Journal of Organometallic Chemistry, 173 (1979) 357—376

TRI-*n*-BUTYLTIN(IV) DERIVATIVES OF L-CYSTEINE ETHYL ESTER, N-ACETYL-L CYSTEINE AND α-GLUTAMYL CYSTEINYL GLYCINE (Glutathione reduced)

G. Domazetis, R.J. Magee and B.D. James.
Dept. of Inorganic and Analytical Chemistry,
La Trobe University, Bundoora, Vic. 3083, Australia.
(Received April 19th, 1979)

SUMMARY

Syntheses and spectroscopic data (^{1}H and ^{13}C N.M.R., I.R. and Mössbauer) are presented for L-cysteine ethyl ester, N-acetyl L-cysteine and Glutathione (reduced) tri-*n*-butyl tin derivatives. The L-cysteine ethyl ester compound appears to be four coordinate with a Sn-S bond while the N-acetyl L-cysteine complex contains a four coordinate $(n\text{-}C_4H_9)_3Sn\text{-}S$ moiety and a $(n\text{-}C_4H_9)_3Sn\text{-}O\text{-}CO$ grouping containing chelating carboxylate. In moderately concentrated solutions, dimeric species exist with hydrogen bonding between NH and CO groups. The Glutathione complex is strongly associated, probably via N→Sn coordination. The $(n\text{-}C_4H_9)_3Sn$ entities in this complex are bonded to the cysteine and glycine residues.

INTRODUCTION

Organotin derivatives of amino-acids and dipeptides have been studied (1-3), but no investigations of sulfur-containing amino-acid derivatives have been reported. The effects of organotins in biological systems include inhibition of mitochondrial phosphorylation (4) and functions of the nervous system (5). It has been reported that binding of organotinsby thiol groups is significant in biological systems (6,7).

Accordingly, we have studied some organotin derivatives of sulfur-containing amino-acids and the tripeptide glutathione reduced. We have reported the preparation of diorganotin complexes (8) and briefly reported results of triorganotin compounds (9). In this report, we present details of preparative procedures for tri-*n*-butyl tin compounds and investigate structural aspects from spectroscopic data.

EXPERIMENTAL

(a) Reagents

Bis(tri-*n*-butyltin) oxide was obtained from Alfa Inorganics Inc. L-cysteine ethyl ester hydrochloride, N-acetyl L-cysteine and glutathione reduced, were all obtained from Aldrich Chemicals, and L-cysteine from B.D.H. Biochemicals. All materials were used as supplied.

(b) Syntheses

(i) α-Glutamyl cysteinato-glycinato (S-, O-,) bis (tri-*n*-butyl stannane)(IV), $[(n\text{-}Bu_3Sn)_2SG]$*

Glutathione reduced (1.54g, 0.005 mol) was dissolved in 120 cm^3 water/ethanol (3:7) solvent through which nitrogen had been bubbled for ½ hour. The nitrogen atmosphere was maintained, and a solution of bis (tri-*n*-butyltin) oxide (2.98g, 0.005 mol) was added slowly. The solution was stirred for 3 hours, and the solvent removed under a stream of air. The gelatinous product was dissolved in chloroform, and the water layer discarded. The chloroform was allowed to air evaporate to 20 cm^3, and the product precipitated out by adding *n*-pentane. The heavy oil was dried in a vacuum desiccator for a week, to yield a clear, brittle, plastic solid. Yield 3.32g (75%), M.pt. 61-63°C. Soluble in chloroform, carbon tetrachloride and ethanol, but insoluble in water. Analysis. Calculated for $C_{34}H_{69}O_6N_3SSn_2$:

---

*Abbreviations used are:
Me = methyl; *n*-Bu = *n*-butyl; SG = Glutathione reduced; N-acet L-cyst = N-acetyl L-cysteine; L-cyst-eth = L-cysteine ethyl ester; gly = glycine.

C, 46.13; H, 7.85; O, 10.84; N, 4.76; S, 3.62; Sn, 26.81%.
Found: C, 45.88; H, 7.98; O, 11.9; N, 4.52; S, 3.0; Sn, 27.3%.
Molecular weight (in 0.005 M solution) = 1204; (in 0.024 M solution) = 1856; corresponding to degrees of association of 1.4 and 2.1 respectively. Calculated molecular weight = 885.30. The color of the solid darkens on heating and gases are evolved in the range 90-150°C. A TG/DTA experiment (Rigaku-Denki Thermoflex instrument/10°C min^{-1}) showed a weight loss starting at *ca.* 170°C (endothermic) under N_2, becoming very rapid at 240°C. Approximately 60% weight loss was observed by 350°C.

(ii) N-acetyl L-cysteinato (S-, O-,) bis(tri-*n*-butylstannane)(IV)

N-acetyl L-cysteine (1.63g, 0.01 mol) and tri-*n*-butyl tin oxide (5.96g, 0.01 mol) were mixed in 100 cm^3 $CHCl_3$. The clear solution was stirred for 3 hours and the solvent removed. The gelatinous product was dried in a vacuum desiccator for a week. Yield 5.6g (76%), M.pt. 64-66°C. Soluble in $CHCl_3$ and CCl_4, but insoluble in water. Analysis. Calculated for $C_{29}H_{61}O_3NSSn_2$: C, 46.99; H, 8.29; Sn, 32.03%. Found: C, 46.78; H, 8.11; Sn, 31.5%. Molecular weight (in 0.015 M solution) = 726 (Calc. = 741.15). The compound decomposes extremely rapidly under nitrogen between 240 and 300°C in a TG/DTA experiment, losing over 90% of the original sample mass.

(iii) Ethyl L-cysteinato S-(tri-*n*-butylstannane)(IV)

A solution of L-cysteine ethyl ester hydrochloride in ethanol (1.86g, 0.01 mol) was titrated with 0.2 M aqueous NaOH to pH 10.5. To this solution was added a solution of tri-*n*-butyltin oxide (2.98g, 0.005 mol) in ethanol and the mixture stirred and warmed to 45°C for ½ hour. The solvent was removed, and the product dissolved in chloroform (50 cm^3). The solution was filtered, washed with 20 cm^3 of water, and the chloroform layer dried with anhydrous magnesium sulfate. Removal of the chloroform yielded a pale yellow oil which darkened on standing. Yield 4.0g (91%). Analysis. Calculated for $C_{17}H_{37}O_2SN$ Sn: C, 46.59; H, 8.50; S, 7.32%. Found: C, 45.86; H, 7.62; S, 6.9%. Soluble in organic solvents.

The product decomposes on standing: after 1½ - 2 weeks, a solid is deposited. The compound decomposes rapidly under nitrogen between 200 and 300° in a TG/DTA experiment, to lose over 90% of the original sample mass. The thermal stability of this compound (slightly less than that of the N-acetyl L-cysteine derivative) stands in contrast with that of the L-cysteine derivative which decomposes rapidly at room temperature to give a mixture of products including L-cysteinato S-(tri-*n*-butyl stannane)(IV), L-cysteinato(S-,O-)bis(tri-*n*-butyl stannane)-(IV) and bis (tri-*n*-butyltin)sulfide.

(c) Spectra

^{1}H N.M.R. Spectra were obtained using a Perkin-Elmer R-32 instrument, operating at 90 MHz and at ambient temperature. Spectra of organotin compounds were obtained from solutions in $CDCl_3$ with TMS as internal standard. Uncomplexed ligands were dissolved in D_2O and TMS was used as an external standard in these cases.

^{13}C N.M.R. spectra were obtained with a JEOL PFT-100FT spectrophotometer as previously described (9).

Infrared spectra were obtained using a Perkin-Elmer 457 instrument calibrated with polystyrene film. For solid samples, KBr pressed disks were employed and for oils a liquid film was pressed between KBr plates. The 600-250 cm^{-1} region for oil samples was recorded from a thin film on polypropylene disks. Solution spectra were recorded using a solution cell with 0.1 mm path length and fitted with KBr windows.

Mössbauer Spectra were taken using a conventional constant acceleration drive connected to an electromechanical transducer. The absorber was mounted in the tail of a variable temperature cryostat. The counting system used a Kr-CO_2 proportional counter with preamp., amplifier and SCA to accumulate a spectrum into 1024 channels of a multi-channel analyzer. Curve fitting was carried out using a least

squares computer programme, fitting either one or two doublets, as required. The $(n\text{-}Bu_3Sn)_2SG$ spectrum was taken with the absorber at liquid nitrogen temperature whilst the spectrum of $(n\text{-}Bu_3Sn)_2$(N-acet-L-cyst) was taken while both absorber and source were at liquid N_2 temperature. No detectable spectra could be obtained at room temperature.

RESULTS AND DISCUSSION

^1H N.M.R. Spectra

The 2-4 p.p.m. region of the ^1H N.M.R. spectrum of freshly-prepared $n\text{-}Bu_3Sn$(L-cyst-eth) in $CDCl_3$ is shown in Fig. 1a together with the corresponding region for the ligand $[C_2H_5O_2CCH(NH_2)CHS^-]$ at pH 12 in D_2O. The 3-8 p.p.m. regions of the spectrum of $(n\text{-}Bu_3Sn)_2$(N-acet-L-cyst) at various concentrations in $CDCl_3$ are shown in Fig. 1b.

The three spin systems, and the four spin systems (at 15% w/w concentration) were analysed with the LAOCOON III program (Table 1). Peaks due to the butyl groups tended to obscure peaks of low intensity arising from the ligand protons. Consequently the accuracy of the results from the butyltin derivatives are poorer than those from the trimethyltin derivative (9) and the L-cysteine ethyl ester anion, both of which showed excellent correlation between experimental and calculated spectra.

The residence times of the rotational isomers (Fig. 2) were calculated by Pachler's method (11,13). The larger proportion of isomer type I for the ligand anion may be due partly to electrostatic interactions. The compounds exist largely as isomers of type I, with isomer III also somewhat favored. These configurations permit closer approach of nitrogen to the tin atom and, as a result, the isomers may be stabilized by a Sn----N interaction. As shown in Fig. 1b, the spectrum of $(n\text{-}Bu_3Sn)_2$(N-acet L-cyst) changes on dilution, probably due to disruption of hydrogen bonding. At 15% w/w concentration,

hydrogen bonding is still present, and the results indicate that the isomer of type III predominates. The species present at this concentration are postulated to be cyclic dimers (as shown by the I.R. spectra - see below) and it is possible that the presence of the species (IV) accounts for the large residence time obtained.

More detailed investigations are needed to clarify this matter, since solvent effects and temperature could also play an important role (13,14). From the ^{3}J(NH-CH) value of 7.2 Hz, a dihedral angle of *ca.* 30° can be estimated for the CH-NH fragment (15).

The spectrum of $(n\text{-}Bu_3Sn)_2SG$ which consists of a series of broad unresolved peaks, is not discussed here.

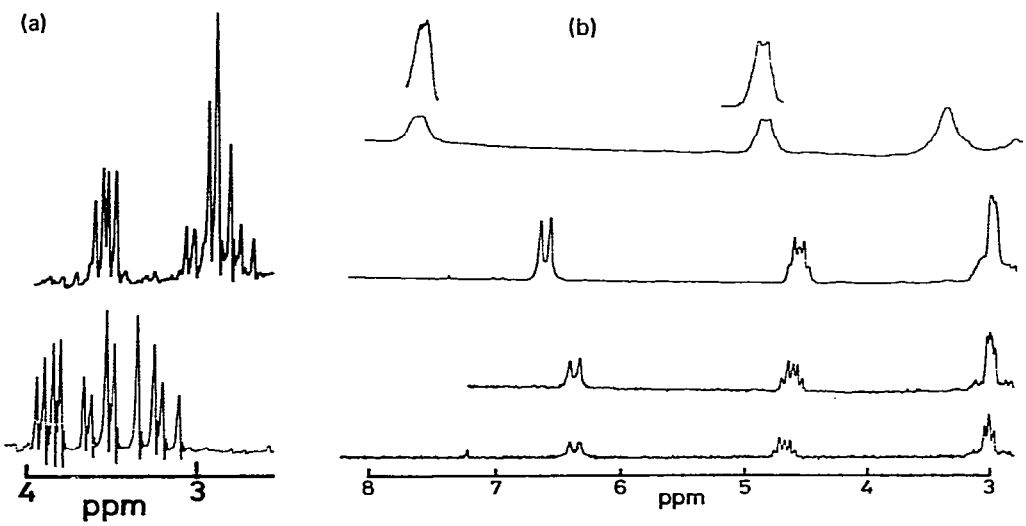
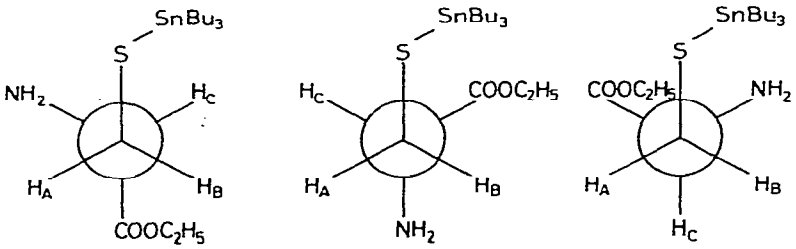


Fig. 1a ^{1}H N.M.R. spectra in the 2-4 p.p.m. region.
Upper: $n\text{-}Bu_3Sn$(L-cyst-eth)
Lower: L-cysteine ethyl ester at pH 12.

Fig. 1b ^{1}H N.M.R. spectra in the 3-8 p.p.m. region for $(n\text{-}Bu_3Sn)_2$(N-acet L-cyst) at various concentrations in CCl_4: 35% w/w (top); 25% w/w; 15% w/w; 5% w/w (bottom).



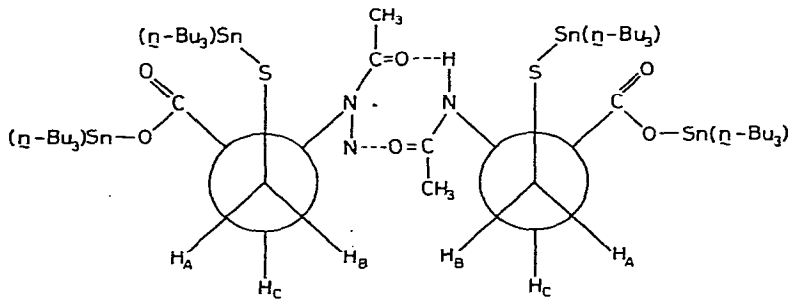


Fig. 2 Rotational isomers for n-Bu_3Sn(L-cyst-eth) (I, II and III) and $(n\text{-}Bu_3Sn)_2$(N-acet L-cyst) (IV).

TABLE 1

Compound	J_{AB} (Hz)	J_{AC} (Hz)	J_{BC} (Hz)	a(I)	b(II)	c(III)
L-cyst-eth (pH 12)	-12.6	3.8	8.6	0.76	0.14	0.10
Me_3Sn(L-cyst-eth)	-13.1	3.5	7.7	0.64	0.10	0.26
n-Bu_3Sn(L-cyst-eth)	-12.4	3.8	7.7	0.64	0.14	0.22
$(n\text{-}Bu_3Sn)_2$(N-acet-L-cyst) (15% w/w)	-11.6	3.6	3.5	0.11	0.11	0.79

^{13}C N.M.R. Spectra

This technique enables the n-Bu_3Sn-S moiety to be identified from the αC shift values observed around 13.5 p.p.m. and the n-Bu_3Sn-O

TABLE 2

^{13}C N.M.R. SPECTRA

Chemical shifts given relative to internal TMS, ±0.1 ppm. Coupling constants ±0.5 Hz., $^{1}J = \begin{cases} ^{119}Sn - ^{13}C \\ ^{117}Sn - ^{13}C \end{cases}$

Compound	Chem. Shifts				Coupling Const.			Ligand Shifts
	αC	βC	γC	δC	^{1}J	^{2}J	^{3}J	
n-Bu_3Sn(L-cyst-eth)[1]	13.9	28.8	27.2	13.7	332.6 317.4	-	61	173.6, 60.9, 57.1, 31.9, 16.8
(n-Bu_3Sn)$_2$(N-acet L-cyst)[2]	17.1 13.7	28.0	27.2	13.7	358.9 344.3 332.0 317.4	-	-	169.4, 174.7 54.7 28.7, 23.4
(n-Bu_3Sn_2)SG[2]	17.1 13.8	28.0	27.2	13.8	366.1 349.1 329.1 315.0	-	63	170.6, 174.3, 173.0 56.0, 54.4, 42.7, 33.0, (28.8), (27.2)

Values for ligands in D_2O solution, using external TMS, are:
N-acetyl L-cystine: 175.2, 174.5, 55.8, 26.3, 22.9
Glutathione (red): 175.9, 174.6, 173.6, 56.8, 54.8, 42.7, 32.2, 27.2, 26.6

1. Spectrum taken 30 hrs. after preparation. Small peaks (<10% intensity) present due to decomposition products.
2. n-$Bu_3SnSCH_2CH_2OH$ αC = 13.5, $^{1}J(^{119}Sn-^{13}C)$ = 330 Hz*
   n-$Bu_3SnO_2CCl_3$ αC = 17.3, $^{1}J(^{119}Sn-^{13}C)$ = 342 Hz*
   n-$Bu_3SnO_2CCH_3$ αC = 16.3, $^{1}J(^{119}Sn-^{13}C)$ = 361 Hz (ref. 9)

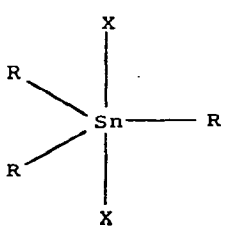
   * unpublished results

moiety from δ(αC) values *ca.* 17 p.p.m. (Table 2). Data from simpler organotin compounds which may be used for comparison is also presented. The δ(αC) and $^{1}J(^{119/117}Sn-^{13}C)$ values are indicative of the coordination state of the tin in solution (9).

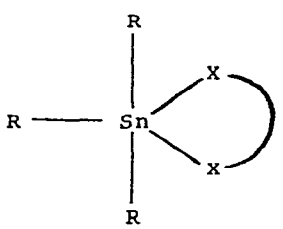
The shift values for the free ligands are also given. These data have been obtained from solutions in D_2O. Since the pH dependence of chemical shifts of amino-acids and peptides (16), complex solvent-solute interactions (13,17) and group electronegativity effects (18) have already been demonstrated, direct comparisons of the free ligand shifts with those of the organotin derivatives are not possible. The organotin derivatives may be useful for the study of steric factors and also the effects of protic and non-protic solvents on the properties of amino-acids and peptides of this type.

Mossbauer Spectra

The spectrum of $(n\text{-}Bu_3Sn)_2SG$ is shown in Fig. 3, and Table 3 also contains isomer shift and quadrupole splitting values of related compounds. The inner doublets of both $(n\text{-}Bu_3Sn)_2SG$ and $(n\text{-}Bu_3Sn)_2$-(N-acet L-cyst), can be assigned to the $n\text{-}Bu_3Sn$-S moiety and the outer doublets to $n\text{-}Bu_3Sn$-O. Values of the parameter ρ (the ratio of quadrupole splitting to isomer shift) below 2.1 are indicative of essentially tetrahedral structures about the tin atom; while ρ>2.1 indicates higher coordination number (19). Quadrupole splitting values for pentacoordinate structures have been reported, (21) and attempts to differentiate between five-coordinate structures such as (A) and (B) using quadrupole splitting values have been made, but these have met with limited success (20).



(A)



(B)

The associated nature of $(n\text{-}Bu_3Sn)_2SG$ indicates that the outer doublet is likely to have originated from a structure of type (A). The monomeric nature of $(n\text{-}Bu_3Sn)_2$(N-acet L-cyst) and the position of ν(C=O) (see below) would suggest a structure of type (B).

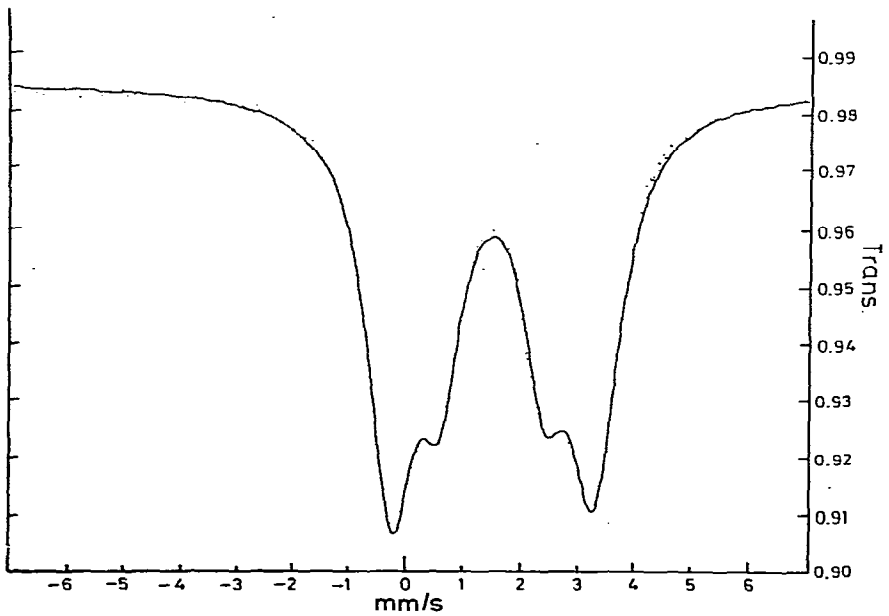


Fig. 3 Mössbauer spectrum of $(n\text{-}Bu_3Sn)_2SG$.

The areas of the doublets (Fig. 3) of $(n\text{-}Bu_3Sn)_2SG$ are in the ratio 1:1.75, while those of $(n\text{-}Bu_3Sn)_2$(N-acet L-cyst) are 1:1.30. The stronger association observed in $(n\text{-}Bu_3Sn)_2SG$ is shown to be due to Sn←N coordination (see below), and probably accounts for the different ratios observed. The $(n\text{-}Bu_3Sn)_2$(N-acet L-cyst) is associated in the solid *via* intermolecular hydrogen bonding. No simple relationships appear to exist between coordination number and the recoil-free fraction (20,22), but recent variable temperature studies have shown a relationship between association in the lattice structure and the recoil-free fraction (22).

TABLE 3

Compound	I.S$_{(mm\ s^{-1})}$	Q.S$_{(mm\ s^{-1})}$		Ref.
$(n\text{-}Bu_3Sn)_2SG$	1.43	1.76	1.23	
	1.44	3.43	2.38	
$(n\text{-}Bu_3Sn)_2$(N-acet L-cyst)	1.34	1.62	1.21	
	1.38	3.59	2.60	
$(n\text{-}Bu_3Sn)_2(SCH_2COO)$	1.40	1.75	1.25	32
	1.40	3.77	2.69	
$n\text{-}Bu_3SnSC_{12}H_{25}$	1.50	1.44	0.96	32
$n\text{-}Bu_3SnO_2C(CH_2)_{11}CH_3$	-	3.62	-	20
$n\text{-}Bu_3Sn$(gly)	1.42	3.21	2.26	1

Infrared Spectra

Solid and solution spectral data are contained in Table 4. Discussion of the results will be centred on the ν(N-H) and ν(C=O) modes.

(i) ν(N-H) region

The position of the ν(N-H) bands is influenced by hydrogen bonding and by coordination of the nitrogen to tin. The shift to lower wavenumber caused by coordination has been discussed (1,23). Studies related to hydrogen bonding in amino-acids, peptides and model systems have been extensive (15,24-27).

n-Bu_3Sn(L-cyst-eth) exhibits broad bands of relatively low intensity which are typical of hydrogen bonded NH_2 groups (21). The instability of this compound prevented detailed studies on solutions. The spectrum of $(n\text{-}Bu_3Sn)_2$(N-acet L-cyst) was recorded over a wide concentration range (Fig. 4a) and provided some very interesting data. In the solid there is one band of medium intensity in the infrared due to a hydrogen bonded N-H group. At decreasing concentrations in CCl_4, a second band due to free N-H is observed. The latter increases in intensity on dilution while that due to bonded N-H decreases.

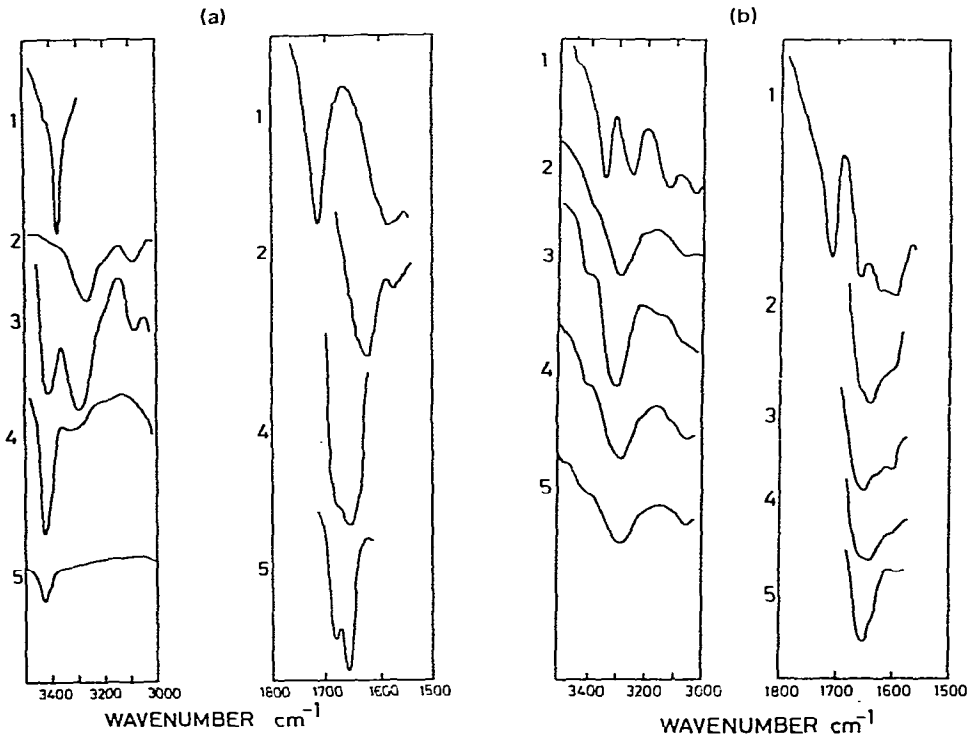


Fig. 4a The ν(N-H) (left) and ν(C=O) (right) regions in the i.r. spectrum of $(n\text{-Bu}_3\text{Sn})_2$(N-acet L-cyst)
1. solid ligand. 2. solid complex. 3. complex, 50% w/w solution in CCl_4. 4. complex, 20% w/w. 5. complex, 2.5% w/w.

Fig. 4b The ν(N-H) (left) and ν(C=O) (right) regions in the i.r. spectrum of $(n\text{-Bu}_3\text{Sn})$SG.
1. solid ligand. 2. complex, thin film. 3. complex, 20% w/w solution in CCl_4. 4. complex, 12% w/w.
5. complex 5% w/w.

Treatment of these results according to the method outlined by Werner *et al.* (28) suggests that the hydrogen bonded species are cyclic dimers. The disappearance of the bonded ν(N-H) band at a concentration 0.06M effectively rules out double hydrogen bonding in an extended form (27). The presence of dimeric species as shown by structure (IV), would require a *cis* arrangement of the amide group. Such an arrangement may be forced on the molecule by the steric requirements of the bulky organotin

moieties. The virtual disappearance of the bonded N-H stretching frequency at 12% w/w concentration indicates that the association is relatively weak (27,30).

The spectrum of $(n\text{-}Bu_3Sn)_2SG$ is shown in Fig. 4b and is recorded over a wide concentration range (50% - 5% w/w solutions). The ν(N-H) peaks do not show appreciable concentration dependence, which rules out the presence of intermolecular hydrogen bonding. Molecular weight determinations show that the complex is associated in solution (the solution employed in molecular weight determinations were also used to record I.R. spectra). Thus this portion of the spectrum could be due to the presence of intramolecularly hydrogen bonded N-H groups and/or due to N-H coordination to the tin atom. The association in solution must certainly be due to N→Sn coordination, and complexes of glutathione with nickel, palladium, cobalt and copper show bands at 3260-3300 cm^{-1} which have been assigned to coordinated amino or amide groups (30).

(ii) ν(C=O) region

The ν(C=O) bands of $(n\text{-}Bu_3Sn)_2$(N-acet L-cyst) and $(n\text{-}Bu_3Sn)_2SG$ are shown in Figs. 4a and 4b respectively. The 1625 cm^{-1} peak of the N-acetyl L-cysteine derivative shows a shift, until at 12% solution both amide and carboxylate C=O bands are observed. The shift of the amide band is consistent with the loss of hydrogen bonding. The carboxylate band appears to be analogous to those reported for tribenzyltin acetate (32), tricyclohexyltin glycinate (1) and bis(tributyltin)-thioglycolate (32), all of which are thought to contain intramolecular interacting groups. The solution spectra certainly rule out carboxylate bridging: the difference $[\nu(C{=}O)_{asym} - \nu(C{=}O)_{sym}]$ being relatively constant (Table 4) and similar to values reported for unassociated organotin carboxylates (33).

This region for the glutathione derivative is complicated by the presence of two carboxylate and two amide carbonyl groups. The

TABLE 4

Infra-red Spectra[1] (in cm^{-1})

(i) *Solid phase and oils*

Compound	ν(N-H)	ν(C=O)[2]	ν(Sn-C)	ν(Sn-S)	ν(S-H)
n-Bu_3Sn(L-cyst-eth)	3375(m) 3200(w)	1743(s)	600(s) 513(w)	330(m)	absent
(*n*-$Bu_3Sn)_2$(N-acet L-cyst)	3270(m) 3090(w)	1625(s.br)	595(m) 515(m)	-	absent
(*n*-$Bu_3Sn)_2$SG	3395(m.br) 3295(s.br)	1645(s.br)	600(s) 518(m)	390(w)	absent
N-acetyl L-cysteine	3372(s) 3280(w.br)	1723(s) 1585(s.br)	-	-	2548(s)
Glutathione (red)	3344(s) 3245(s) 3124(s) 3024(s)	1715(s) 1655†(s)	-	-	2525(m)

(ii) *Solution spectra (in CCl_4)*

Compound	ν(N-H)	ν(C=O) asym	ν(C=O) sym	Δ*	ν(Sn-C)	ν(Sn-S)
(*n*-$Bu_3Sn)_2$(N-acet L-cyst) (50% w/w)	3418(m) 3295(m) 3090(w)	1645(s,v.br)	-	-	595(m) 518(m)	-
(20% w/w)	3425(m) 3300(w,br)	1675†(sh) 1660(vs)	1382(s)	278	590(m) 523(m)	- -
(12% w/w)	3425(m)	1685†(s) 1662(s)	1381(s)	281	590(m) 525(m)	385(w)
(2.5% w/w)	3428(m)	1685†(s) 1662(s)	1379(s)	283	590(m) 525(m)	385(w/w
(*n*-$Bu_3Sn)_2$SG (>50% w/w, film)	3400(w,sh) 3293(m) 3070(w,br)	1645(s,br)	1395(s)	250	600(m) 515(w)	-
(20% w/w)	3400(w) 3293(m) 3060(sh,br)	1650(s,v.br)	1392(s)	258	600(m) 520(w)	-

TABLE 4 (Cont'd)

Compound	ν(N-H)	ν(C=O)asym	ν(C=O)sym	Δ*	ν(Sn-C)	ν(Sn-S)
(12% (w/w)	3400(w) 3293(m) 3060(w)	1650(s,v.br)	1392(s) (1380?)	258 (270?)	600(m) 515(vw)	-
(5% w/w)	3410(w,br) 3293(m) 3060(w,br)	1658(s)	1390(s)	268	600(w) -	-

1. Assignments based on published values and by comparison with spectra of the ligand and simpler organotin compounds.

2. The $\delta(NH_2)$ modes also appears in the 1600 cm^{-1} region (ref. 23).

† amide carbonyl group

* $\Delta = [\nu(C=O)asym - \nu(C=O)sym]$

S = strong; m = medium; w = weak; br = broad; sh = shoulder.

disappearance of the 1715 cm^{-1} band in the free ligand, due to the glycine residue, shows that bonding has occurred at this carboxylate group. The broad band observed in the complex (Fig. 4b) shows a small shift in solution. The $\nu(C=O)_{sym}$ bands are observed at 1390 cm^{-1} (or 1380 cm^{-1}). These do not show any appreciable shift in solution, thus eliminating the possibility of carboxylate bridging.

STRUCTURES OF THE ORGANOTIN DERIVATIVES

From the results presented, a number of deductions can be made concerning the structures of the compounds reported.

1. Ethyl L-cysteinato S-(tri-*n*-butyl stannane)(IV)

Since the ν(C=O) band appears at 1743 cm^{-1}, the carbonyl oxygen does not coordinate with the tin atom. In addition, the ^{13}C N.M.R. spectrum is indicative of four coordinate tin in solution.

The infrared spectrum, however, shows that the NH_2 group is involved in hydrogen bonding.

The ^1H N.M.R. results indicate that the preferred conformer is (I). It is apparent that the chemical shift of the $-SCH_2-$ protons is markedly affected by the tributyltin moiety in comparison with the spectrum of the free ligand. This effect is probably due to the electronegativity of the tributylstannyl group (10,11).

2. N-Acetyl L-Cysteinato (S,O)-bis(tri-*n*-butyl stannane)(IV)

The ^{13}C N.M.R. spectrum of a solution *ca.* 30% w/w (in $CDCl_3$) and the Mössbauer spectrum at liquid N_2 temperature show that the n-Bu_3Sn-S moiety is four coordinate about tin and the n-Bu_3Sn-O grouping is similar to that in tributyltin carboxylates. In dilute solution, the molecular weight corresponds to a nomomer while infrared and ^1H N.M.R. spectra reveal the presence of intermolecular hydrogen bonding. Progressive dilution causes changes in the ^1H N.M.R. spectral peaks and the predominance of rotational isomer(III) in a 15% w/w solution may be deduced.

The ν(C=O) values in both solid and solution infrared spectra compare well with those from structures containing chelating carboxylate groups. A dimeric formulation (structure IV), with association *via* hydrogen bonding between the NH and CO groups of neighbouring molecules is consistent with the solution infrared spectra. Such a structure would be consistent with the high residence time observed for isomer (III). The dihedral angle (*ca.* 30^o) estimated from the ^1H N.M.R. data is also consistent with this model, in which the NH-CH fragment can move into a position to allow the tributylstannyl groups of the two molecules to be furthest apart.

The hydrogen bonding association in solution is fairly weak (as shown by its disappearance below 12% w/w), but in the solid such association is probably more extensive. The structure of the compound may therefore be represented by Fig. 5.

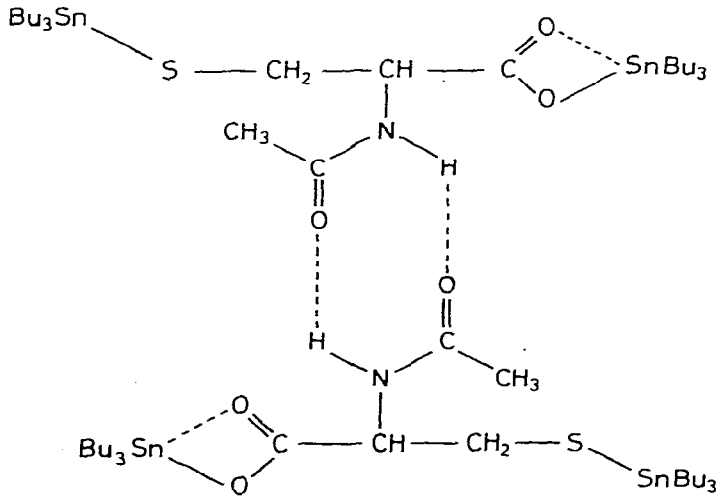


Fig. 5 Structure of $(n\text{-}Bu_3Sn)_2$(N-acet L-cyst).

3. α-Glutamyl cysteinato-glycinato(S-,O-)bis(tri-*n*-butylstannane) (IV)

For this particularly interesting complex, the infrared spectrum shows the organotin entities are bonded to the cysteine and glycine residues. One tin atom is four coordinate and the other pentacoordinate, as shown by both ^{13}C N.M.R. and Mössbauer spectra. The occurrence of intramolecular association is shown by the infrared spectrum, molecular weight determinations, and indicated by the increased area of the outer doublet in the Mössbauer spectrum. The infrared spectrum rules out carboxylate bridging or intermolecular hydrogen bonding and shows that the strong association observed in dilute solutions is due to N→Sn coordination.

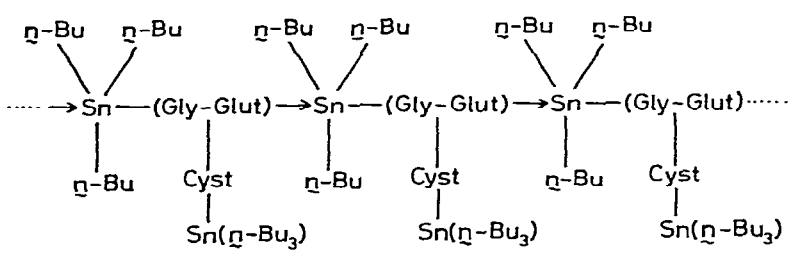
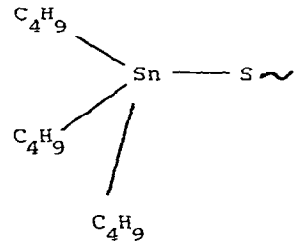
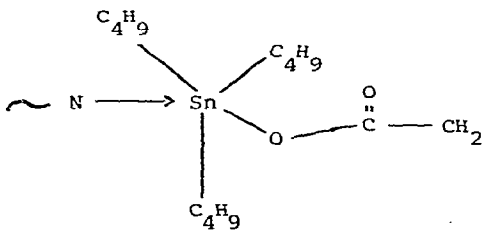


Fig.6 Structure of $(n\text{-}Bu_3Sn)_2SG$.

It is therefore proposed that the organotin units consist of:



[Cysteine residue]



[Glycine residue]

Overall, the structure may be written as in Fig. 6.

ACKNOWLEDGEMENTS

We express our thanks to Dr. J. Cashion of Monash University, for the Mössbauer spectra. G.D. acknowledges receipt of a Commonwealth of Australia Postgraduate Research Award.

REFERENCES

1. B.Y.K. Ho and J.J. Zuckerman, Inorg. Chem., 12, 1552, (1973).
2. L. Pellerito, M.T. LoGuidice, G. Ruisi, N. Bertazzi and R. Barbieri, Inorg. Chim. Acta, 17, L21, (1976).
3. W.T. Hall and J.J. Zuckerman, Inorg. Chem., 16, 1239, (1977).
4. W.N. Aldridge in "Organotin Compounds: New Chemistry and Applications" (J.J. Zuckerman, Ed.), Advances in Chemistry Series, Vol. 151, pp.186-195. American Chemical Society, Washington, D.C. 1976.

5. P.N. Magee, H.B. Stone and J.M. Barnes, J. Path. Bact., 73, 107, (1957).

6.(a) B.G. Farrow and A.P. Dawson, Eur. J. Biochem., 86, 85, (1978).

(b) K. Cain, M.D. Partis and D.E. Griffiths, Biochem. J., 166, 593, (1977).

7. J.G.A. Luijten in "Organotin Compounds" (A.K. Sawyer, Ed.), Vol.3, p.93, Marcel Dekker Inc., New York, NY, (1972).

8. G. Domazetis, R.J. Magee and B.D. James, J. Organometal. Chem., 162, 239, (1978).

9. G. Domazetis, R.J. Magee and B.D. James, Inorg. Chim. Acta, 32, L48, (1979).

10. G. Domazetis, R.J. Magee and B.D. James, J. Organometal Chem., 148, 339, (1978).

11. K.G.R. Pachler, Spectrochim. Acta, 20, 581 (1964).

12. W.G. Schneider in "Hydrogen Bonding" (D. Hadzi, Ed.) Pergamon Press, New York, pp.55-69, (1959).

13. W.A. Thomas, Ann. Repts. NMR Spectros., 6B, 1, (1976).

14. V. Madison and J. Schellman, Biopolymers, 9, 511, (1970).

15. V.F. Bystrov, S.L. Portnova, T.A. Balashova, V.I. Tsetlin, V.T. Ivanov, P.V. Kostetzky and Yu. A. Ovchinnikov, Tetrahedron Letts., 5283, (1969).

16. J. Feeney, P. Parktington and G.C.K. Roberts, J. Mag. Res., 13, 268 (1974).

17. R.A. Newmark and M.A. Miller, J. Phys. Chem., 75, 505 (1971).

18. K.D. Bartle, J.C. Fletcher, D.W. Jones and R.L'Amie, Biochim. Biophys. Acta., 160, 106 (1968).

19. J.J. Zuckerman, Adv. Organometal. Chem., 9, 22 (1970).

20. G.M. Bancroft and R.H. Platt, Adv. Inorg. Chem. Radiochem., 15, 59 (1972).

21. G.M. Bancroft, V.G. Kumar Das, T.M. Sham and M.G. Clark, J.C.S. Chem. Comm., 236 (1974).

22. P.G. Harrison, R.C. Phillips and E.W. Thornton, J.C.S. Chem. Comm., 603 (1977).

23. G.F. Svatos, C. Curran and J.V. Quagliano, J. Amer. Chem. Soc., 77, 6159 (1955).

24. J.F. Pearson and M.A. Slifkin, Spectrochim. Acta., 28A, 2403 (1972).

25. N. Sheppard, in "Hydrogen Bonding", (D. Hadzi, Ed.), Pergamon Press, New York, pp.85-105, (1959).

26. C.M. Huggins and G.C. Pimentel, J. Phys. Chem., 60, 1615 (1956).

27. S. Mizushima, T. Shimanouchi, M. Tsuboi, T. Sugita, E. Kato and E. Kondo, J. Amer. Chem. Soc., 73, 1330 (1951); ibid, 75, 1863 (1953).

28. R.L. Wener, J.K. Haken and D.T. Heggie, Spectrochim. Acta, 29A, 1509 (1973).

29. M. Arnaudov, L. Shishkova, A. Dobrev and C. Ivanov, Spectrochim. Acta., 33A, 437 (1977).

30. S.T. Chow, C.A. McAuliffe and B.J. Sayle, J. Inorg. Nucl. Chem., 37, 451 (1975).

31. N.W. Alcock and R.E. Timms, J. Chem. Soc. A, 1876 (1968).

32. C.H. Stapfer and R.H. Herber, J. Organometal. Chem., 56, 175 (1973).

33. B.F.E. Ford and J.R. Sams, J. Organometal. Chem., 21, 345 (1970).