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Synthesis, structural and biocidal activity studies of triorganotin(IV) compounds of some *N*-protected amino-acids

M Adediran Mesubi, U Basil Eke and T Tunde Bamgboye
Department of Chemistry, University of Ilorin, PMB 1515, Ilorin, Nigeria

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Seven new triorganotin(IV) complexes of the type R_3SnL (L = *N*-phthaloyl derivatives of glycine, DL-alanine or *N*-acetyl- and *N*-benzoyl-glycine and -cysteine; R = n-C_4H_9 or C_6H_5) have been prepared by reacting the sodium salt of the ligand and the triorganotin(IV) chloride in 1:1 molar ratio in methanol. The complexes have been characterized by elemental analysis, molecular mass determination, IR and ^{1}H NMR spectroscopy. The complexes are monomeric in molten camphor and are moderately soluble in the common organic solvents. The spectral data support *cis* five-coordinate complexes with an unsymmetrical bidentate coordination of the carboxylate group to tin.

The complexes exhibit some insecticidal effect on Bean Weevils (*Sitophilus granaria*) even at low concentration and they also show fungicidal activity on *Aspergillus niger* and *Helminthosporium taulosum*. Some of the complexes are found to be more effective than tri-n-butyltin and triphenyltin chlorides.

Keywords: Synthesis, structure, biocides, *N*-protected amino-acids, triorganotin(IV) compounds, insecticides, fungicides

INTRODUCTION

While studies on several organotin(IV) compounds of amino-acids and their derivatives[1–6] have been published, only relatively few organotin(IV) complexes of *N*-protected amino-acids have been reported.[7–9] In particular, very few triorganotin(IV) complexes of these *N*-protected amino-acids are known. Some of them have been found to be biocides.[10] It seemed desirable to extend this study by synthesizing other new complexes in this class. Therefore, we report here the synthesis, characterization and the biocidal properties of the following complexes: R_3SnL [L = *N*-phthaloylglycinate (PhthGlyO), *N*-phthaloyl-DL-alaninate (phthAlaO), *N*-acetylglycinate (AcGlyO), *N*-acetyl-L-cysteinate (AcCysO), *N*-benzoylglycinate (BzGlyO) or *N*-benzoyl-L-cysteinate (BzCysO); R = C_6H_5 or n-C_4H_9.]

EXPERIMENTAL

Triphenyltin and tri-n-butyltin chlorides were obtained from Alfa Products, USA, and were used without further purification. The *N*-protected amino-acids were prepared by the published procedures.[11] Their sodium salts were obtained by neutralization with sodium carbonate.

Preparation of the complexes

All the complexes were prepared by the same general procedure, as described below for triphenyltin(IV) phthaloylglycinate, Ph_3Sn(PhthGlyO),

Ph_3SnCl (1.0 g, 2.59 mmol) dissolved in 30 cm^3 of methanol was mixed with 70 cm^3 of a methanol solution of sodium *N*-phthaloyl-glycinate (0.71 g, 2.59 mmol). The mixture was refluxed for 3 h and later filtered to remove the precipitated sodium chloride. The filtrate was evaporated to dryness under reduced pressure using a rotary evaporator. The resulting solid was recrystallized from hot benzene, dried in a vacuum oven at 40°C and stored in a desiccator over calcium chloride. Physical data are reported in Tables 1–3.

Physical measurements

Melting points were determined in open capillaries using an electrothermal melting point

Table 1 Physical and analytical data for the complexes

Complex	Yield (%)	M.p. (°C)	Analysis: Found (Calcd) (%) C	H	N	Molar mass: Found (Calcd) ($g\,mol^{-1}$)
1 $Ph_3Sn(PhthGlyO).3H_2O$	77.84	>300	55.20	3.59	2.30	533
($C_{28}H_{21}NO_4Sn.3H_2O$)			(55.29)	(4.48)	(2.30)	(608)
2 $Bu_3Sn(PhthGlyO)$	34.62	85	53.49	7.31	2.41	401
$C_{22}H_{33}NO_4Sn$)			(53.46)	(6.74)	(2.83)	(495)
3 $Ph_3Sn(PhthAlaO).H_2O$	57.56	179–180	60.34	3.98	1.55	548
($C_{29}H_{23}NO_4Sn.O.0.5H_2O$)			(60.34)	(4.20)	(2.43)	(578)
4 $Ph_3Sn(AcGlyO)$	60.74	129–131	56.45	4.39	2.49	442
($C_{22}H_{21}NO_3Sn$)			(56.70)	(4.54)	(3.01)	(467)
5 $Ph_3Sn(AcCysO).4.5H_2O$	56.67	138–140	46.87	4.00	2.54	554
($C_{23}H_{23}NSO_3Sn.4.5H_2O$)			(47.56)	(5.40)	(2.36)	(593)
6 $Ph_3Sn(BzGlyO).H_2O$	61.97	98–100	59.92	4.34	1.74	562
($C_{27}H_{23}NO_3Sn.H_2O$)			(59.33)	(4.61)	(2.56)	(546)
7 $Ph_3Sn(BzCysO).1.5H_2O$	60.90	54–56	55.89	4.28	1.84	682
($C_{28}H_{25}NSO_3Sn.1.5H_2O$)			(55.95)	(4.69)	(2.33)	(601)

Table 2 Infrared spectral data (KBr, cm^{-1}) for the complexes

Complex[a]	ν_s(C=O)	ν_a(C=O)	ν_a(COO)	ν_s(COO)	$\Delta\nu$	ν(Sn—O)	ν_a(Sn—C)	ν_s(Sn—C)	ν(NH)	ν(CN)
1 $Ph_3Sn(PhthGlyO)$	1780m	1722vs	1590s	1378s	212	455w	266w	230w,sh	—	—
2 $Bu_3Sn(PhthGlyO)$	1776m	1724vs	1582vs	1376s	206	414vw	258vw	230vw	—	—
3 $Ph_3Sn(PhthAlaO)$	1778s	1713s	1598s,sh	1392vs	206	448s	263s	228m,sh	—	—
	ν(C=O)amido									
4 $Ph_3Sn(AcGlyO)$	1638s,sh	—	1608s	1388s	220	454s	263s	229s,sh	3278m,br	1563s
5 $Ph_3Sn(AcCysO)$	1725s	—	1623m	1383s	240	458w	260m	226m,sh	3368vs,br	1523s
6 $Ph_3Sn(BzGlyO)$	1642s,sh	—	1626s,br	1393m	233	448m	266s	230s,sh	3408m,br	1563s
7 $Ph_3Sn(BzCysO)$	1662s,sh	—	1623s,br	1393s	230	448s	258s	223s,sh	3388s,br	1523m

[a]Water content not shown.

apparatus and are uncorrected. Microanalyses of the complexes were performed at the microanalytical laboratory of the Department of Chemistry, University College London. Molecular masses of the complexes were determined in molten camphor by the Rast method[12] (Table 1).

The infrared spectra were recorded between 4000 and 200 cm^{-1} on a Perkin–Elmer 283B spectrophotometer in potassium bromide pellets. The spectra were calibrated with polystyrene. Improved resolution of the bands was obtained between 4000 and 400 cm^{-1} using a Fourier Transform 1710 IR spectrophotometer (Table 2).

The ^1H NMR spectra were run in saturated $CDCl_3$ solution with TMS as internal standard on a JEOL GX270 FT spectrometer (Table 3).

All the IR and NMR spectra were run at the Department of Chemistry, University College, Dublin (UCD), Republic of Ireland.

Biocidal tests

(a) Insecticidal

The complexes were prepared for application on Bean Weevils (*Sitophilus granaria*) using two methods: (i) wetting filter paper; and (ii) spotting,[13] as described below for a 5×10^{-3} mol dm^{-3} suspension of $Ph_3Sn(PhthGlyO)$.

$Ph_3Sn(PhthGlyO)$ (0.6928 g, 1.74 mmol) was

Table 3 ^{1}H NMR data ($CDCl_3$) for the complexes

Complex[a]	Chemical shifts, δ(ppm)				Coupling constants. J(119Sn—C—^{1}H) (Hz)
	Ligand aromatic proton	Sn—R[b]	—CONH	Other protons	
1 Ph_3Sn(PhthGlyO)	7.80–7.70 td	7.66m, 7.27m	—	4.5s (—NCH_2)	—
2 Bu_3Sn(PhthGlyO)	7.80–7.70 td	1.67m, 1.28m	—	4.4s (—NCH_2) 1.75d (—CH_3)	76.96
3 Ph_3Sn(PhthAlaO)	7.85–7.69m	7.68, 7.24m	—	5.03q (—CH) 1.90s (—$OCCH_3$)	—
4 Ph_3Sn(AcGlyO)	—	7.80–7.24m	6.10br	4.05d (—$OOCCH_2$) 1.25s (—$OCCH_3$)	—
5 Ph_3Sn(AcCysO)	—	7.66–7.25m	—	2.10br (CH_2S) 3.20dd (—OOCCH)	—
7 Ph_3Sn(BzCysO)	7.80–7.69m	7.58–7.19m	6.35d	2.97m (—CH_2S) 4.37q (—OOCCH)	—

[a]Water content not shown. [b]R = C_4H_9 or C_6H_5; s = singlet, d = doublet, dd = doublet doublet, td = triplet doublet, q = quartet, m = multiplet, br = broad.

placed in a 250 cm^3 volumetric flask and a 30% $MeOH/H_2O$ solution was added to the mark. This stock solution was appropriately diluted to obtain 2.5×10^{-3} and 1.25×10^{-3} mol dm^{-3} suspensions.

(i) The Bean Weevils were introduced into a petri-dish containing a filter paper previously wetted thoroughly with a suspension of the organotin(IV) complex. The petri-dishes were monitored for the time lapse before all the insects died. A control experiment was similarly set up by wetting a dry filter paper with the pure 30% $MeOH/H_2O$ solution.

(ii) Each of a known number of the insects introduced into a petri-dish was carefully spotted with the suspension of the complexes in the $MeOH/H_2O$ solution. A control experiment was set up by spotting an equal number of the weevils with the pure $MeOH/H_2O$ solution. The petri-dishes were monitored for the time lapse before all the insects under observation died.

(b) Fungicidal

The complexes were tested for antifungal activity on two fungi namely *Aspergillus niger* and *Helminthosporium taulosum* using the poisoned food technique. The complexes were prepared in concentrations of 500 ppm and 100 ppm as follows.

A sample of 0.125 g (0.212 mmol) of Ph_3Sn(PhthGlyO) was placed in a 250 cm^3 volumetric flask. A 10% $MeOH/H_2O$ solution was added to the flask and made up to the mark to give a 500 ppm suspension. This stock solution was appropriately diluted to obtain the 100 ppm concentration.

The organisms (*Aspergillus niger* and *Helminthosporium taulosum*) were cultured on potato dextrose agar (PDA) and incubated at 30°C for seven days.[14] The medium was prepared by adding 1.0 cm^3 of the suspension of the compound to 9.0 cm^3 of the PDA in a sterile petri-dish. The plates were inoculated with a 5 mm-diameter agar disc of a five-day-old culture in the centre of the petri-dish. A control was set up by suspending 1.0 cm^3 of the $MeOH/H_2O$ solution in 9.0 cm^3 of PDA and inoculated as described above. The inoculated plates were then incubated at 30°C and the radial growth measured after seven days. The number of spores in each culture was also counted using a haemocytometer.

RESULTS AND DISCUSSION

General properties

All the complexes isolated are solids, white in colour except for Ph_3Sn(AcCysO) and Ph_3Sn(BzCysO) which are off-white and light yellow, respectively. They are air- and moisture-stable. Their melting points and microanalytical data are shown in Table 1. The complexes are

almost completely soluble in methanol and ethanol but less soluble in the other common organic solvents. The molar masses of the complexes determined in molten camphor are given in Table 1. The data compare favourably, within the limits of experimental error, with those calculated from the formulated compositions of the complexes, thus suggesting that the complexes are monomeric in molten camphor.

Infrared spectra

For structural elucidation purposes the most informative spectral data are given in Table 2. Assignments of bands have been made by comparing observed frequencies with those of known organotin carboxylates and complexes.[7–9,15–19] The absence of a strong broad band due to the O—H stretching mode of the carboxylic group in the 3000–2500 cm^{-1} region indicates the deprotonation of the COOH group. The broad bands observed in the range 3479–3408 cm^{-1} in the spectra of complexes **1**, **3** and **5–7** are clear evidence of the presence of water molecules in the complexes.

The very strong–medium bands observed in the 1782–1773 cm^{-1} and 1710 cm^{-1} regions in complexes **1–3** are due to the symmetric and asymmetric imido C=O stretching modes.[9,20] A comparison of these frequencies with those of ν_s(C=O) = 1780–1770 cm^{-1} and ν_s(C=O) = 1720 cm^{-1} for diorganotin(IV) complexes of *N*-phthaloyl-L-leucine, -DL-alanine and -L-phenylalanine,[9,20] ν_s(C=O) = 1775 cm^{-1} and ν_a(C=O) = 1740 cm^{-1} for the free ligand *N*-phthaloyl-DL-alanine and ν_s(C=O) = 1775 cm^{-1} and ν_a(C=O) = 1742 cm^{-1} for phthalimide,[21] clearly shows that the imido C=O groups are not involved in complex formation.

As Kumar Das[22] has pointed out the metal coordination compounds of *N*-acetyl- and *N*-benzoyl-amino-acids, which are potentially polydentate carboxylic acids, can give rise to several interesting structural possibilities. Coordination could occur through the carboxylate oxygen atoms, the amido nitrogen atom and one of the carboxylate oxygen atoms, or the ketonic oxygen atom and one of the carboxylate oxygen atoms. The type of coordination which actually occurs can readily be detected from the infrared spectra. According to the literature the N—H stretching frequency is expected to be the same or slightly higher than that of the free ligand if the amido nitrogen is uncoordinated. The C=O stretching frequency generally shifts to higher values with respect to the free acid if the ketonic CO group is uncoordinated but a lowering of the ν(C=O) frequency would be expected upon coordination.

The N—H stretching frequencies of complexes **4–7** in Table 2 are in the range 3408–3278 cm^{-1}, which compare well with the ν(N—H) frequencies of the free acids (3480–3278 cm^{-1}).[19] The observed broadening of the bands probably implies that the N—H group is hydrogen-bonded to the ketonic oxygen atom. This would lead to some lowering of the N—H stretching frequency. It is inferred from these data that the amido nitrogen is not coordinated to tin.

The ketonic CO stretching frequencies (1725–1638 cm^{-1}) observed for this series of triorganotin complexes are relatively higher than those expected for the free ligand.[8,22] This implies that the ketonic oxygen atom is uncoordinated to tin.

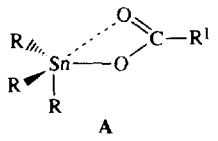
The strong–medium intensity ν_a(COO) acid and ν_s(COO) acid bands in the spectra of all the complexes are observed in the range 1626–1582 cm^{-1} and 1393–1376 cm^{-1} respectively. The $\Delta\nu$ values [$\Delta\nu = \nu_a(COO) - \nu_s(COO)$] of 197–240 cm^{-1} are indicative of an unsymmetrical bidentate coordination of the carboxylate group of the amino-acid to tin.[8,9,19]

The number of Sn—C stretching bands can be used to deduce the geometry of the $-SnR_3$ moiety.[16,17,19] The presence of both ν_a(Sn—C) and ν_s(Sn—C) bands in the spectra of all the complexes implies a non-planar $-SnR_3$ configuration. No bands assignable to Sn—N and Sn—O—Sn bonds are found, thus implying no coordination of nitrogen atom to tin and the absence of polymeric structure with a bridging carboxylate group.

^{1}H NMR data

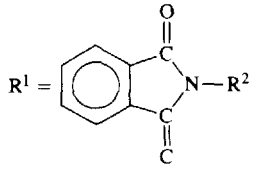
The ^{1}H NMR data are reported in Table 3. We could not run the spectrum of Ph_3Sn(BzGlyO) due to the instability of the complex in solution. The absence of any signal between 9.1 and 8.5 ppm in the spectra of all the complexes provides additional evidence for the absence of the carboxylic proton in the complexes. For each complex the integrated area is equivalent to the number of protons calculated on the basis of the proposed structure.

A set of multiplets due to the ligand aromatic or the phenyl ring protons of the $-SnPh_3$ moiety is observed in the range 7.85–7.19 ppm for all the complexes. Another set of multiplets due to n-C_4H_9 protons is observed between 1.57 and 0.89 ppm for the tributyltin derivatives. The magnitude (76.96 Hz) of the coupling constants $J(^{119}Sn—C—^1H)$ for the tributyl complex in Table 3 suggests a coordination number greater than four for tin.



A

R = *n*-C_4H_9 or C_6H_5



(R^2 = CH_2 or $CH(CH_3)$), $CH_3CONHCH_2$, $C_6H_5CONHCH_2$, $CH_3CONHCH(CH_2SH)$ or $C_6H_5CONHCH(CH_2SH)$.

Proposed structure

On the basis of the available infrared and ^1H NMR data a *cis* five-coordinate structure (**A**) is proposed for the complexes.

A similar geometry with X-ray structural corroboration has been encountered for other triphenyltin(IV) complexes with chelating ligands as well as for some triphenyltin(IV) ester derivatives.[22]

Biocidal properties of the complexes

Fungicidal activity

The organotin(IV) compounds were tested for fungicidal activity on two organisms (*Aspergillus niger* and *Helminthosporium taulosum*) using the poisoned-food technique in PDA media. Radial growth and sporulation after incubating for seven days were used as an indication of the fungicidal

Table 4 Radial growth and sporulation of *Aspergillus niger* and *Helminthosporium taulosum* in suspensions of the complexes after seven days

		Aspergillus niger		*Helminthosporium taulosum*	
Complex[a]	Concn (ppm)	Radial growth (mm)	Sporulation ($\times 10^6$)	Radial growth (mm)	Sporulation ($\times 10^6$)
Control	10% MeOH/H_2O	18.0	480.0	10.0	160.0
Ph_3SnCl	100	7.0	280.0	10.0	80.0
	500	5.0	80.0	5.0	20.0
Bu_3SnCl	100	4.0	200.0	6.0	0.008
	500	2.0	80.0	2.0	0
1 Ph_3Sn(PhthGlyO)	100	11.0	80.0	3.0	40.0
	500	9.0	60.0	1.0	10.0
2 Bu_3Sn(PhthGlyO)	100	5.0	40.0	9.0	20.0
	500	3.0	20.0	1.0	12.0
3 Ph_3Sn(PhthAlaO)	100	7.0	80.0	8.0	250.0
	500	5.0	80.0	7.0	100.0
4 Ph_3Sn(AcGlyO)	100	5.0	40.0	8.0	25.0
	500	2.0	12.0	7.0	8.0
5 Ph_3Sn(AcCysO)	100	10.0	80.0	4.0	40.0
	500	8.0	20.0	3.0	40.0
6 Ph_3Sn(BzGlyO)	100	7.0	40.0	7.0	12.0
	500	5.0	20.0	5.0	8.0
7 Ph_3Sn(BzCysO)	100	15.0	150.0	10.0	200.0
	500	7.0	80.0	3.0	60.0

[a]Water content not shown.

activity of the compounds. The results are given in Table 4.

Ph_3Sn(PhthAlaO) and Ph_3Sn(BzCysO) exhibit poor antifungal activity compared with tri-n-butyltin chloride, Bu_3SnCl. On the other hand, Ph_3Sn(PhthGlyO) and Ph_3Sn(AcCysO) are poor radial growth inhibitors for *Aspergillus niger* but good inhibitors for its sporulation. They do however effectively inhibit both the radial growth and sporulation of *Helminthosporium taulosum*. The data in the Table clearly showed that (i) the antifungal activity generally increases with increase in concentration of the compounds and (ii) Bu_3Sn(PhthGlyO) is the most effective followed by Bu_3SnCl, Ph_3Sn(AcGlyO), Ph_3Sn(AcCysO), Ph_3Sn(BzGlyO) and Ph_3SnCl. Thus, the complexation of *N*-protected amino-acids has enhanced the antifungal activity of Ph_3SnCl.

Insecticidal activity

Mortality rates of the insects were used as a measure of the insecticidal ability of the complexes. The results of the insecticidal activity tests for the complexes of Bean Weevils are shown in Table 5. The data show that: (i) the wet filter paper method is more effective (killing time: 5–18 min) than the spotting method (45–60 min)—this may be due to the continuous contact between the insects and fresh suspensions of the complexes as the insects moved to fresher areas of the wetted filter paper; (ii) the insecticidal effect increases with increasing

Table 5 Mortality rate of Bean Weevils on application of a suspension of the complexes; number of weevils used for each test = 5

Complex[a]	Concn ($\times 10^{-3}$ mol dm^{-3})	Time lapse before all died (min)	
		Wetting filter paper method	Spotting method
Control	30% MeOH/H_2O	480.0	480.0
Ph_3SnCl	5.0	180.0	360.0
	2.5	225.0	480.0
	1.25	240.0	540.0
Bu_3SnCl	5.0	45.0	240.0
	2.5	65.0	300.0
	1.25	70.0	300.0
1 Ph_3Sn(PhthGlyO)	5.0	10.0	50.0
	2.5	10.0	50.0
	1.25	15.0	60.0
2 Bu_3Sn(PhthGlyO)	5.0	7.0	45.0
	2.5	10.0	50.0
	1.25	12.0	50.0
3 Ph_3Sn(PhthAlaO)	5.0	8.0	50.0
	2.5	10.0	50.0
	1.25	12.0	55.0
4 Ph_3Sn(AcGlyO)	5.0	10.0	50.0
	2.5	12.0	45.0
	1.35	15.0	50.0
5 Ph_3Sn(AcCysO)	5.0	6.0	50.0
	2.5	10.0	55.0
	1.25	12.0	55.0
6 Ph_3Sn(BzGlyO)	5.0	5.0	60.0
	2.5	10.0	60.0
	1.25	18.0	60.0
7 Ph_3Sn(BzCysO)	5.0	7.0	60.0
	2.5	12.0	60.0
	1.25	17.0	60.0

[a]Water content not shown.

concentration of the complex; (iii) tri-n-butyltin chloride is more effective than triphenyltin chloride; (iv) the complexes are more effective than the parent triorganotin(IV) chlorides (Bu_3SnCl and Ph_3SnCl); and (v) the most effective complexes are Bu_3Sn(PhthGlyO), Ph_3Sn(PhthAlaO) and Ph_3Sn(AcCysO) and their toxicity effect is about the same.

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