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Synthesis, Characterization and Fungicidal Activity of Triphenyltin Derivatives of Sarcosine: Crystal Structures of $[Ph_3Sn(OCOCH_2NH_2CH_3)_2]Cl$ and $[Ph_3Sn(OCOCH_2NH_2CH_3)_2]NCS$

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Two new sarcosine triphenyltin complexes formulated as $[Ph_3Sn(OCOCH_2NH_2CH_3)_2]X$ (X = Cl, NCS) were prepared and characterized via IR, proton NMR and Mössbauer spectroscopies, and their fungicidal properties against *Ceratocystis ulmi* were determined. The crystal structures of bis(methylammonioacetato)triphenyltin chloride and isothiocyanate are also reported.

Keywords: organotin; crystal structures; fungicidal activity; Dutch elm disease

INTRODUCTION

The reactions of zwitterions such as *N*-aryl(alkyl)salicylideneimines and picolinic acid with triorganotin and diorganotin halides and pseudohalides have been shown to give 1:1, 2:1 or 3:2 (ligand:tin) adducts.[1-5] We recently investigated the electron-donating effect of a methyl group attached to a zwitterion on the tin atom by treating triphenyltin chloride or isothiocyanate with N,N-dimethylglycine.[6] The adducts exhibit 1:1 stoichiometry even though a pair of $Me_2NHCH_2COO \cdot Ph_3SnCl$ molecules are consolidated by two N—H···O hydrogen bonds into a centro-symmetric dimer. In addition, these complexes have been shown to possess biological activity.

In this paper we describe the synthesis, characterization and fungicidal activity of the triphenyltin sarcosine complexes in which the ligand to triphenyltin ratio is 2:1. The crystal structures of bis(methylammonioacetato)triphenyltin chloride and isothiiocyanate, $[Ph_3Sn(OCOCH_2NH_2CH_3)_2]X$ [X = Cl (**1**), NCS (**2**)] are given.¶

EXPERIMENTAL

The starting materials were of reagent or analytical grade and used as received. Sarcosine and triphenyltin chloride were purchased from Aldrich Chemicals, USA. Triphenyltin isothiocyanate (m.p. 168–170 °C) was prepared according to the literature method[7] and recrystallized from benzene before use. Proton NMR spectra were recorded in DMSO-d_6 on Perkin–Elmer R12B spectrometer using tetramethylsilane (TMS) as a reference. Infrared spectra were recorded for KBr pellets on a Perkin–Elmer Model 1725FT-IR spectrometer. Conductance measurements in methanol were made at room temperature using a Horiba DS-14 conductivity bridge with a cell constant of 1.028 (1 cm). Microanalyses were performed in the Chemistry Department, National University of Singapore. The Mössbauer spectra were measured at 80 K on a Mössbauer spectrometer, Model MS-900 (Ranger Scientific Co., Burelson, TX 70682,

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¶ Atomic coordinates for the title structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.

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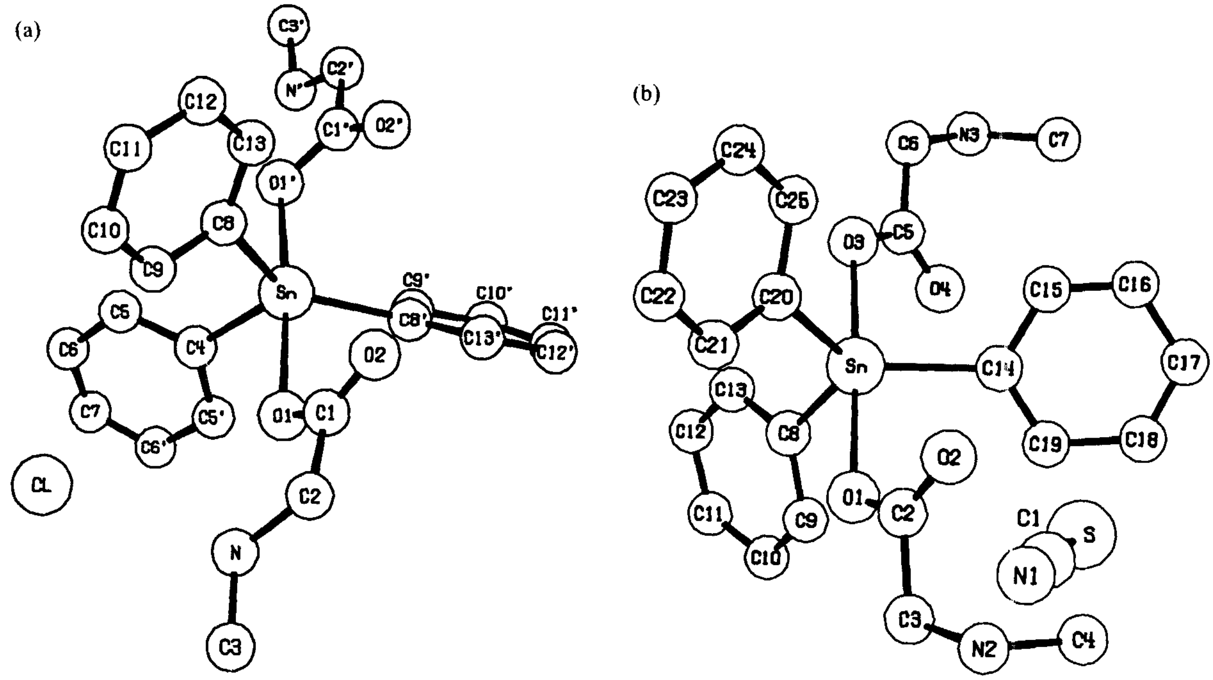

Figure 1 Molecular structure and crystallographic numbering scheme (parentheses have been omitted for clarity) for (a) $[Ph_3Sn(OCOCH_2NH_2CH_3)_2]Cl$, symmetry code ', x, $1/2-y$, $1/2-z$, and (b) $[Ph_3Sn(OCOCH_2NH_2CH_3)_2]NCS$.

USA) in the acceleration mode with a moving source geometry using a liquid nitrogen cryostat (CYRO Industries of America Inc., Salem, NH 03811, USA). The samples were mounted in Teflon holders. The source was 15 mCi $Ca^{119m}SnO_3$, and the velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and tin foil (splitting, 2.52 mm s^{-1}). The resultant spectra were analysed by a least-squares fit to Lorenzian-shaped lines.

Table 1 Atomic coordinates for **1** ($\times 10^4$ for Sn and Cl; $\times 10^3$ for others) and equivalent isotropic temperature factors[a] ($Å^2 \times 10^3$) for others

Atom	x	y	z	U_{eq}/U_{iso}
Sn	952(3)	2500	2500	29(2)
Cl	2500	0	4237(7)	47(9)
O(1)	106(2)	199(1)	411(1)	36(4)
O(2)	-127(2)	188(1)	406(1)	38(5)
N	140(2)	112(1)	565(1)	27(5)
C(1)	-15(3)	178(1)	443(2)	26(6)
C(2)	-2(3)	133(1)	540(2)	26(6)
C(3)	154(3)	79(1)	672(2)	40(7)
C(4)	321(4)	250	250	58(11)
C(5)	395(3)	218(1)	169(2)	42(7)
C(6)	543(3)	220(1)	173(2)	50(8)
C(7)	603(5)	250	250	48(9)
C(8)	15(3)	163(1)	176(2)	29(6)
C(9)	88(3)	107(1)	210(1)	38(7)
C(10)	42(3)	48(1)	171(2)	40(7)
C(11)	-63(3)	45(1)	102(2)	42(7)
C(12)	-140(3)	99(1)	71(2)	47(8)
C(13)	-101(3)	159(1)	110(2)	35(7)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U tensor.

Preparation of 2 : 1 adducts, $[Ph_3Sn(OCOCH_2NH_2CH_3)_2]X$ (X = Cl, NCS)

To a warmed solution of sarcosine (0.5 g, 6 mmol in 30 ml of 95% ethanol) was added 1.1 g (3 mmol) of triphenyltin chloride. The mixture was stirred and warmed gently. As soon as all of the triphenyltin chloride was dissolved, a precipitate started to form. Recrystallization of the product (1.4 g, yield 88%) in ethanol at room temperature overnight afforded colourless crystals, m.p. 238–240 °C. Analysis: Calcd for $C_{24}H_{29}ClN_2O_4Sn$: C, 51.16; H, 5.20; N, 4.97%. Found: C, 51.00; H, 5.08; N, 4.83%. IR (KBr; ν, cm^{-1}): 2750br, 2720br ($-NH_{2\,\mathrm{asym/sym}}^{+}$); 1615sh, 1610 ($OCO_{\mathrm{asym}}$); 1390 ($OCO_{\mathrm{sym}}$). ^{1}H NMR ($\delta$, ppm): 2.35 (s, 6H, $2CH_3$); 3.35 (s, 4H, $2CH_2$); 4.5 (br, 4H, NH/OH); 7.3–8.1 (m, 15H, aromatic).

The triphenyltin isothiocyanate–sarcosine complex (m.p. 228–230 °C) was similarly prepared. A 90% yield resulted from recrystallization from 95% ethanol. Analysis: Calcd for $C_{25}H_{29}N_3O_4SSn$: C, 51.21; H, 5.00; N, 7.17%. Found: C, 51.08; H, 4.89; N, 7.02%. IR (KBr; ν, cm^{-1}); 2812, 2790br ($-NH_2^+{}_{asym/sym}$); 2062 (NCS_{asym}); 1660, 1639 (OCO_{asym}); 1372 (OCO_{sym}). ^1H NMR (δ, ppm): 2.40 (s, 6H, $2CH_3$); 3.45 (s, 4H, $2CH_2$); 5.0 (br, 4H, NH/OH); 7.4–8.0 (m, 15H, aromatic).

Preparation of stock organotin solutions and fungicidal activity

The preparation of the organotin stock solutions and fungus for the toxicity studies has been previously described.[8] 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, MD 20852, 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.

X-ray crystallography of 1 and 2

Crystal data were as follows.

1: $C_{24}H_{29}ClN_2O_4Sn$, M_r 563.4, orthorhombic, space group *Pnna*, $a = 9.583(4)$ Å, $b =$

Table 2 Bond lengths (Å), angles (°) and torsion angles (°) for **1**[a]

Bond lengths			
Sn–C(4)	2.16(4)	Sn–C(8)	2.18(2)
Sn–O(1)	2.28(1)	O(1)–C(1)	1.31(3)
O(2)–C(1)	1.19(3)	N–C(2)	1.46(3)
N–C(3)	1.51(3)	C(1)–C(2)	1.53(3)
C(4)–C(5)	1.40(3)	C(5)–C(6)	1.42(4)
C(6)–C(7)	1.29(3)	C(8)–C(13)	1.39(3)
C(8)–C(9)	1.42(3)	C(9)–C(10)	1.40(3)
C(10)–C(11)	1.32(3)	C(11)–C(12)	1.39(3)
C(12)–C(13)	1.40(3)	N–O(2″)	2.76(2)
N–Cl	3.12(2)		
Angles			
O(1)–Sn–O(1′)	174.9(10)	O(1)–Sn–C(4)	87.4(5)
O(1)–Sn–C(8)	90.1(7)	O(1)–Sn–C(8′)	91.7(7)
C(4)–Sn–C(8)	110.5(6)	C(8)–Sn–C(8′)	139.0(13)
Sn–O(1)–C(1)	113(2)	Sn–C(4)–C(5)	121(2)
Sn–C(8)–C(13)	126(2)	Sn–C(8)–C(9)	113(2)
C(2)–N–C(3)	114(2)	O(1)–C(1)–O(2)	128(2)
O(2)–C(1)–C(2)	19(2)	O(1)–C(1)–C(2)	113(2)
N–C(2)–C(1)	115(2)	C(5)–C(4)–C(5′)	119(4)
C(4)–C(5)–C(6)	118(3)	C(5)–C(6)–C(7)	119(3)
C(6)–C(7)–C(6′)	127(5)	C(9)–C(8)–C(13)	121(2)
C(8)–C(9)–C(10)	118(2)	C(9)–C(10)–C(11)	120(2)
C(10)–C(11)–C(12)	124)2)	C(11)–C(12)–C(13)	118(3)
C(8)–C(13)–C(12)	119(2)	O(2″)–N–C(2)	128(1)
Cl–N–C(2)	115(1)	O(2″)–N–C(3)	94(1)
Cl–N–C(3)	98(1)	Cl–N–O(2″)	104(1)
N–Cl–N‴	111.8(3)		
Torsion angles			
Sn–O(1)–C(1)–C(2)	169(1)	O(1)–C(1)–C(2)–N	−12(3)
C(1)–C(2)–N–C(3)	168(2)		

[a] Symmetry: ′, x, $1/2-y$, $1/2-z$; ″, $1/2+x$, y, $1-z$; ‴, $1/2-x$, $-y$, z

20.903(8) Å, $c = 12.504(5)$ Å, $V = 2505(2)$ Å^3, $Z = 4$, $D_{cal} = 1.494$ Mg m^{-3} and $F(000) = 1143$.

2: $C_{25}H_{29}N_3O_4SSn$, M_r 586.3, monoclinic, space group $P2_1/a$, $a = 15.637(3)$ Å, $b = 9.729(2)$ Å, $c = 17.676(4)$ Å, $\beta = 96.031(11)°$, $V = 2674(1)$ Å^3, $Z = 4$, $D_{cal} = 1.456$ Mg m^{-3} and $F(000) = 1192$.

Diffraction data were collected on a Huber diffractometer using the ω–2θ technique, then integrated and corrected for Lorentz and polarization factors and for absorption. The structures were solved by direct methods[9] and in the least-squares refinements hydrogen atoms were kept in calculated positions (C–H, N–H = 0.95 Å) with isotropic temperatures factors 20% greater than that of the atom to which they were attached. The weighting scheme used was $w^{-1} = [\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|$. Computations were carried out using the KRYSTAL programme package[10] and the atomic scattering factors and anomalous dispersion corrections were taken from Ref. 11.

For **1**, a crystal of dimensions 1.027 mm × 0.039 mm × 0.006 mm was used; 1828 unique reflections were measured ($2\theta_{max} = 48°$, 50 steps/scan, ω-scan width $0.6 + 0.346 \tan\theta$, 4″/step) of which 521 were considered to be significant ($I > 3\sigma(I)$). Because of the low number of reflections only the tin and chlorine atoms were refined anisotropically. Final R_F and R_{wF} values were 0.060 and 0.059 for 73 variables. The final difference map showed values between −0.8(2) and 0.8(2) e Å^{-3}.

For **2**, a crystal of dimensions 0.458 mm × 0.130 mm × 0.043 mm was used; 3332 unique reflections were measured ($2\theta_{max} = 50°$, 50 steps/scan, ω-scan width $1.0 + 0.346 \tan\theta$, 2″/step for $2\theta < 40°$, otherwise 4″/step) of which 1835 were considered to be significant ($I > 3\sigma(I)$). All non-hydrogen atoms were refined anisotropically. The crystal was twinned on (001) so that reflections h, k, l and h, $-k$, $-(l + h/4)$ were overlapped for $h = 4n$. The intensities for the overlapped reflections were unscrambled using $\alpha = I(\text{twin } 2)/I(\text{twin } 1) = 0.277$, α was measured from the intensities of 2, k, l reflections which were measured for both twins. Final R_F and R_{wF} values were 0.055 and 0.064 for 307 variables. The final difference map showed values between −1.4(1) and 1.28(1) e Å^{-3}.

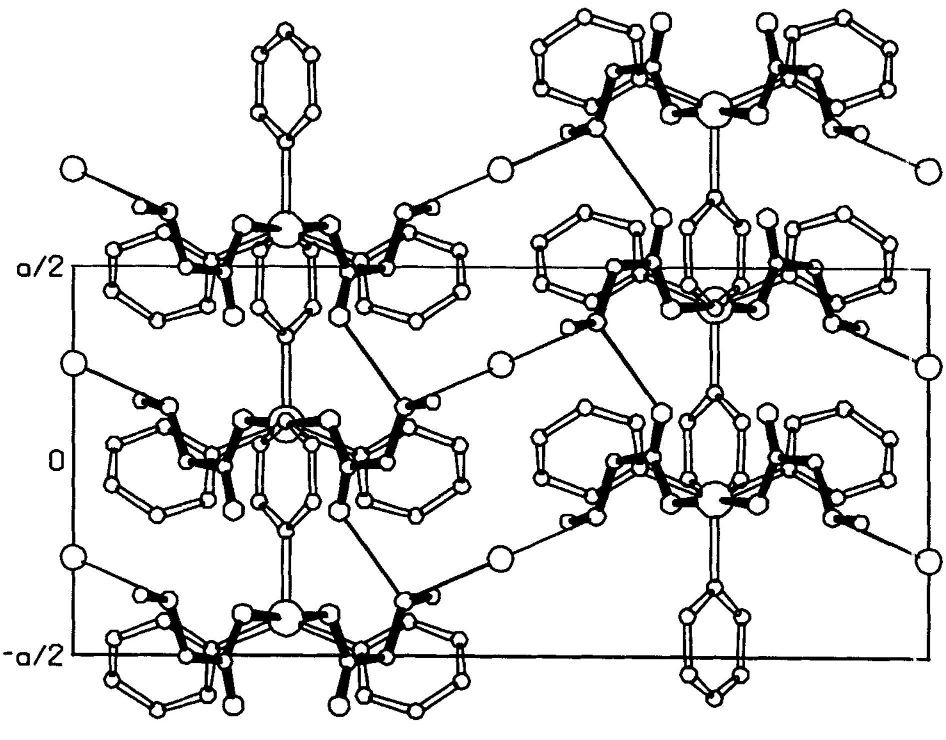

Figure 2 Hydrogen bonding in $C_{24}H_{29}ClN_2O_4Sn$.

RESULTS AND DISCUSSION

Regardless of the proportions of sarcosine (L) and triphenyltin chloride or isothiocyanate used, the adducts of composition $(Ph_3SnL_2)X$ (X = Cl, NCS) all crystallized in a 2:1 ligand:tin stoichiometry. This was confirmed by the elemental microanalyses data and the comparison of the integrated intensities of the ligand and organotin protons. These complexes are colourless, decompose on melting and are soluble in alcohol.

The IR evidence suggests that the sarcosine, reacted in the zwitterionic form, behaves as a monodentate ligand via coordination through the carboxylate oxygen. This is based on the stretching vibrations of alkylammonium ions [$—NH_2^+—$] which are observed in the range of 2812–2720 cm^{-1}, as well as the magnitude of the $\nu_{asym}(OCO) - \nu_{sym}(OCO)$ [i.e. $\Delta\nu$] separation. The observed values of $\Delta\nu$ for **1** and **2**, which are in the range of 220–288 cm^{-1}, indicate a unidentate bonding mode for the carboxylate moiety.[12, 13] The recorded Mössbauer quadrupole splitting values of 2.84 ± 0.7 and 3.06 ± 0.7 mm s^{-1} for **1** and **2**, respectively, are in the range commonly found for *trans*-trigonal bipyramidal triorganotin compounds.[14] Thus, a *trans*-R_3SnO_2 structure for **1** and **2** would infer participation of two monodentate ligands resulting in the formation of a five-coordinate tin cation, $(Ph_3SnL_2)^+$, together with either Cl^- (for **1**) or SCN^- (for **2**) as the counter-ion. The molar conductance observed for the complexes was 84.69 and 90.80 Ω^{-1} mol^{-1} cm^2 for **1** and **2**, respectively, in 10^{-3} M methanol. This suggests a 1:1 electrolyte.[15] The present X-ray structural investigations of **1** and **2** confirmed the 2:1 adduct formulation with the organic ligand in the zwitterionic form, and the halogen/pseudohalogen as the X^- ion.

Table 3 Atomic coordinates for **2** ($\times 10^5$ for Sn; $\times 10^4$ for others) and equivalent isotropic temperature factors[a] ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
Sn	64 992(7)	66(20)	69 534(5)	27(4)
S	5915(4)	4825(9)	8626(4)	79(3)
O(1)	7538(7)	1543(12)	6943(6)	40(6)
O(2)	8544(7)	385(10)	7709(7)	45(7)
O(3)	5450(7)	−1535(11)	6917(6)	39(7)
O(4)	4660(8)	−0371(10)	7692(7)	46(8)
N(1)	7524(10)	5298(15)	8147(8)	49(9)
N(2)	9517(9)	2712(14)	7976(7)	40(10)
N(3)	3693(8)	−2614(13)	7959(8)	38(9)
C(1)	6851(13)	5066(29)	8324(9)	58(14)
C(2)	8237(12)	1406(16)	7348(10)	43(12)
C(3)	8770(11)	2737(16)	7404(10)	39(11)
C(4)	9282(20)	2789(28)	8771(12)	86(27)
C(5)	4824(11)	−1419(17)	7350(9)	36(9)
C(6)	4341(11)	−2706(16)	7402(10)	42(11)
C(7)	4097(15)	−2646(25)	8767(13)	68(17)
C(8)	5694(11)	1513(17)	6356(9)	35(10)
C(9)	5806(11)	2933(17)	6507(9)	39(11)
C(10)	5270(13)	3892(20)	6141(11)	57(14)
C(11)	4634(13)	3471(20)	5604(11)	51(13)
C(12)	4483(14)	2097(25)	5437(10)	66(14)
C(13)	5003(11)	1121(20)	5832(10)	46(10)
C(14)	6631(9)	32(28)	8171(7)	38(10)
C(15)	6589(15)	−1210(27)	8561(13)	49(13)
C(16)	6670(17)	−1300(25)	9309(15)	59(19)
C(17)	6825(16)	−108(37)	9740(11)	87(18)
C(18)	6890(16)	1094(28)	9401(15)	68(13)
C(19)	6779(16)	1197(20)	8578(14)	41(15)
C(20)	7151(10)	−1433(15)	6308(8)	29(9)
C(21)	7756(12)	−1001(18)	5821(9)	43(11)
C(22)	8190(15)	−1951(22)	5427(11)	64(16)
C(23)	8070(15)	−3338(25)	5528(11)	72(17)
C(24)	7513(13)	−3816(20)	6028(11)	54(13)
C(25)	7075(12)	−2887(18)	6443(8)	43(12)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\boldsymbol{U}$ tensor.

The molecular structure and atomic numbering scheme of **1** is shown in Fig. 1(a). The fractional atomic coordinates and equivalent isotropic temperature factors are listed in Table 1 and selected bond lengths and angles are given in Table 2. The tin(IV) atom is five-coordinate, with three phenyl groups occupying the equatorial positions of a trigonal bipyramid and with carboxyl oxygen atoms at the apices. The cation has an exact two-fold symmetry since Sn, C(4) and C(7) are situated on a crystallographic two-fold axis. The nitrogen atom is hydrogen-bonded to Cl [$N\cdots Cl = 3.12(2)$ Å] and to $O(2'')$ [$N\cdots O(2'') = 2.76(2)$ Å] which together with C(2) and C(3) form a tetrahedral arrangement about the N atom. The Cl^- ions are hydrogen-bonded to two nitrogen atoms, i.e. Cl to N and N''', so that the hydrogen bonds link both cation and anion in a three-dimensional network (Fig. 2).

The molecular structure and atomic numbering scheme of **2** is shown in Fig. 1(b). The fractional atomic coordinates and equivalent isotropic temperature factors are listed in Table 3 and selected bond lengths and angles are given in Table 4. The tin(IV) atom is again five-coordinate, with the three phenyl groups occupying the equatorial positions of a trigonal bipyramid and with carboxyl oxygen atoms at the apices. The cation has

Table 4 Bond lengths (Å), angles (°) and torsion angles (°) for **2**[a]

Bond lengths			
Sn-O(1)	2.210(11)	Sn-O(3)	2.219(11)
Sn-C(8)	2.138(15)	Sn-C(14)	2.140(12)
Sn-C(20)	2.133(15)	S-C(1)	1.63(2)
N(1)-C(1)	1.15(2)	O(1)-C(2)	1.25(2)
O(2)-C(2)	1.25(2)	O(3)-C(5)	1.31(2)
O(4)-C(5)	1.23(2)	N(3)-C(6)	1.49(2)
N(3)-C(7)	1.50(3)	N(2)-C(4)	1.49(3)
N(2)-C(3)	1.46(2)	C(2)-C(3)	1.54(2)
C(5)-C(6)	1.47(2)	C(8)-C(13)	1.40(2)
C(8)-C(9)	1.41(2)	C(9)-C(10)	1.37(2)
C(10)-C(11)	1.36(3)	C(11)-C(12)	1.38(3)
C(12)-C(13)	1.39(3)	C(14)-C(19)	1.35(3)
C(14)-C(15)	1.40(3)	C(15)-C(16)	1.32(3)
C(16)-C(17)	1.40(3)	C(17)-C(18)	1.32(3)
C(18)-C(19)	1.45(3)	C(20)-C(21)	1.41(2)
C(20)-C(25)	1.44(2)	C(21)-C(22)	1.38(2)
C(22)-C(23)	1.38(3)	C(23)-C(24)	1.39(3)
C(24)-C(25)	1.39(2)	N(2)-O(4')	2.65(2)
N(2)-S'	3.42(2)	N(3)-O(2''')	2.74(2)
N(3)-N(1'')	2.94(2)		
Angles			
O(1)-Sn-O(3)	177.9(4)	C(8)-Sn-C(14)	118.6(7)
C(8)-Sn-C(20)	118.4(6)	C(14)-Sn-C(20)	123.0(7)
O(1)-Sn-C(8)	85.8(6)	O(1)-Sn-C(14)	90.4(7)
O(1)-Sn-C(20)	92.7(5)	O(3)-Sn-C(8)	93.1(6)
O(3)-Sn-C(14)	91.7(7)	O(3)-Sn-C(20)	86.2(5)
Sn-O(1)-C(2)	122(1)	Sn-O(3)-C(5)	121(1)
Sn-C(8)-C(9)	121(1)	Sn-C(8)-C(13)	121(1)
Sn-C(14)-C(15)	119(2)	Sn-C(14)-C(19)	123(2)
Sn-C(20)-C(21)	121(1)	Sn-C(20)-C(25)	120(1)
C(3)-N(2)-C(4)	113(2)	C(6)-N(3)-C(7)	112(1)
O((1)-C(2)-O(2)	130(2)	O(3)-C(5)-O(4)	125(2)
O(2)-C(2)-C(3)	117(2)	O(4)-C(5)-C(6)	123(2)
O(1)-C(2)-C(3)	113(2)	O(3)-C(5)-C(6)	113(2)
N(2)-C(3)-C(2)	115(1)	N(3)-C(6)-C(5)	112(1)
C(9)-C(8)-C(13)	118(2)	C(15)-C(14)-C(19)	119(1)
C(8)-C(9)-C(10)	121(2)	C(14)-C(15)-C(16)	123(2)
C(9)-C(10)-C(11)	119(2)	C(15)-C(16)-C(17)	119(2)
C(10)-C(11)-C(12)	122(2)	C(16)-C(17)-C(18)	120(2)
C(11)-C(12)-C(13)	118(2)	C(17)-C(18)-C(19)	121(2)
C(8)-C(13)-C(12)	121(2)	C(14)-C(19)-C(18)	118(2)
C(21)-C(20)-C(25)	118(2)	C(20)-C(21)-C(22)	120(2)
C(21)-C(22)-C(23)	121(2)	C(22)-C(23)-C(24)	121(2)
C(23)-C(24)-C(25)	120(2)	C(20)-C(25)-C(24)	120(2)
S-C(1)-N(1)	176(2)	C(3)-N(2)-O(4')	86(1)
C(3)-N(2)-S'	133(1)	C(4)-N(2)-O(4')	99(1)
C(4)-N(2)-S'	86(1)	O(4')-N(2)-S'	135(1)
C(6)-N(3)-O(2''')	84(1)	C(6)-N(3)-N(1'')	127(1)
C(7)-N(3)-O(2''')	99(1)	C(7)-N(3)-N(1'')	97(1)
O(2''')-N(3)-N(1'')	137(1)		
Torsion angles			
Sn-O(1)-C(2)-C(3)	−166(1)	Sn-O(3)-C(5)-C(6)	−164(1)
O(1)-C(2)-C(3)-N(2)	169(1)	O(3)-C(5)-C(6)-N(3)	174(1)
C(2)-C(3)-N(2)-C(4)	−73(2)	C(5)-C(6)-N(3)-C(7)	−74(2)

[a] Symmetry: ', $1/2-x, 1/2+y, z$; '', $+1/2-x, 1/2+y, z$; ''', $-1/2-x, -1/2+y, z$.

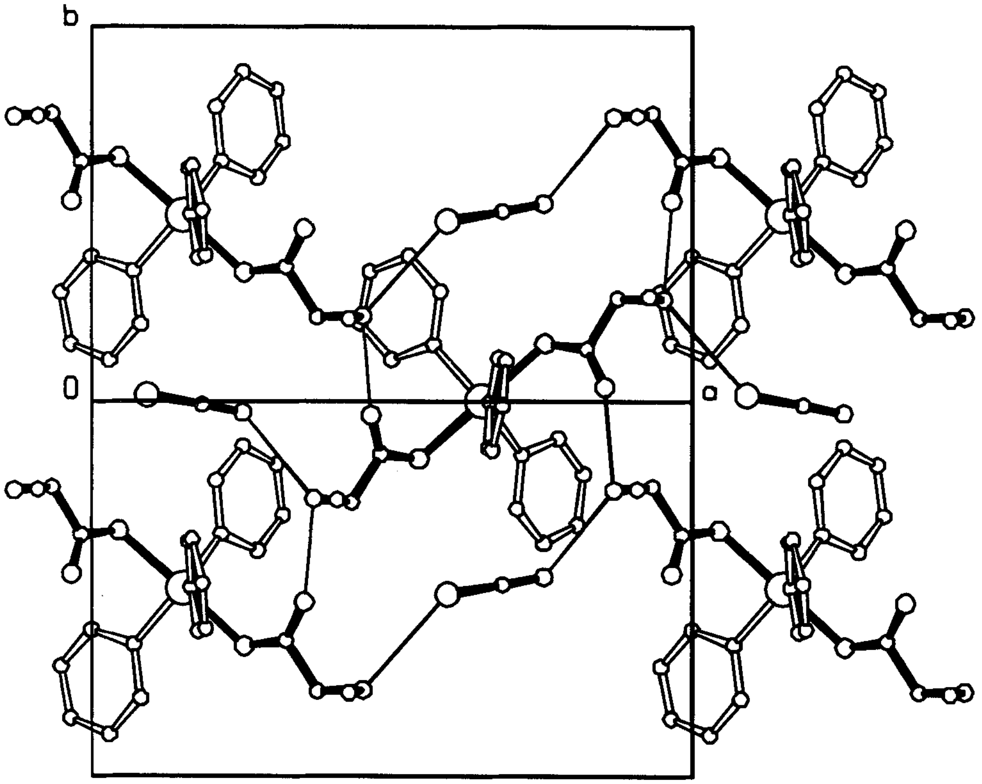

Figure 3 Hydrogen bonding in $C_{25}H_{29}N_3O_4SSn$.

an approximate two-fold symmetry with Sn, C(14) and C(17) close to the pseudo-symmetry axis. The nitrogen atoms of the ligands are hydrogen-bonded to carboxyl oxygen atoms of the neighbouring molecules [N(2)···O(4) = 2.65(2) Å and N(3)···O(2) = 2.74(2) Å] and there are also weak hydrogen bonds to the thiocyanate ion [N(2)···S = 3.42(2) Å and N(3)···N(1) = 2.94(2) Å] forming an infinite sheet of cations and anions parallel to the (001) plane (Fig. 3).

These structures are unusual in that the organotin moiety retains a positive charge, and not a negative charge as is usually the case.[4] The only other example is bis(triphenylarsine oxide)(*p*-chlorophenyl)diphenyltin(IV) tetraphenylborate.[16] Whereas the sarcosine ligands are approximately planar in **1** [torsion angle C–C–N–C = 168(2)°] this is not the case for **2** [C–C–N–C = −73(2)° and −74(2)°]. The planar conformation is the most common [values from the Cambridge Structural Database[17]] but the bent conformation has been observed in a telluric acid adduct.[18]

The two triorganotin complexes were screened *in vitro* against *Ceratocystis ulmi*, the causative agent of Dutch elm disease (DED). The inhibitory concentration (the concentration at which 50% of the fungus is inhibited) for complexes **1** and **2** is 2.51 and 2.37 $\mathrm{mg\,l^{-1}}$, respectively. The values indicate that these compounds are not as effective in the inhibition of *C. ulmi* as the parent compound, triphenyltin chloride (1.1 $\mathrm{mg\,l^{-1}}$). It has been postulated that the species responsible for the inhibition of *C. ulmi* is the Ph_3Sn^+ cation or its hydrated form,[19,20] and the inhibition has been attributed to the interaction between the cation and the cell wall of the fungus.[20] Thus, the reduced activity of the complexes is most likely due to the inability of the $Ph_3SnL_2^+$ species to dissociate as effectively as triphenyltin chloride. The size of the $Ph_3SnL_2^+$ species may also play a role in its reduced activity as the substantially large dimensions of this species may prevent it from interacting with the fungal cell membrane. However, a more systematic study must be performed before any definitive conclusions can be reached pertaining to this class of compounds as possible DED fungicides.

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