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Organotin biocides. XII.* Synthesis and structural characterization of organotin derivatives of 3-indolylacetic acid, including the crystal structures of tributylstannyl 3-indolylacetate and tricyclohexylstannyl *N*-methyl-3-indolylacetate

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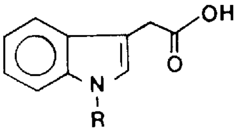
INTRODUCTION

3-Indoyl acetic acid (**I**; R = H; IAAH) is a plant growth hormone, important for cell enlargement in shoots and lateral root initiation. It is believed to act by stimulating polysaccharide synthesis which leads to loosening of the cell membrane and facilitating cell enlargement.[2] Our interest in the biocidal nature of organotin compounds has prompted us to prepare compounds which incorporate both active metal and ligand entities and we report our findings herein relating to a series of derivatives of IAAH. In a previous publication, we have described the structure of Cy_3SnIAA (Cy = cyclo-C_6H_{11}) which, in the solid state, consists of tetrahedral organotin units held in a one-dimensional H-bonded chain by intermolecular N—H...O=C interactions.[3] In view of the important role of hydrogen bonding in this system, we have prepared for comparison derivatives of *N*-methyl-3-indolylacetic acid (**I**; R = CH_3; N-MeIAAH) in which such a structural feature is precluded.



(**I**)

In addition to a full report on both the synthesis and structural chemistry of the titled organometallic carboxylates, we also include in this contribution details of screening tests undertaken to assess the potential pesticidal and fungicidal activity of representative compounds.

EXPERIMENTAL

Spectra were recorded using the following instruments: Perkin-Elmer 599B (infrared), Perkin-Elmer R24B (^1H nmr), JEOL FX60Q (^{119}Sn NMR), V.G. 70–70E (mass spectra). Details of our Mössbauer spectrometer and related procedures are given elsewhere.[4] 3-Indolylacetic acid was of commercial origin (Aldrich) and was used without further purification. The *N*-methyl analogue was prepared by the method of Rosemund *et al.*[5] The synthesis of organotin esters of these acids follows two routes, typified by the examples given below. Additional experimental details including recrystallization solvents, yields, analytical and physical data are collected in Table 1.

Synthesis of tricyclohexylstannyl-3-indolylacetate (Method 1)

Cy_3SnOH (3.0 g, 7.8 mmol) and IAAH (1.39 g, 7.9 mmol) were refluxed together in toluene (100 cm^3) for 45 min, during which time the water formed as a result of the reaction was azeotropically removed using a Dean and Stark trap. The solution was allowed to cool to *ca*

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*For Part XI see ref. 1.

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Table 1 Physical data[a]

Compound	Preparation method[b]	Yield (%)	M.P (°C)	Calculated (%) C	H	N	Found (%) C	H	N
$Me_3Sn(IAA)$	2	26[c]	166–168	46.20	5.07	4.14	45.87	4.90	3.95
$Bu_3Sn(IAA)$	1	93[d]	58–60	56.92	7.59	3.02	55.80	7.32	2.94
$Cy_3Sn(IAA)$	1	55[e]	150–152	62.01	7.62	2.58	61.82	7.59	2.50
$Me_3Sn(N\text{-}MeIAA)$	1	73[c]	150–152	47.77	5.44	3.98	47.09	5.30	3.89
$Bu_3Sn(N\text{-}MeIAA)$	1	91[d]	75–76	57.76	7.80	2.92	57.84	7.95	3.23
$Cy_3Sn(N\text{-}MeIAA)$	1	50[f]	89–90	62.60	7.81	2.52	61.80	7.71	2.50
$Me_3Pb(IAA)$	2	30[c]	180(d)	36.61	4.02	3.28	36.26	3.93	3.14

[a] Abbreviations: Bu = n-C_4H_9; Cy = cyclo-C_6H_{11}. [b] See Experimental for code. [c] Recrystallized from EtOH. [d] Recrystallized from 40:60 petroleum ether. [e] Recrystallized from toluene. [f] Recrystallized from MeOH.

55°C, filtered and the filtrate concentrated to approximately half its volume. Overnight crystallization yielded the desired product, which was subsequently recrystallized from hot toluene (2.42 g, 55%).

Synthesis of trimethylstannyl-3-indolylacetate (Method 2)

IAAH (1.0 g, 5.8 mmol) was dissolved in a methanolic solution (20 cm^3) containing sodium (0.13 g, 6.2 mmol). To this was added Me_3SnCl (1.13 g, 5.7 mmol) in methanol (10 cm^3). The resulting mixture was stirred, first at room temperature for 1 h, then at reflux for 2 h before being evaporated to dryness and the residue recrystallized from hot toluene. The product obtained in this manner was further recrystallized from ethanol to yield the desired compound as a colourless, crystalline material (0.5 g, 26%).

X-ray crystal structure of $Bu_3Sn(IAA)$

Suitable crystals for X-ray studies were grown from 40:60 petroleum ether.

Crystal data: $C_{22}H_{35}NO_2Sn$, mol.wt = 464.3, monoclinic $P2_1/n$, $a = 13.388(6)$, $b = 10.278(4)$, $c = 17.350(6)$ Å, $\beta = 98.6(3)°$, $V = 2360.84$ Å^3, $Z = 4$, $D_c = 1.31$ g cm^{-3}, $F(000) = 928$, $\mu(\text{Mo}-K\alpha) = 9.94$ cm^{-1}.

Data collection was carried out at room temperature on a Hilger–Watts Y290 four-circle automatic diffractometer using Mo – Kα radiation. Of the 3787 reflections measured, 3358 had $I \geqq 3\sigma(I)$ and were considered to be observed. Data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by conventional methods using the SHELX[6] program suite to final values of $R = 0.0362$ and $R_W = 0.0405$. The asymmetric unit with atomic labelling is shown in Fig. 1. Final positional parameters for non-hydrogen atoms and bond distances and angles are given in Tables 5 and 6 respectively.

X-ray crystal structure of $Cy_3Sn(N\text{-}MeIAA)$

Suitable crystals for X-ray analysis were grown from toluene.

Crystal data: $C_{29}H_{43}NO_2Sn$, mol. wt = 556.4, monoclinic $P2_1/n$, $a = 9.888(4)$, $b = 15.288(8)$, $c = 18.326(7)$ Å, $\beta = 91.8(2)°$, $V = 2768.89$ Å^3, $Z = 4$, $D_c = 1.33$ g cm^{-3}, $F(000) = 1160$, $\mu(\text{Mo}-K\alpha) = 8.57$ cm^{-1}.

In a manner similar to that described above, the structure was solved using diffraction data for 3024 observed reflections from a total data set of 3995, to final values of $R = 0.0651$ and $R_W = 0.0680$. Final fractional atomic coordinates, bond distances and angles for non-hydrogen atoms are given in Tables 8 and 9. The asymmetric unit is shown in Fig. 4. For both structures, full listings of atomic coordinates and thermal parameters are available upon request from the authors.

Biocidal testing

$Me_3Sn(IAA)$ and $Cy_3Sn(IAA)$ were tested against selected organisms by ICI Plant Protection (Jealotts Hill) following methodlogy described elsewhere.[7] Results of these tests are given in Table 10.

DISCUSSION

Synthesis and spectroscopy

Triorganotin derivatives of IAAH and N-MeIAAH have been synthesized by reactions between the free acid and an organotin oxide or hydroxide [Eqns 1 and 2]

$$R_3SnOH + HX \rightarrow \quad R_3SnX + H_2O \qquad [1]$$

$$R = Me,Cy \qquad X = N\text{-}MeIAA$$

$$R = Cy \qquad X = IAA$$

$$(R_3Sn)_2O + 2HX \rightarrow \quad 2R_3SnX + H_2O \qquad [2]$$

$$R = Bu \qquad X = IAA,\ N\text{-}MeIAA$$

or by the reaction between an organotin halide and the sodium salt of the ligand (Eqn 3):

$$Me_3SnCl + Na(IAA) \rightarrow Me_3Sn(IAA) + NaCl \qquad [3]$$

This latter reaction has also been used to prepare $Me_3Pb(IAA)$, although in general yields are lower by this route than in reactions involving the acid form of the ligand.

Mass spectra, obtained under EI (electron ionization) conditions, confirm the composition of the compounds prepared, although parent ions are either weak or completely unobserved (Table 2). Under milder CI (chemical ionization, isobutene) fragmentation, a parent ion was observed for $Bu_3Sn(IAA)$ along with substantial abundances for the high-mass ions $Bu_2Sn(IAA)$ and Bu_3Sn. In all spectra the most abundant (100%) ion is the ligand $-CO_2$. A general feature of these data is that even-electron ions decompose with loss of a neutral group to give other even-electron fragments. Loss of odd-electron fragments from even-electron ions is not common, as indicated by the absence of odd-electron ions such as $R_2Sn^{+\cdot}$ or $RSnL^{+\cdot}$ as current carriers. R_2SnH^+ species are observed, indicating the preferred loss of neutral alkene rather than alkyl [Eqn 4]:

$$Bu_3Sn^+ \rightarrow Bu_2SnH^+ + CH_3CH_2CH{=}CH_2 \quad [4]$$

For example, in the mass spectrum of $Bu_3Sn(N\text{-}MeIAA)$, Bu_2SnH^+ is observed at 6.9% abundance.

Vibrational spectra (Table 3) segregate the compounds into two groupings. The two tricyclohexyltin compounds form the first group, in which $\Delta\nu_{asym}(CO_2)$ between solid and solution phases is $\leq 20\,cm^{-1}$. For $Cy_3Sn(IAA)$, dissolution in $CHCl_3$ induces an upfield shift of $\nu(N{-}H)$ of

Table 2 Selected mass spectral (70 eV EI) data

Compound	Parent$^+$	R_2SnL^+	R_3Sn^+	LSn^+	RSn^+	Sn^+/SnH^+
$Cy_3Sn(IAA)$						
m/z	—	460	369	294	203	120/121
Abundance(%)		85.5	3.3	19	30	10/12
$Cy_3Sn(N\text{-}MeIAA)$						
m/z	—	474	369	308	203	120/121
Abundance (%)		15	1	3	24	3.2/6
$Bu_3Sn(IAA)$[a]						
m/z	—	408[b]	291	294	177	120/121
Abundance (%)		60	8	3	18	3/5
$Bu_3Sn(N\text{-}MeIAA)$						
m/z	479	422	291	308	177	120/121
Abundance (%)	1.3	35	5	4.5	10	2/4
$Me_3Sn(IAA)$						
m/z	339	324	165	295[c]	135	120/121
Abundance (%)	3.2	4	12.6	1	2	1/0
$Me_3Sn(N\text{-}MeIAA)$						
m/z	353	338	165	308	135	—
Abundance (%)	3.2	3	5	1	1	

[a] Under C.I. conditions: 466(44%), 408(60%)[b], 291(94%), 120/121(3.6/4.2%).
[b] Parent ion minus C_4H_{10}. [c] HSn(IAA).

Table 3 Vibrational spectroscopic data (cm^{-1})[a]

Compound	Matrix	ν(N—H)	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	ν_{asym}(Sn—C)	ν_{sym}(Sn—C)
IAAH	KBr	3390	1690	1400		
	$CHCl_3$	3470	1710	1410		
N-MeIAAH	KBr		1700			
Me_3Sn(IAA)	KBr	3358	1574br	1400	558	—
	$CHCl_3$	3470	1640	1330	550	545
Me_3Sn(N-MeIAA)	KBr		1565	1400	542[b]	520 vw[b]
	$CHCl_3$		1645	1330	542	540
Bu_3Sn(IAA)	KBr	3350br	1575br	1380		
	$CHCl_3$	3470	1637	1340		
Bu_3Sn(N-MeIAA)	KBr		1575br	1390		
	$CHCl_3$		1642	1335		
Cy_3Sn(IAA)	KBr	3295	1615	1445		
	$CHCl_3$	3480	1635	1440		
Cy_3Sn(N-MeIAA)	KBr		1640	1340		
	$CHCl_3$		1640	1340		
Me_3Pb(IAA)	KBr	3395, 3275 br	1562	1380	495[c]	488w[c]

[a]IR data unless indicated otherwise. [b]Raman: 543vw, 518. [c]$\nu_{asym,sym}$(Pb—C) respectively.

185 cm^{-1} with a change in band profile from broad (solid state) to sharp. Taken collectively, these data imply N—H...O=C hydrogen bonding in this compound, a situation confirmed by an X-ray structure of this species.[3] For Cy_3Sn(N-MeIAA) where H-bonding is precluded, $\nu_{asym}(CO_2)$ is phase-independent and at a frequency characteristic of a unidentate ligand, thereby implying tetrahedral coordination here also.

For each of the four compounds based upon trimethyl- or tributyltin residues, $\nu_{asym}(CO_2)$ moves *ca* 80 cm^{-1} to higher wavenumber upon going from solid to solution states. The low frequency of $\nu_{asym}(CO_2)$ in the solid state ($\sim$1570 cm^{-1}) coupled with the planarity or near-planarity of the C_3Sn moiety inferred from the pattern of bands observed for $\nu_{sym,asym}$(Sn—C) in the IR/Raman spectra dictates that in the solid state the carboxylate acts in a bridging, bidentate manner, enforcing a local *trans*-O_2SnC_3 geometry at tin. This structure is, as is now well established, disrupted into a collection of monomeric fragments in dilute solution. In addition to the C=O:→Sn coordination, infrared data also suggest a non-passive structural role for the N—H unit in derivatives of IAAH. In the free acid, the N—H moiety is not involved in hydrogen bonding,[8] so the shift $\Delta\nu$(N—H) between solid and solution spectra of 80 cm^{-1} must arise purely from solid-state (packing) effects. Taking these data as indicating a non-H-bonding role for N—H, and $\Delta\nu$(N—H) = 185 cm^{-1} as diagnostic of strong H-bonding as in Cy_3Sn(IAA),[3] values of 112 cm^{-1} and 120 cm^{-1} for Me_3Sn(IAA) and Bu_3Sn(IAA) respectively imply that weak H-bonds involving N—H and presumably an oxygen of the carboxylate group are also present in the solid-state structures of the two R_3Sn(IAA) (R=Me, Bu) compounds. This analysis is vindicated by the X-ray structure of the latter compound, discussed below.

Me_3Pb(IAA) also belongs to this second structural grouping based upon IR data, but a splitting of the N—H stretching band in the solid state may suggest a more complex H-bonding array than in either of the two corresponding tin compounds.

Mössbauer (solid-state) and NMR (solution) data (Table 4) support the structural implications of the vibrational spectroscopy discussed above. Mössbauer quadrupole splitting (QS) values for the four methyl- and butyl-tin compounds (3.43–3.61 mm s^{-1}) lie in a range generally associated with the *trans*-O_2SnC_3 trigonal bipyramidal geometry at tin.[9] Direct comparison can be made with, for example, Ph_3SnO_2CH (QS = 3.48 mm s^{-1}) which is known to adopt this structure.[10] On the other hand, both tricyclohexyltin compounds have reduced QS values (3.01, 2.67 mm s^{-1}) and can arise from either tetrahedral or *cis*-O_2SnC_3 stereochemistry about tin.[9] In view of the established tetrahedral

Table 4 ^{1}H, ^{119}Sn NMR and ^{119}Sn Mössbauer spectroscopic data

Compound	$^2J(^1H—C—^{119}Sn)$ (Hz)	$\delta^{119}Sn$ (ppm)[a]	IS (mm s^{-1})[b]	QS (mm s^{-1})[b]	Γ[c] (mms^{-1})
$Me_3Sn(IAA)$	60[d,e]	135.2	1.32	3.61	1.06, 1.05
$Me_3Sn(N\text{-}MeIAA)$	56[d]	131.6	1.35	3.43	0.93, 0.91
BuSn(IAA)		111.0	1.44	3.46	0.87, 0.82
$Bu_3Sn(N\text{-}MeIAA)$		105.3	1.35	3.46	0.87, 0.82
$Cy_3Sn(IAA)$		5.1[g]	1.55	3.01	0.95, 0.94
$Cy_3Sn(N\text{-}MeIAA)$		3.6[f]	1.48	2.67	0.99, 1.01
$Me_3Pb(IAA)$	84[g]				

[a]Relative to Me_4Sn. [b]$\pm$0.03 mm s^{-1}. [c]Full width at half height. [d]In $CDCl_3$. [e]67 Hz in $(CD_3)_2CO$. [f]In toluene. [g]$^2J(^1H—C—^{207}Pb)$.

nature of $Cy_3Sn(IAA)$,[3] and in the light of other spectral data, it would seem most likely that $Cy_3Sn(N\text{-}MeIAA)$ is also four-coordinate at tin. However, it is somewhat surprising that a relatively minor modification to the indole acetic acid ligand should induce such a sizeable change in Mössbauer QS value. ^{119}Sn NMR chemical shifts for all six organotin compounds are consistent with coordination numbers of four at tin.[11,12] In the case of $Cy_3Sn(N\text{-}MeIAA)$, given the constancy of $\nu_{asym}(CO_2)$ in solid and solution states (Table 3), these data support a tetrahedral geometry at tin in the solid state as well as in solution. We have used a similar rationale in discussing the structures of triphenyltin benzoates,[13] whose crystallographic data can be interpreted in terms of either four- or five-coordinate *cis*-O_2SnC_3 arrangements about tin.[14,15]

$^2J(^1H—G—^{207}Pb)$ coupling in the ^{1}H NMR of $Me_3Pb(IAA)$ is typical of five-coordinate lead,[16] but this may well arise from solvent (MeOH) coordination to the metal. Coupling constants for Me_3PbCl in donor solvents have values similar to that for $Me_3Pb(IAA)$ in methanol, e.g. 81 Hz (pyridine), 78 Hz (acetone).[16] However, the sparing solubility of this material even in donor solvents supports the contention that this compound is a coordination polymer in the solid state.

Table 5 Final fractional coordinates[a] for non-hydrogen atoms in $Bu_3Sn(IAA)$

Atom	x	y	z
Sn	78122(3)	20045(3)	21346(2)
N(1)	10462(5)	−1449(5)	−137(3)
O(1)	8397(3)	434(3)	1467(2)
O(2)	7839(3)	−1027(4)	2227(2)
C(1)	8697(5)	1676(7)	3246(3)
C(2)	9733(5)	1117(8)	3274(4)
C(3)	10328(6)	1017(11)	4071(5)
C(4)	11317(7)	483(10)	4131(6)
C(5)	8372(4)	3415(6)	1493(4)
C(6)	9497(5)	3673(6)	1612(3)
C(7)	9885(5)	4641(7)	1064(4)
C(8)	10997(6)	4884(8)	1249(5)
C(9)	6278(4)	1432(7)	1890(4)
C(10)	5735(8)	1576(16)	1211(7)
C(11)	4595(12)	1150(24)	1099(10)
C(12)	4021(15)	1440(21)	692(12)
C(13)	8220(4)	−739(5)	1644(3)
C(14)	8452(5)	−1803(5)	1094(4)
C(15)	9401(5)	−1633(5)	745(4)
C(16)	9471(5)	−1565(6)	−33(4)
C(17)	10390(5)	−1551(6)	1151(4)
C(18)	10808(6)	−1563(8)	1924(5)
C(19)	11820(7)	−1475(11)	2134(6)
C(20)	12441(6)	−1300(11)	1558(7)
C(21)	12065(6)	−1314(9)	779(6)
C(22)	11036(5)	−1411(6)	579(4)

[a]Values tabulated are $\times 10^5$ for Sn, $\times 10^4$ for the other atoms, with e.s.d. (estimated standard deviation) in parentheses.

The structures of $Bu_3Sn(IAA)$ and $Cy_3Sn(N\text{-}MeIAA)$

The structure of $Bu_3Sn(IAA)$ is shown in Fig. 1. The coordination sphere about tin is *trans*-O_2SnC_3 type as indicated spectroscopically, and follows the most common structural motif for triorganotin carboxylates. The intermolecular linkage [Sn—O(2′): 2.524(3) Å] is strong in comparison with that involving bulkier R_3Sn moieties (e.g. R = Cy), but weaker than is often

Table 6 Final bond distances (Å) and angles (°) for Bu$_3$Sn(IAA)[a]

Distances[b]

Sn—O(1)	2.199(3)	C(1)—C(2)	1.596(8)
Sn—O(2′)	2.524(3)	C(2)—C(3)	1.492(10)
Sn—C(1)	2.135(6)	C(3)—C(4)	1.423(11)
Sn—C(5)	2.134(5)	C(5)—C(6)	1.518(8)
Sn—C(9)	2.118(6)	C(6)—C(7)	1.520(8)
O(1)—C(13)	1.275(6)	C(7)—C(8)	1.496(10)
O(2)—C(13)	1.235(6)	C(9)—C(10)	1.296(11)
C(13)—C(14)	1.514(7)	C(10)—C(11)	1.571(16)
C(14)—C(15)	1.497(8)	C(11)—C(12)	1.009(22)
C(15)—C(16)	1.368(8)	C(16)—N(1)	1.371(8)
C(15)—C(17)	1.406(9)	C(22)—N(1)	1.361(8)
C(17)—C(18)	1.374(9)	C(20)—C(21)	1.371(12)
C(18)—C(19)	1.352(11)	C(21)—C(22)	1.373(10)

Angles[b]

O(1)—Sn—O(2′)	173.5(2)	C(1)—Sn—C(5)	116.6(3)
O(1)—Sn—C(1)	99.6(2)	C(1)—Sn—C(9)	121.9(3)
O(1)—Sn—C(5)	90.1(2)	C(5)—Sn—C(9)	119.0(3)
O(1)—Sn—C(9)	95.8(2)	Sn—O(1)—C(13)	118.2(3)
O(2′)—Sn—C(1)	84.9(2)	Sn″—O(2)—C(13)	139.8(2)
O(2′)—Sn—C(5)	83.8(2)	O(1)—C(13)—O(2)	122.6(5)
O(2′)—Sn—C(9)	85.6(2)	O(1)—C(13)—C(14)	117.9(5)
Sn—C(1)—C(2)	118.6(4)	O(2)—C(13)—C(14)	119.4(5)
C(1)—C(2)—C(3)	114.9(6)	C(13)—C(14)—C(15)	115.9(5)
C(2)—C(3)—C(4)	117.2(8)	C(14)—C(15)—C(16)	126.3(6)
—	—	C(14)—C(15)—C(17)	126.6(5)
Sn—C(5)—C(6)	113.6(4)	C(16)—C(15)—C(17)	107.1(5)
C(5)—C(6)—C(7)	112.6(5)	C(15)—C(16)—N(1)	110.2(6)
C(6)—C(7)—C(8)	113.4(6)	C(15)—C(17)—C(18)	134.9(6)
Sn—C(9)—C(10)	123.1(6)	C(15)—C(17)—C(22)	106.4(6)
C(9)—C(10)—C(11)	118.9(11)	C(18)—C(17)—C(22)	118.7(7)
C(19)—C(20)—C(21)	122.1(8)	C(17)—C(19)—C(20)	119.5(9)
C(19)—C(20)—C(21)	122.1(8)	—	—
C(20)—C(21)—C(22)	117.1(7)	—	—
C(21)—C(22)—C(17)	121.7(8)	—	—
C(17)—C(22)—N(1)	108.5(6)	—	—
C(21)—C(22)—N(1)	129.8(7)	—	—
C(16)—N(1)—C(22)	107.9(5)	—	

[a] Primed atoms are related to their umprimed counterparts (x, y, z) by $\frac{3}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$, while doubly primed atoms are similarly related by $\frac{3}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$. [b] E.s.d. in parentheses.

encountered in these systems. Table 7 collates structural data for selected organotin carboxylates for comparison. The unit cell of Bu$_3$Sn(IAA) shown in Fig. 2 also reveals that the polymer chains are held together by intermolecular hydrogen bonds N(1)···O(1) to produce an overall sheet structure. Two points are worth making about this H-bonding scheme in comparison with that previously described for Cy$_3$Sn(IAA), whose lattice structure is shown in Fig. 3 for reference. Firstly, the H-bonds in Bu$_3$Sn(IAA) [N(1)···O(1): 3.128 Å] are weak and of secondary importance in terms of bonding to the intermolecular Sn—O bonds along the chain, while in Cy$_3$Sn(IAA) a stronger H-bond (2.891 Å) exists only at the expense of any C═O:→Sn interactions. Secondly, in Bu$_3$Sn(IAA) the oxygen of the carboxylate which engages in the H-

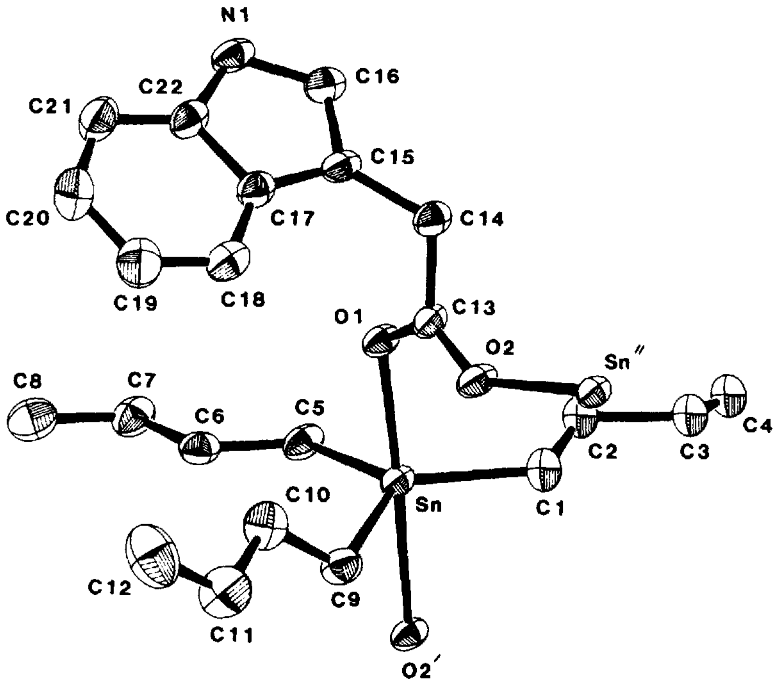

Figure 1 The asymmetric unit of tributylstannyl 3-indolylacetate showing the labelling scheme used in the text.

Table 7 Comparative structural data (Å) for selected organotin carboxylates

		Sn—O					
Compound	Sn—O	Intra	Inter	C=O	C—O	H-bond[a]	Ref.
IAAH				1.223	1.298	2.665	8
$Bu_3Sn(IAA)$	2.199(3)	3.120	2.524(3)	1.235(6)	1.275(6)	3.128	This work
$Cy_3Sn(N\text{-}MeIAA)$	2.05(1)	2.78(1)	—	1.25(2)	1.26(2)	—	This work
$Cy_3Sn(IAA)$	2.086(3)	2.929	—	1.213(7)	1.302(7)	2.891	3
$Cy_3SnO_2CCH_3$	2.12(3)	2.94(4)	3.84	1.25(9)	1.39(8)	—	20
$Cy_3SnO_2CCF_3$	2.08(4)	3.11	3.70	1.20(5)	1.28(4)	—	21
$Ph_3SnO_2CC_6H_4(N_2R)$-*o*[b]	2.070(5)	2.463(7)	—	1.224(1)	1.296(8)	2.94[c]	22
$Ph_3SnO_2CC_6H_4(OH)$-*o*	2.083	3.071	3.035	1.232	1.301	2.71	15
$Ph_3SnO_2CC_6H_4(NMe_2)$-2	2.115(6)	2.564(7)	—	1.22(1)	1.272(9)	—	14
$Ph_3SnO_2CC_6H_4(NH_2)$-4	2.072(2)	2.629(2)	—	1.236(4)	1.306(4)	—	14
$Ph_3SnO_2CCH_3$	2.185	3.206(3)	2.349(3)	1.251(5)	1.263(5)	—	4
$Me_3SnO_2CCH_2NH_2$	2.21(1)	3.23(2)	2.46[d]	1.23(3)	1.34(3)	2.74	23
$Me_3SnO_2CCH_3$	2.205(3)	3.23	2.391(4)	1.240(6)	1.269(5)	—	24

[a] CO···HO or CO···HN. [b] R = 2-hydroxy-5-methylphenyl. [c] Also contains two OH···N bonds at 2.62, 2.58 Å. [d] N:→Sn.

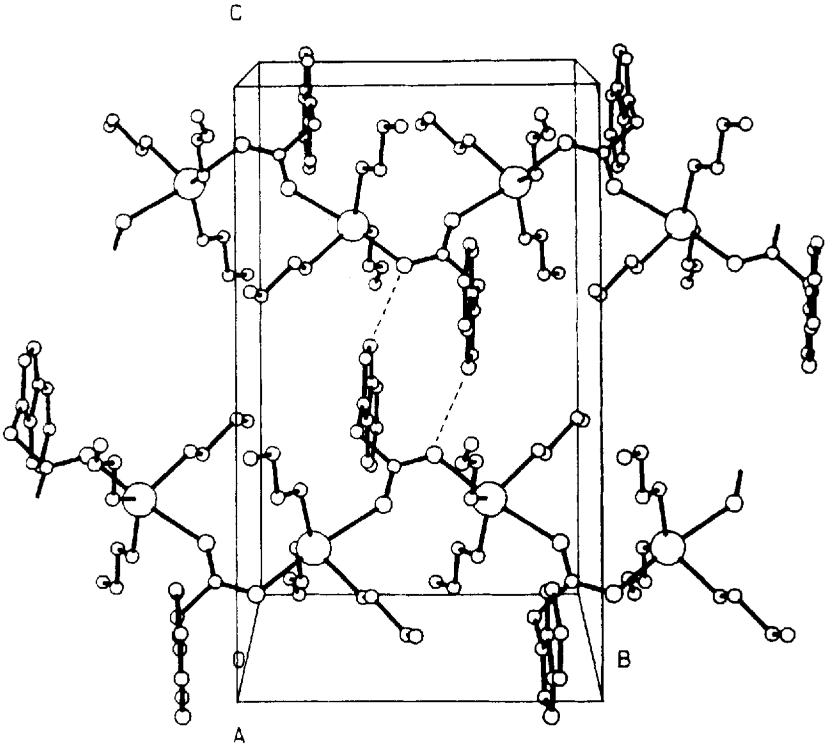

Figure 2 The unit cell of $Bu_3Sn(IAA)$, viewed along the *a*-axis. H-bonds are marked ---

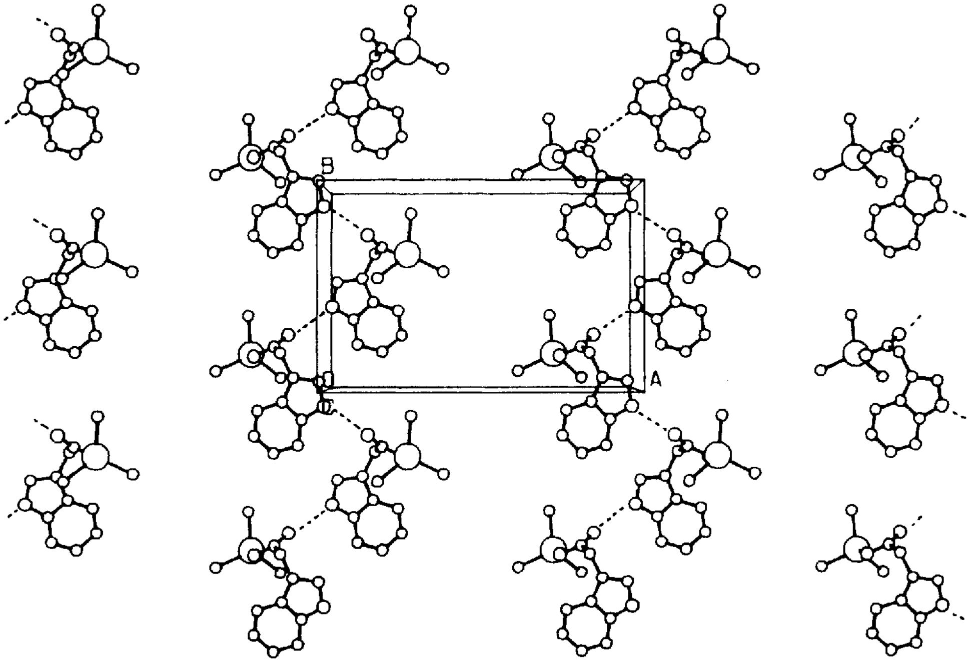

Figure 3 The unit cell of $Cy_3Sn(IAA)$, viewed along the *c*-axis. Data are taken from ref. 3. H-bonds are marked ---

bonding array [O(1)] is covalently rather than coordinatively bonded to tin, and is formally the oxygen *singly* bonded to carbon in the RCO$_2$-rouping. This contrasts with the more usual C=O···HN arrangement which occurs in Cy$_3$Sn(IAA) and again underlines the fact that in Bu$_3$Sn(IAA) the formation of H-bonds is secondary to build-up of the coordination polymer.

Given the similar Lewis acidity of tin in both Bu$_3$Sn(IAA) and Cy$_3$Sn(IAA), the contrasting structures adopted by these two compounds must arise from the different steric requirements of Bu versus Cy. Bulky hydrocarbon groups on tin inhibit polymer formation by increasing the steric clashes between themselves and the substituent on the carboxylate group, in this case (C$_8$H$_6$N)CH$_2$. We have discussed this phenomenon more fully on a previous occasion[10] when comparing the structures of Ph$_3$SnO$_2$CR (R = H, Me). We have also suggested, from an MO viewpoint, that where the preferred *trans*-O$_2$SnC$_3$ geometry at tin is inhibited on steric grounds, formation of a tetrahedral geometry is the likely result, rather than the alternative five-coordinate structure *cis*-O$_2$SnC$_3$.[1]

The extent to which H-bonding influences the tin coordination sphere in Cy$_3$Sn(IAA) can be determined by comparing the structure of Cy$_3$Sn(N-MeIAA) (Fig. 4). The intramolecular, 'chelating' Sn—O(2) bond is shorter in the *N*-methylated derivative [2.780 versus 2.929 Å], but the pattern of bond angles about tin is remarkably similar in the two cases. As with Cy$_3$Sn(IAA), which has already been fully discussed,[3] there are no systematic angular changes to imply that a tetrahedral-to-trigonal bipyramidal transition is in effect with close approach of O(2) to tin. The C—Sn—C angles are larger than those for C—Sn—O, but this is to be expected under the rehybridization ideas of Bent.[17] The only piece of evidence to support a chelating carboxylate ligand is the equality of the two C—O bonds within the CO$_2$ unit, a result which is quite out of keeping with, for example, the shortness of the Sn—O(1) bond [2.05(1) Å]. The large standard deviations in the C—O bonds may be clouding the issue here, but clearly interpretation of the structural data is somewhat subjective. The data for Cy$_3$Sn(N—MeIAA) is paralleled in a series of triphenyltin benzoate structures which follow a similar structural pattern and which have been discussed as having less than ~25% trigonal bipyramidal character.[14,15] In the case of both the benzoates[13] and Cy$_3$Sn(N-MeIAA), our recourse is to follow the implications of the spectroscopic data which incline us toward describing these compounds as tetrahedral at tin. What is clear, however, is that the H-bonding in Cy$_3$Sn(IAA) alone does not prevent formation of a five-coordinate tin (of whatever geometry) but merely acts as a useful source of bond energy when C=O:→Sn coordination is sterically and/or electronically disfavoured.

Table 8 Final fractional coordinates ($\times 10^4$) for non-hydrogen atoms in Cy$_3$Sn(N-MeIAA)[a]

Atom	*x*	*y*	*z*
Sn	5564(1)	2452(1)	1515(1)
N(1)	9300(14)	−908(9)	345(7)
O(1)	6462(11)	1300(8)	1229(6)
O(2)	4360(12)	849(8)	1186(6)
C(1)	4246(12)	2892(9)	628(7)
C(2)	4747(13)	1636(10)	−116(7)
C(3)	3811(15)	2966(10)	−724(9)
C(4)	3605(14)	3920(10)	−671(8)
C(5)	3077(15)	4197(11)	47(8)
C(6)	4010(14)	3863(10)	690(8)
C(7)	4689(13)	2315(9)	2571(7)
C(8)	3142(14)	2169(11)	2512(9)
C(9)	2528(17)	2034(13)	3249(10)
C(10)	3266(15)	1336(12)	3698(9)
C(11)	4717(15)	1494(13)	3760(9)
C(12)	5379(15)	1555(11)	3006(8)
C(13)	7431(14)	3190(14)	1557(8)
C(14)	8375(15)	2934(11)	2167(9)
C(15)	9665(19)	3437(15)	2177(11)
C(16)	10234(18)	3634(15)	1531(9)
C(17)	9308(15)	3954(12)	932(9)
C(18)	7982(16)	3398(13)	927(10)
C(19)	5596(16)	697(13)	1149(8)
C(20)	6047(16)	−247(11)	1016(10)
C(21)	7466(15)	−457(10)	891(8)
C(22)	8624(15)	−334(10)	1383(8)
C(23)	8775(15)	41(10)	2075(8)
C(24)	10077(17)	81(12)	2387(11)
C(25)	11181(17)	−213(12)	2006(10)
C(26)	11076(18)	−540(12)	1330(10)
C(27)	9749(16)	−618(12)	1026(9)
C(28)	7958(17)	−814(12)	281(10)
C(29)	10183(18)	−1340(14)	−187(10)

[a] E.s.d. in parentheses.

Biocidal testing

The biocidal activity of Me$_3$Sn(IAA) and Cy$_3$Sn(IAA) against a range of organisms is given

Table 9 Final bond distances (Å) and angles (°) for $Cy_3Sn(N\text{-}MeIAA)^a$

Distances			
Sn—C(1)	2.16(1)	C(11)—C(12)	1.55(2)
Sn—C(7)	2.16(1)	C(13)—C(14)	1.49(2)
Sn—C(7)	2.16(1)	C(13)—C(14)	1.49(2)
Sn—C(13)	2.16(1)	C(13)—C(18)	1.33(2)
Sn—O(1)	2.05(1)	C(14)—C(15)	1.49(2)
Sn—O(2)	2.78(1)	C(15)—C(16)	1.36(2)
C(1)—C(2)	1.52(2)	C(16)—C(17)	1.49(2)
C(1)—C(6)	1.51(2)	C(17)—C(18)	1.56(2)
C(2)—C(3)	1.51(2)	O(1)—C(19)	1.26(2)
C(3)—C(4)	1.48(2)	O(2)—C(19)	1.25(2)
C(4)—C(5)	1.49(2)	C(19)—C(20)	1.53(2)
C(5)—C(6)	1.56(2)	C(20)—C(21)	1.46(2)
C(7)—C(8)	1.55(2)	C(21)—C(22)	1.45(2)
C(7)—C(12)	1.56(2)	C(21)—C(28)	1.35(2)
C(8)—C(9)	1.51(2)	C(22)—C(23)	1.40(2)
C(9)—C(10)	1.52(2)	C(22)—C(27)	1.38(2)
C(10)—C(11)	1.46(2)	C(23)—C(24)	1.39(2)
C(28)—N(1)	1.34(2)	C(24)—C(25)	1.39(2)
C(29)—N(1)	1.48(2)	C(15)—C(26)	1.34(2)
	—	C(26)—C(27)	1.41(2)
	—	C(27)—N(1)	1.39(2)

Angles			
C(1)—Sn—C(7)	117.1(5)	C(7)—C(8)—C(9)	112.5(13)
C(1)—Sn—C(13)	111.1(6)	C(8)—C(9)—C(10)	112.3(15)
C(7)—Sn—C(13)	112.7(6)	C(9)—C(10)—C(11)	112.4(16)
C(1)—Sn—O(1)	109.4(5)	C(10)—C(11)—C(12)	112.5(14)
C(7)—Sn—O(1)	109.6(5)	C(11)—C(12)—C(7)	108.1(13)
C(13)—Sn—O(1)	94.7(6)	Sn—C(13)—C(14)	113.8(12)
Sn—C(1)—C(2)	112.9(8)	Sn—C(13)—C(18)	117.7(12)
Sn—C(1)—C(6)	110.0(9)	C(14)—C(13)—C(18)	116.9(14)
C(2)—C(1)—C(6)	112.2(13)	C(13)—C(14)—C(15)	112.9(15)
C(1)—C(2)—C(3)	111.5(11)	C(14)—C(15)—C(16)	118.8(17)
C(2)—C(3)—C(4)	111.3(13)	C(15)—C(16)—C(17)	116.9(17)
C(3)—C(4)—C(5)	113.0(14)	C(16)—C(17)—C(18)	108.8(15)
C(4)—C(5)—C(6)	116.0(13)	C(17)—C(18)—C(13)	119.4(15)
C(5)—C(6)—C(1)	110.8(12)	Sn—O(1)—C(19)	111.1(11)
Sn—C(7)—C(8)	112.1(9)	O(1)—C(19)—O(2)	121.2(19)
Sn—C(7)—C(12)	110.6(9)	O(1)—C(19)—C(20)	120.4(14)
C(8)—C(7)—C(12)	110.1(12)	O(2)—C(19)—C(20)	118.3(16)
C(19)—C(20)—C(21)	121.1(14)	C(24)—C(25)—C(26)	123.3(17)
C(20)—C(21)—C(22)	128.1(15)	C(25)—C(26)—C(27)	116.1(18)
C(20)—C(21)—C(28)	126.2(15)	C(26)—C(27)—C(22)	122.6(16)
C(22)—C(21)—C(28)	105.6(14)	C(26)—C(27)—N(1)	130.5(16)
C(21)—C(22)—C(23)	132.8(14)	C(22)—C(27)—N(1)	106.7(13)
C(21)—C(22)—C(27)	107.4(14)	C(27)—N(1)—C(28)	109.5(14)
C(23)—C(22)—C(27)	119.7(14)	C(27)—N(1)—C(29)	123.8(15)
C(22)—C(23)—C(24)	117.5(15)	C(28)—N(1)—C(29)	126.4(15)
C(23)—C(24)—C(25)	120.6(17)		

[a] E.s.d. in parentheses.

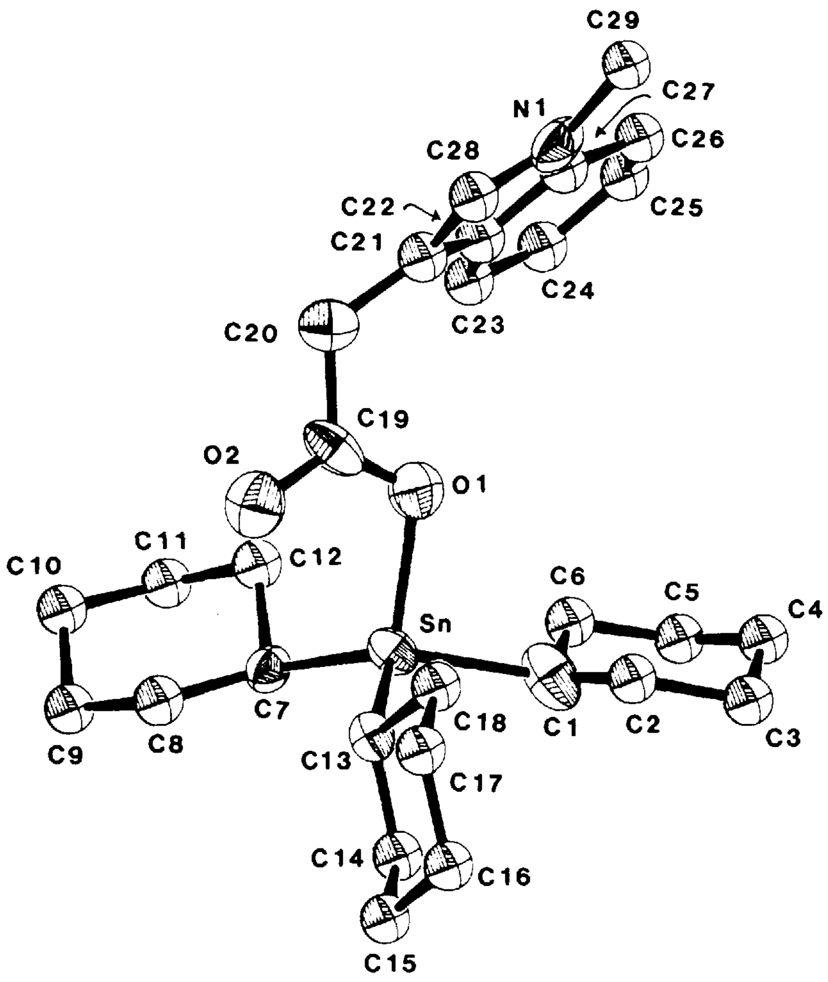

Figure 4 The asymmetric unit of tricyclohexylstannyl *N*-methyl-3-indolylacetate showing the labelling scheme used in the text.

in Table 10. Both compounds show broad-spectrum activity, with the trimethyltin compound generally being the more active of the two. Unfortunately, however, the high mammalian toxicity of methyltin compounds in general[18] largely negates these results in terms of commercial exploitation. In pesticidal tests, $Me_3Sn(IAA)$ proved active against *Myzus persicae* (potato peach aphid), *Musca domestica* (housefly) and *Chilo partellus* (maize and sorghum stem borer) while $Cy_3Sn(IAA)$ was totally inactive, but against *Blattella germanica* (German cockroach) the reverse was found to be true. Both compounds exhibited >80% kill of *Tetranychus urticae* (two-spotted mite) and have similar activity levels in this respect to Cy_3SnOH (Plictran®). $Cy_3Sn(IAA)$ is thus much less active than $Cy_3Sn(mbt)$[7] (mbt = anion of 2-mercaptobenzthiazole) against both *Musca domestica* and *Chilo partellus* at the same concentration level. In fungicidal and bactericidal tests, $Cy_3Sn(IAA)$ again proved to be slightly less active than $Cy_3Sn(mbt)$ against *Aspergillus niger* and *Botrytis cinerea* (grey mould), though similarly active against *Plasmopora viticola* (vine downy mildew) and *Venturia inaequalis* (apple scab).

The general level of activity of these two organotin 3-indolylacetate derivatives is in keeping with the idea that four-coordinate tin monomers or five-coordinate tin polymers are often more active than chelated, five-coordinate

Table 10 Biocidal testing of $Me_3Sn(IAA)$ and $Cy_3Sn(IAA)$

Organism	Concentration (ppm, $\mu g\,g^{-1}$)	$Me_3Sn(IAA)$	$Cy_3Sn(IAA)$
Pesticidal testing[a]			
Tetranychus urticae	500	9	9
Myzus persicae	500	9	0
Musca domestica	500	9	0
Chilo paretellus	500	9	0
Nilaparvata lugens	500	0	0
Blatella germanica	500	0	9
Fungicidal and bactericidal activity[b]			
Cladosporium sphaerospermum	25		2
Aspergillus niger	25		0
Botrytis cinerea	25		0
Septoria nodurum	25		4
Plasmopara viticola (vine)[c]	100		4
Venturla inaequalis (apple)[c]	100		4
Pyricularia oryzae (rice)[c]	100		3[d]

[a] 0=0–49%, 9=80–100% kill. [b] 4=no disease, 3=trace–5%, 2=6–25%, 0=>60% disease. [c] *In vivo* tests. [d] Slightly phytotoxic.

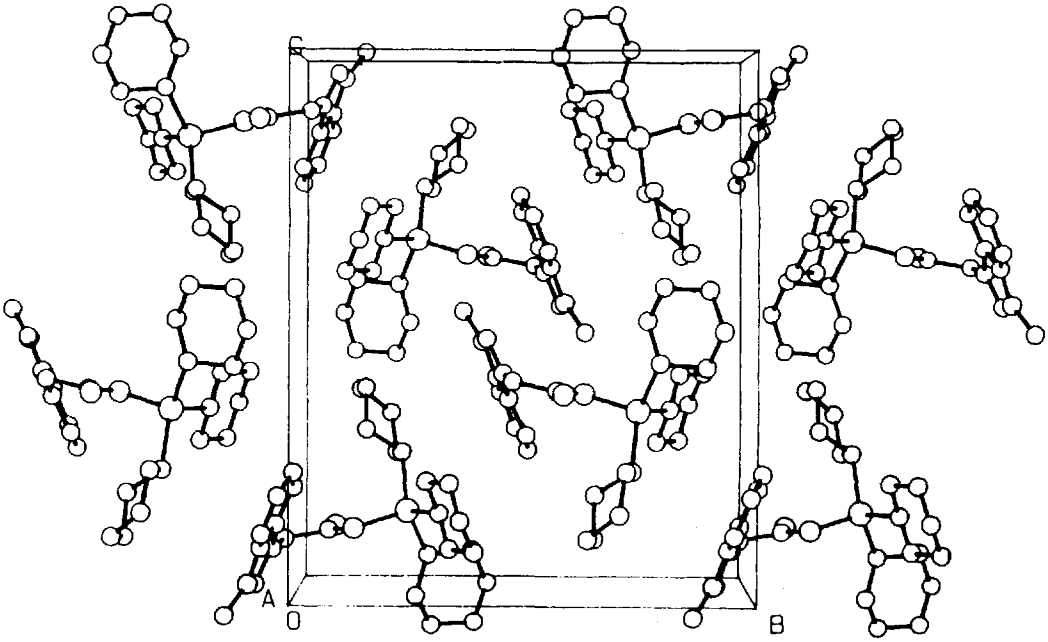

Figure 5 The unit cell of $Cy_3Sn(N\text{-}MeIAA)$ viewed along the *a*-axis.

tin species.[19] The unifying feature of the two active groupings in contrast to the third is that these more readily give four-coordinate entities in solution (the coordination polymer by fragmentation) or are more likely to be easily hydrolysed to $R_3Sn(H_2O)_2{}^+$-type species. The anion in these systems is thus of secondary importance, since in this and other studies using biocidally active ligands we have been unable to exceed the activity of simple Cy_3SnOH. The ligand thus probably only affects the rate of formation of a ligand-free active organotin entity—most probably $R_3Sn(H_2O)_2{}^+$ since Sn–O, Sn–S, Sn–N bonds are more readily hydrolysed than Sn–C bonds—or possibly the pre-hydrolysis transport of the intact compound to the active site of the system. Either way, the ligand is not *totally* irrelevant as comparison of the activity of $Cy_3Sn(IAA)$ and $Cy_3Sn(mbt)$ (above) shows.

In order to obtain possible synergistic activity between an organotin and a ligand of complementary activity, it would seem to us that the ligand must be incorporated into the R_3Sn— system. That is, it should be C-bonded to tin, rather than through readily hydrolysable Sn–O, Sn–S or Sn–N (etc) bonds. Future publications in this series will report our synthetic and structural findings in this area.

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