylates synthesized are shown in Table 8. Corresponding data for the triphenyltin complexes have been reported previously.[8] All the carboxylates listed in Table 8 were isolated as yellow solids that were stable in air. Tributyltin *N*-salicylideneglycinate was isolated as a liquid which decomposed on distillation under reduced pressure (188–240 °C/0.06 mm Hg) and is not included in the table.

The NMR signal from the azomethine proton in each of the free ligands (δ = 8.40–8.80 ppm) did not shift significantly on complex formation.[8] For all the complexes, a broad signal observed at δ = 11–14 ppm was assigned to the phenolic proton. This assignment was substantiated by the broad infrared absorptions in the region 2600–3400 cm^{-1} which are reported to be due to intramolecular hydrogen bonding between the phenolic proton and the azomethine nitrogen.[16]

The quadrupole splitting (q.s.), isomer shift (c.s.) and the ρ (= q.s/c.s) values from the Mössbauer spectra of $Bu_3SnOCO(CH_2)_nN = CHAr$ and $Ph_3SnOCO(CH_2)_nN = CHAr$ are listed in Table 9. For all examples of both triphenyltin and tributyltin carboxylates, the recorded ρ ratio values (ranging from 2.21 to 2.53) in Table 9 are greater than 2.1, indicating that the coordination of the tin atom is greater than four.[17,18] This is further substantiated by the X-ray structural determinations, where a *trans*-R_3SnO_2 moiety with phenolic bridging was found for $Ph_3SnOCO(CH_2)_nNCH = CHAr$, n = 5.[8] The observed Mössbauer quadrupole splitting values (3.49–3.61 mm s^{-1}) and the ρ ratio values (2.41–2.53) for tributyltin carboxylates are in the range commonly found for *trans* trigonal bipyramidal triorganotin compounds.[17–19] Thus a *trans*-R_3SnO_2 structure would infer a bridging participation from either the phenolic or the carboxylate carbonyl oxygen present in the ligand,

Table 9 Mössbauer data, carboxylate IR frequencies and the inhibitory concentrations (IC_{50} values) against *Ceratocystis ulmi* for $ArCH = N(CH_2)_nCOOSnBu_3$ and $ArCH = N(CH_2)_nCOOSnPh_3$

Compound		Mossbauer (mm s^{-1})[a]			Carboxylate frequencies (cm^{-1})			
Ar	*n*	q. s.	c. s.	ρ	ν_{asym}(OCO)	ν_{sym}(OCO)	$\Delta\nu$	IC_{50} (mg l^{-1})
Tributyltin carboxylates								
$2\text{-}OHC_{10}H_6$	1	3.49 ± 0.02	1.40 ± 0.01	2.49	1655	1305	305	0.5
$2\text{-}OHC_{10}H_6$	2	3.61 ± 0.02	1.43 ± 0.01	2.52	1575	1405	170	0.5
$2\text{-}OHC_{10}H_6$	3	3.59 ± 0.02	1.44 ± 0.01	2.49	1550	1400	150	1.0
$2\text{-}OHC_6H_4$	2	3.52 ± 0.02	1.46 ± 0.01	2.41	1595	1405	190	0.8
$2\text{-}OHC_6H_4$	3	3.57 ± 0.02	1.41 ± 0.01	2.53	1590	1395	195	1.0
Triphenyltin carboxylates[b]								
$2\text{-}OHC_{10}H_6$	1	2.72 ± 0.04	1.18 ± 0.01	2.31	1640	1355	285	0.6
$2\text{-}OHC_{10}H_6$	2	2.15 ± 0.09	0.93 ± 0.02	2.31	1645	1295	350	0.4
$2\text{-}OHC_{10}H_6$	3	2.64 ± 0.04	1.19 ± 0.01	2.22	1635	1405	230	0.4
$2\text{-}OHC_6H_4$	1	2.74 ± 0.05	1.20 ± 0.01	2.28	1640	1325	315	0.4
$2\text{-}OHC_6H_4$	2	2.69 ± 0.02	1.18 ± 0.01	2.28	1640	1350	290	1.8
$2\text{-}OHC_6H_4$	3	2.41 ± 0.04	1.09 ± 0.01	2.21	1630	1370	260	0.7

[a] q.s., Quadrupole splitting; c.s., isomer shift; ρ = q.s./c.s.
[b] IR data from Ref. 8.

resulting in the formation of a five-coordinate tin geometry.

The observed infrared absorption frequencies for the carboxylate antisymmetric, ν_{asym}(OCO), and symmetric, ν_{sym}(OCO), stretching vibrations for $Bu_3SnOCO(CH_2)_nNCH = CHAr$ are shown in Table 9. The assignment of the ν_{asym}(OCO) band is complicated by the presence of the $\nu(C = N)$ stretching vibration which is observed in the 1615–1625 cm^{-1} region. Nevertheless, the magnitude of the ν_{asym}(OCO)–ν_{sym}(OCO) (i.e. $\Delta\nu$) separation is of interest. With the exception of compound 1, for which $\Delta\nu = 305\ cm^{-1}$, the observed values of $\Delta\nu$, which are in the range 150–195 cm^{-1}, indicate a bridging or chelating carboxylate moiety.[20] This is widely observed in the infrared spectra of triorganotin carboxylates.[21] For a unidentate bonding mode for the carboxylate group $\Delta\nu$ would be expected to be $>200\ cm^{-1}$ [22] as observed for $Ph_3SnOCO(CH_2)_nNCH = CHAr$, $n = 5$[8]. Thus the infrared spectroscopic data, when considered together with the Mössbauer data which suggest a *trans*-R_3SnO_2 moiety for all the complexes in Table 9, would indicate that the structure for the tributyltin carboxylates listed in Table 9 would be carboxylate-bridged except for **1**, which may involve bridging by phenolic oxygen. This conclusion was confirmed by the results of the X-ray structural analyses for compounds **1** and **2**.

Screening

The toxicity results for the tributyltin and triphenyltin carboxylates against *Ceratocystis ulmi*, the causative agent of Dutch Elm disease, are listed in Table 9. As is evident from the data, both series of carboxylates are effective inhibitors of the fungus since the observed results are lower than for commercially known tributyltin and triphenyltin fungicides.[15] This is consistent with the fact that organotin carboxylates are known to possess biocidal properties.[1–3] Furthermore, a comparison of the activity of **1**, which has a phenolic oxygen bridged structure, against the rest of the compounds, with the carboxylate bridged structure found in both series of carboxylates, indicates that there is no significant difference in the toxicity results. While tributyltins are known to induce phytotoxic effects on plants when used at concentrations where they are effective,[23] this particular series of tributyltin carboxylates has been shown to be different. Previous phytotoxic studies on elm seedlings using four out of the five tributyltin carboxylates indicated that no phytotoxic effects were observed, even at a concentration of 20 mg l^{-1}, which is far above the inhibitory concentration for these compounds. This suggests that this series of compounds, as well as the triphenyltin carboxylates, can be considered as candidates for the control of Dutch Elm disease.

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