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Synthesis, Spectroscopic Characterization and Fungicidal Activity of Triphenyltin Derivatives of *N,N*-Dimethylglycine: Crystal Structure of [Dimethyl(carboxylatomethyl)ammonium]-chlorotriphenylstannate

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Two new triorganotin complexes formulated as $Me_2HNCH_2COO \cdot Ph_3SnX$, X = Cl, NCS were prepared and spectroscopically characterized, and their fungicidal properties against *Ceratocystis ulmi* were determined. An X-ray structure for [dimethyl(carboxylatomethyl)ammonium] chlorotriphenylstannate is also reported.

Keywords: Organotin, fungicidal, crystal structure

INTRODUCTION

Triorganotin and diorganotin halides and pseudohalides have been reported to form molecular adducts with zwitterions such as *N*-alkyl and *N*-arylsalicylidenes,[1-5] picolinic acid[6, 7] and quinaldic acid.[8] With Schiff bases, the 1:1 and 1:2 adducts normally have trigonal and octahedral geometries, respectively, for the tin atoms, although some unusual structures have been reported.[9, 10] With carboxylic acids, hydrated complexes are generally obtained. The acid in its zwitterion form binds to the triphenyltin moiety and generates a trigonal bipyramidal geometry around the tin atom. Hydrogen bonding involving uncoordinate water molecules serves to bind the five coordinate units together in the form of a dimer. These compounds, besides displaying a most unusual structure,[6-10] have also shown promising fungicidal activity.[11] We are therefore prompted to attempt the synthesis of analogous complexes between triphenyltin chloride or isothiocyanate and other protonated α-amino carboxylic acids.

We describe here the synthesis, spectroscopic characterization and fungicidal activity of triphenyltin derivatives with *N,N*-dimethylglycine along with the crystal structure of [dimethyl(carboxylatomethyl)ammonium]chlorotriphenylstannate.

EXPERIMENTAL

The starting materials were of reagent or analytical grade and used without further purification. *N,N*-Dimethylglycine and triphenyltin chloride were from Aldrich Chemicals, USA. Triphenyltin isothiocyanate (m.p. 168–170 °C) was prepared by the literature method[12] and recrystallized from benzene before use. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer Model 1725 FT–IR spectrometer. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$–DMSO-d_6 on a Bruker AC-P300 spectrometer. The ^{119}Sn Mössbauer spectral data were obtained with the apparatus and data reduction techniques described in a preceding paper.[13]

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Atomic coordinates for this structure 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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Preparation of 1 : 1 adducts $[(CH_3)_2HNCH_2COO\cdot Ph_3SnX]$ with X = Cl, NCS

To 5.1 g of triphenyltin chloride in 40 ml of 95% ethanol was added to 1.7 g *N*,*N*-dimethylglycine dissolved in 20 ml of ethanol. The mixture was heated to boiling, which was stopped when precipitates started to form. Recrystallization of the solid (5.4 g) in ethanol at room temperature overnight afforded colourless crystals (3.1 g), m.p. 181–182 °C. Elemental analysis (NUS, Singapore)—Calculated (found) for $C_{22}H_{24}NO_2SnCl$ (%) C, 54.08 (53.98); H, 4.96 (5.03); N, 2.87 (2.70).

The triphenyltin isothiocyanate *N*,*N*-dimethylglycine adduct (m.p. 186–188 °C) was similarly prepared in 82% yield and recrystallized in 95% ethanol. Elemental analysis—calculated (found) for $C_{23}H_{24}N_2O_2SSn$ (%): C 54.03 (53.87); H, 4.74 (4.77); N, 5.48 (5.24).

Fungicidal activity

The compounds were screened against *Ceratocystis ulmi* using the method previously described.[14]

X-ray crystallography

Crystal data: $C_{22}H_{24}ClNO_2Sn$, M_r 488.6, orthorhombic, space group *Pbca*, $a = 15.609(3)$ Å, $b = 15.811(3)$ Å, $c = 17.561(4)$ Å, $V = 4334(2)$ Å^3, $Z = 8$, $D_{cal} = 1.497$ Mg/m^3 and $F(000) = 1968$.

A selected crystal of dimensions 0.08 mm × 0.14 mm × 0.16 mm was used. Diffraction data ($2\theta_{max} = 50°$, 2852 unique reflections) collected on a Siemens P4 diffractometer using the ω-scan mode (2.00–29.3° min^{-1}) were processed with a profile-fitting procedure[15] and corrected for adsorption using ψ-scan data ($\mu r = 0.08$, transmission factors 0.841–0.905).[16] A total of 1606 independent reflections with $|F| > 4\sigma|F|$ were considered as observed data and used in the structure analysis. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically (C–H = 0.96 Å) and included in structure-factor calculations with assigned isotropic thermal parameters. Final R_F and R_{wF2} values are 0.0703 and 0.0737 for 254 variables with the weight scheme $w = [\sigma^2(|F_0|) + 0.0012|F_0|^2]^{-1}$. The residual extrema in the final difference map are in the range of +0.88 to -1.08 e Å^{-3}. Computations were performed using the SHELXTL-PC programme package.[17] Analytic expressions of neutral atomic scattering factors were used, and anomalous-dispersion corrections were incorporated.[18]

Copies of lists of bond lengths, bond angles and torsion angles, anisotropic thermal parameters, calculated hydrogen coordinates and observed and calculated structure factors can be obtained from the authors.

RESULTS AND DISCUSSION

Picolinic acid and quinaldic acid, by virtue of their capability to adopt zwitterionic configurations, are reported to form hydrated adducts with Ph_3SnCl and Ph_3SnNCS in which the carboxylate

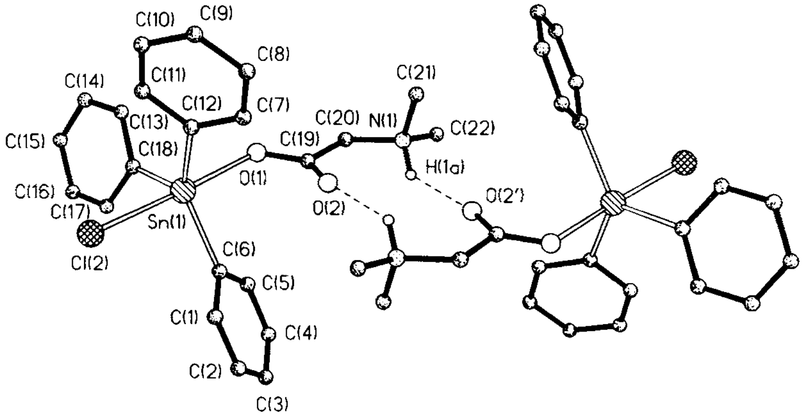

Figure 1 Molecular structure and crystallographic numbering scheme employed for $[Me_2HNCH_2COO\cdot Ph_3SnCl]$. The broken lines represent hydrogen bonds that link a pair of molecules to form a centrosymmetric dimer.

oxygen coordinates to the tin atom.[6–8] It was anticipated that the ligand *N,N*-dimethylglycine would behave likewise. However, the present X-ray structural investigation of $Me_2HNCH_2COO \cdot Ph_3SnCl$ confirmed the 1:1 adduct formulation with the organic ligand in the zwitterionic form.

The molecular structure is illustrated in Fig. 1, which shows the numbering scheme employed. The fractional atomic coordinates with equivalent isotropic thermal parameters are listed in Table 1 and the bond lengths and bond angles are given in Table 2.

As expected, the tin(IV) atom is found to be five-coordinate, with three phenyl groups occupying the equatorial positions of a trigonal bipyramid and the apical sites taken by the chlorine atom and a carboxyl oxygen from *N,N*-dimethylglycine. The pyramidal arrangement of N–C bonds at N(1) and the location of the H(1a) atom from a difference map both substantiate the fact that *N,N*-dimethylglycine is coordinated in the form of a zwitterion. The measured intermolecular H(1a)· · ·O(2′) [where ′ denotes the symmetry-related position −x, −y, −z] distance and N(1)—H(1a)· · ·O(2′) angle are 1.97(2) Å and 139(2)°, respectively. Accordingly a pair of $Me_2HNCH_2COO \cdot Ph_3SnCl$ molecules are consolidated by two N—H· · ·O hydrogen bonds to form a centrosymmetric dimer as illustrated in Fig. 1.

Table 1 Atomic coordinates (×10^5 for Sn; ×10^4 for others) and equivalent isotropic temperature factors[a] ($Å^2 \times 10^4$ for Sn; $Å^2 \times 10^3$ for others)

Atom	*x*	*y*	*z*	U_{eq}[a]
Sn(1)	25584(6)	19027(7)	6081(6)	494(4)
Cl(2)	3476(2)	3095(3)	−14(2)	60(1)
O(1)	1796(5)	869(6)	1212(5)	47(4)
O(2)	769(6)	722(6)	330(6)	54(4)
N(1)	−15(6)	−562(7)	1088(7)	45(4)
C(1)	2725(8)	1445(10)	−1128(8)	48(6)
C(2)	2845(9)	915(11)	−1725(10)	58(6)
C(3)	2966(10)	58(12)	−1632(12)	72(8)
C(4)	2979(9)	−277(12)	−902(11)	62(7)
C(5)	2830(9)	260(11)	−301(10)	55(6)
C(6)	2709(8)	1133(9)	−371(8)	43(6)
C(7)	739(9)	2738(9)	664(9)	54(6)
C(8)	147(11)	3363(11)	853(10)	65(7)
C(9)	403(10)	4078(11)	1253(9)	60(7)
C(10)	1241(10)	4170(10)	1464(9)	60(7)
C(11)	1822(9)	3531(10)	1275(9)	48(6)
C(12)	1578(9)	2823(9)	860(8)	47(6)
C(13)	3393(10)	1974(10)	2216(10)	66(7)
C(14)	4064(11)	1973(10)	2725(9)	67(7)
C(15)	4866(10)	1727(10)	2490(12)	65(7)
C(16)	4997(10)	1448(10)	1764(10)	59(7)
C(17)	4358(9)	1475(9)	1244(9)	53(6)
C(18)	3526(9)	1729(8)	1462(8)	42(5)
C(19)	1152(9)	508(10)	910(10)	47(6)
C(20)	830(8)	−255(10)	1372(9)	53(6)
C(21)	−717(8)	27(9)	1322(9)	58(6)
C(22)	−204(9)	−1434(9)	1397(10)	66(7)

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

Table 2 Selected bond lengths (Å) and bond angles (deg) of $Me_2HNCH_2COO \cdot Ph_3SnCl$

Sn(1)–Cl(2)	2.607(4)	Sn(1)–O(1)	2.285(9)
Sn(1)–C(6)	2.12(2)	Sn(1)–C(12)	2.157(1)
Sn(1)–C(18)	2.15(1)	O(1)–C(19)	1.27(2)
O(2)–C(19)	1.23(2)	N(1)–C(20)	1.50(2)
N(1)–C(21)	1.50(2)	N(1)–C(22)	1.51(2)
N(1)–H1A	0.960	C(19)–C(20)	1.54(2)
Cl(2)–Sn(1)–O(1)	176.9(2)	Cl(2)–Sn(1)–C(6)	90.8(4)
O(1)–Sn(1)–C(6)	91.3(4)	Cl(2)–Sn(1)–C(12)	89.3(4)
O(1)–Sn(1)–C(12)	91.0(4)	C(6)–Sn(1)–C(12)	129.2(5)
Cl(2)–Sn(1)–C(18)	89.9(4)	O(1)–Sn(1)–C(18)	87.2(4)
C(6)–Sn(1)–C(18)	114.6(5)	C(12)–Sn(1)–C(18)	116.2(5)
Sn(1)–O(1)–C(19)	122.6(9)	C(20)–N(1)–C(21)	110.7(10)
C(20)–N(1)–C(22)	110.4(11)	C(21)–N(1)–C(22)	109.1(10)
Sn(1)–C(6)–C(1)	124.2(11)	Sn(1)–C(6)–C(5)	120.7(11)
Sn(1)–C(12)–C(7)	124.3(11)	Sn(1)–C(12)–C(11)	117.2(10)
Sn(1)–C(18)–C(13)	121.5(10)	Sn(1)–C(18)–C(17)	119.6(10)
O(1)–C(19)–O(2)	127.4(14)	O(1)–C(19)–C(20)	112.9(13)
O(2)–C(19)–C(20)	119.6(13)	N(1)–C(20)–C(19)	111.5(11)

The similarities of the spectroscopic data indicate that a five-coordinate structure should be proposed for the 1:1 $Ph_3SnCl:Me_2NCH_2COOH$ (**1**) and $Ph_3SnNCS:Me_2NCH_2COOH$ (**2**) complexes.

The recorded Mössbauer isomer shift values of 1.31 ± 0.02 and 1.23 ± 0.02 for **1** and **2**, respectively are in agreement with the known values for Schiff base complexes with triorganotin chloride and isothiocyanate.[4,5] The ρ values of 2.30 for **1** and 2.61 for **2** are greater than 2.1, indicating that the coordination of the tin atom is greater than four.[19,20] This is further substantiated by the observation that the IR carbonyl stretching vibrations of Me_2NCH_2COOH at $1734\ cm^{-1}$ was shifted to lower frequency by about $100\ cm^{-1}$ at $1636\ cm^{-1}$ for both the complexes, **1** and **2**. The strong absorption at $2055\ cm^{-1}$ (absorption for Ph_3NCS is at $2099\ cm^{-1}$) for the isothiocyanate adduct suggests that the thiocyanate groups are *N*-bonded.[21] The proton and ^{13}C NMR spectra (Table 3) for **1** and **2** are very similar. As com-

Table 3 NMR data for **1**, **2** and *N*,*N*-dimethylglycine

	δ (ppm)							
	^{1}H NMR				^{13}C NMR			
Compound	Me_2N	CH_2	OH/NH	Ar	Me_2N	CH_2	C=O	Ar
Me_2NCH_2COOH	2.76	4.88	3.91		41.32	54.60	165.26	
1	2.59	3.58	2.49	7.3–7.9	42.85	59.18	167.28	127.24: 127.71; 128.22 136.15; 136.46; 145.27
2	2.61	3.67	2.61	7.3–7.8	42.91	58.78	167.65	127.51; 127.98; 128.61 135.70; 136.00; 136.31 143.34

pared with the free ligand, a shift in the methylene proton absorption (*ca* 1.2 ppm) and the methylene ^{13}C absorption (*ca* 4.2 ppm) was observed. The marked similarities in the spectra of the two complexes, which have the same stoichiometry and are prepared in like manner, provide strong evidence that they are isostructural to each other.

The two triorganotin complexes were screened *in vitro* against *Ceratocystis ulmi*. The minimal inhibitory concentration for compounds **1** and **2** are 0.2 ppm and 0.4 ppm, respectively. These values indicate that they are slightly better inhibitors of the fungus than the parent compound, triphenyltin chloride (1.1 ppm). However, a more systematic study must be performed before any definitive conclusions can be reached pertaining to this class of compounds as possible inhibitors of *Ceratocystis ulmi*.

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