Synthesis and Spectroscopic Studies of Inorganic Tin Derivatives of Amino-acids and their Esters

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The nature of the product obtained on reacting $SnCl_2$ with sulphur-containing amino-acids is shown to depend on the reaction conditions. Eleven new inorganic tin(II) or tin(IV) derivatives of sulphur-containing amino-acids and their esters are reported. Three tin(II) complexes of amino-acids that have exclusively Sn–O bonds have also been prepared. The bonding in these compounds is discussed in terms of their i.r. and ^{119}Sn Mössbauer spectroscopic data. Infrared spectra suggest the presence of co-ordination to Sn by the amino-N atoms.

ALTHOUGH organotin derivatives of amino-acids have been the subject of recent interest,[1–5] there has been little work on the corresponding inorganic tin compounds. The only previous reports are by Hall and Zuckerman,[6] on bis(glycinato)tin(II), $Sn(O_2CCH_2NH_2)_2$, by Sumarokova *et al.*,[7,8] on a number of adducts of tin(IV) or tin(II) chloride with glycine, alanine, and leucine, and by Pellerito *et al.*[9] on tin(IV) and tin(II) derivatives of dipeptides. A knowledge of the binding affinities of inorganic tin(II) and tin(IV) compounds for various amino-acid sites is of importance in understanding those applications which involve their use in proteinaceous materials, including flame-resist treatments for woollen fabrics,[10] possible cross-linking agents for photographic gelatin,[11] and radiopharmaceutical scanning agents.[12]

We now report on an extension of our preliminary studies [13] of tin(II) and tin(IV) derivatives of amino-acids and their esters. Fourteen new compounds are described and their structures and bonding discussed in terms of their ^{119}Sn Mössbauer and i.r. data.

EXPERIMENTAL

The reactions between anhydrous $SnCl_2$ and a number of sulphur-containing amino-acids and their esters are studied. The types of product obtained are shown in the Scheme.

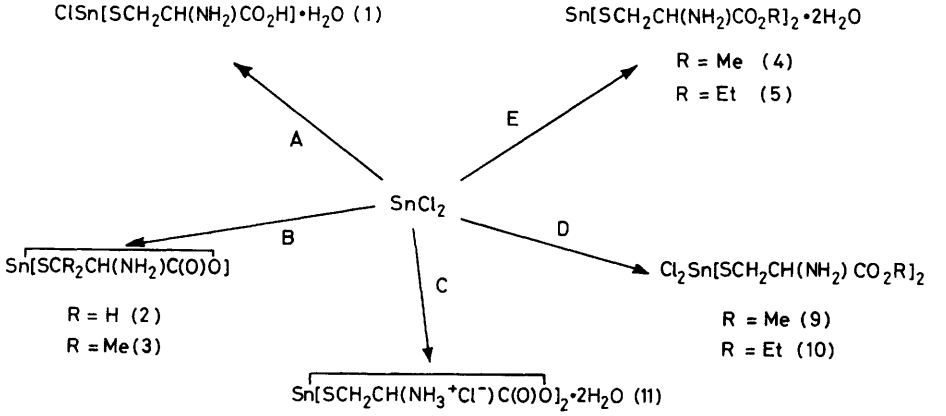
The nature of the products obtained from the aqueous tin(II) chloride/sulphur-containing amino-acid systems depends upon the conditions of the preparation. When concentrated aqueous solutions of tin(II) chloride and L-cysteine are mixed in an equimolar ratio, *monochloro*-(*cysteinato*-S)*tin*(II) *monohydrate* (1) is precipitated as a pale yellow powder (reaction A).

However, when dilute aqueous solutions of L-cysteine or DL-penicillamine hydrochloride (1 mol) are neutralised with sodium bicarbonate solution, followed by the addition of aqueous tin(II) chloride (1 mol), cyclic tin(II) derivatives, (*cysteinato*-OS)*tin*(II) (2) and (*penicillaminato*-OS)*tin*(II) (3), are formed as white and pale brown precipitates respectively (reactions B). The preparation of the L-cysteine derivative (2) was also reported recently by Llopiz and Maire.[14]

An aqueous mixture of L-cysteine (2 mol) and tin(II) chloride (1 mol) allowed to evaporate to dryness at room temperature over 3 d gives the glassy yellow product *bis*-(*cysteinato*-OS)*tin*(IV) *dihydrochloride dihydrate* (11) (reaction C).

When methanolic solutions of tin(II) chloride (1 mol) and L-cysteine methyl (or ethyl) ester hydrochloride (2 mol) are mixed and allowed to stand for 2 d, colourless crystals of the tin(IV) complexes *bis*(O-*alkyl* *cysteinato*-S)*dichlorotin*(IV) (9, 10), are deposited (reactions D). The methyl derivative can also be prepared directly from a tin(IV) compound by allowing a methanolic mixture of bis(acetylacetonato)-dichlorotin(IV) [15] (1 mol) and L-cysteine methyl ester hydrochloride (2 mol) to stand for 2 d.

An aqueous mixture of tin(II) chloride (1 mol) and L-cysteine methyl (or ethyl) ester hydrochloride (2 mol) neutralised with aqueous sodium hydroxide gives a white precipitate of *bis*(O-*alkyl* *cysteinato*-S)*tin*(II) *dihydrate* (4, 5) (reactions E).



SCHEME Synthetic routes to tin(II) and tin(IV) derivatives of sulphur-containing amino-acids

The new compounds (1), (4), and (11) are dehydrated by controlled heating to give three further new tin derivatives: *monochloro*(*cysteinato*-S)*tin*(II) (12), *bis*(O-*methyl cysteinato*-S)*tin*(II) (13), and *bis*(*cysteinato*-OS)*tin*(IV) *dihydrochloride* (14), respectively.

The reactions of anhydrous tin(II) chloride with tributylstannyl esters of L-valine, L-leucine, and L-β-phenylalanine have also been studied. When a solution of tin(II) chloride (1 mol) in acetone is added slowly to a stirred solution of tributyltin valinate,[16] $Bu_3Sn[O_2CCH(NH_2)CHMe_2]$ (2 mol), in toluene, a white precipitate of *bis*(*valinato*)*tin*(II), $Sn[O_2CCH(NH_2)CHMe_2]_2$ (6), is formed immediately. *Bis*(*leucinato*)*tin*(II) (7) and *bis*(β-*phenylalaninato*)*tin*(II) (8), both white powders, are prepared by a similar method.

Microanalytical data for C, H, N, S, and Cl were obtained by the University College London, Microanalytical Laboratory. Tin analyses were performed as follows.

(*a*) *Non-sulphur-containing derivatives*. The samples were dissolved in dilute HCl, tin(IV) was reduced to tin(II) using nickel metal, and the total tin was determined volumetrically with potassium iodate–potassium iodide solution using starch as indicator.

(*b*) *Sulphur-containing derivatives*. The samples were wet-ashed in concentrated HNO_3–H_2SO_4 and, after reduction of tin(IV) to tin(II) with nickel metal, total tin was determined as above.

^{119}Sn Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer (Cryophysics Ltd., Oxford), with a 512-channel data store. A 15-mCi

TABLE 1

Inorganic tin derivatives of amino-acids and their esters

Compound	Yield/%	M.p.[a]/°C	Analysis[b] (%) C	H	N	S	Cl	Sn	H_2O[c]
(1) $ClSn[SCH_2CH(NH_2)CO_2H]\cdot H_2O$	30	119	12.6 (12.3)	2.6 (2.8)	4.8 (4.8)	10.5 (11.0)	12.4 (12.1)	41.6 (40.6)	6.0 (6.2)
(2) $Sn[SCH_2CH(NH_2)C(O)O]$	80	190	15.0 (15.1)	2.2 (2.1)	5.8 (5.9)	13.1 (13.5)		49.2 (49.9)	
(3) $Sn[SCMe_2CH(NH_2)C(O)O]$	50	210	22.4 (22.6)	3.6 (3.4)	5.2 (5.3)	11.3 (12.1)		43.6 (44.6)	
(4) $Sn[SCH_2CH(NH_2)CO_2Me]_2\cdot 2H_2O$	20	158	22.6 (22.7)	4.1 (4.8)	6.7 (6.6)	14.4 (15.1)		28.2 (28.1)	9.0 (8.5)
(5) $Sn[SCH_2CH(NH_2)CO_2Et]_2\cdot 2H_2O$	35	142	26.2 (26.6)	4.7 (5.4)	6.4 (6.2)	13.3 (14.2)		27.0 (26.3)	7.5 (8.0)
(6) $Sn[O_2CCH(NH_2)CHMe_2]_2$	50	253	34.1 (34.2)	6.7 (5.8)	7.2 (8.0)			33.2 (33.8)	
(7) $Sn[O_2CCH(NH_2)CH_2CHMe_2]_2$	80	245	38.1 (38.0)	7.3 (6.4)	7.5 (7.4)			29.3 (31.3)	
(8) $Sn[O_2CCH(NH_2)CH_2Ph]_2$	95	195	49.1 (48.4)	5.1 (4.5)	6.3 (6.3)			29.7 (26.6)	
(9) $Cl_2Sn[SCH_2CH(NH_2)CO_2Me]_2$	20	182	20.8 (21.0)	3.4 (3.5)	6.4 (6.1)	14.0 (14.0)	15.5 (15.5)	25.2 (25.9)	
(10) $Cl_2Sn[SCH_2CH(NH_2)CO_2Et]_2$	35	160	24.6 (24.7)	4.2 (4.2)	5.8 (5.8)	12.6 (13.2)	14.7 (14.6)	24.3 (24.4)	
(11) $Sn[SCH_2CH(NH_3^+Cl^-)C(O)O]_2\cdot 2H_2O$[d]	100	145	16.2 (15.5)	3.6 (3.5)	6.2 (6.0)	14.0 (13.8)	14.9 (15.2)	24.7 (25.5)	7.0 (7.7)

[a] All compounds decompose without melting. [b] Calculated values are given in parentheses. [c] Thermogravimetric analysis values given represent percentage weight losses due to water of hydration. [d] Hydrogen-1 n.m.r. (D_2O): τ 4.65 (s, 10 H, NH_3^+ and H_2O), 5.08 (t, 2 H, CH), and 6.00 (s, br, 4 H, CH_2).

All of the above products were dried *in vacuo* at room temperature and their analytical and physical data are presented in Table 1.

Two compounds were prepared in this work for comparison with the new tin derivatives. These are described below.

(*i*) (*Penicillaminato*-OS)*lead*(II).—An aqueous solution of DL-penicillamine hydrochloride (1 mol) was neutralised with sodium bicarbonate solution, followed by the addition of aqueous lead(II) nitrate (1 mol). The white precipitate obtained was collected, washed with water, and dried in air, yield 65%, m.p. 216 °C (decomp.) (Found: C, 16.5; H, 2.6; N, 3.8; S, 8.6. Calc. for $C_5H_9NO_2PbS$: C, 16.9; H, 2.6; N, 3.9; S, 9.0%).

(*ii*) *Dichlorobis*(2-*pyridinethiolato*)*tin*(IV).—This compound was prepared from tin(II) chloride by the method of Masaki and Matsunami.[17] The pale yellow powder obtained was washed with 1,2-dichloroethane and dried in air, yield 95%, m.p. 276 °C (decomp.) (Found: C, 29.0; H, 2.2; Cl, 17.8; N, 6.8; S, 15.6. Calc. for $C_{10}H_8Cl_2N_2S_2Sn$: C, 29.3; H, 2.0; Cl, 17.3; N, 6.8; S, 15.6%).

$Ba^{119m}SnO_3$ source was used at room temperature and the samples were packed in Perspex discs and cooled to 80 K. The experimental error in the measured values of isomer shift (δ) and quadrupole splitting (Δ) parameters is ±0.05 mm s^{-1}. Infrared spectra were recorded as Nujol mulls on Grubb-Parsons Spectromaster Mk. 1 and DM4 instruments. Hydrogen-1 n.m.r. spectra were recorded on D_2O solutions (using an external $SiMe_4$ standard) at 33 °C, on a Perkin-Elmer R10 60-MHz instrument. Thermogravimetric analyses were carried out on a Stanton Redcroft 750 instrument. The ^{119}Sn Mössbauer data for the new tin derivatives and for some related compounds are given in Table 2 and the i.r. data for the new products are in Table 3.

RESULTS AND DISCUSSION

Tin(II) *Derivatives of Sulphur-containing Amino-acids*.—The i.r. spectra of compounds (1)—(5) (Table 3) all show one or two strong bands in the range 340—376 cm^{-1} due to Sn–S stretching modes [*cf.* $Sn(SMe)_2$, which shows [18] ν_{asym}(Sn–S) at 361 cm^{-1}]. In addition, the

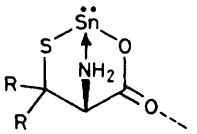
TABLE 2

^{119}Sn Mössbauer data

Compound	δ/ mm s^{-1}	Δ/ mm s^{-1}
(1) $ClSn[SCH_2CH(NH_2)CO_2H]\cdot H_2O$	3.52	1.32
(2) $Sn[SCH_2CH(NH_2)C(O)O]$	3.19	1.93
(3) $Sn[SCMe_2CH(NH_2)C(O)O]$	3.04	2.43
(4) $Sn[SCH_2CH(NH_2)CO_2Me]_2\cdot 2H_2O$	3.12	1.98
(5) $Sn[SCH_2CH(NH_2)CO_2Et]_2\cdot 2H_2O$	3.04	1.88
(6) $Sn[O_2CCH(NH_2)CHMe_2]_2$	3.03	2.05
(7) $Sn[O_2CCH(NH_2)CH_2CHMe_2]_2$	2.95	2.05
(8) $Sn[O_2CCH(NH_2)CH_2Ph]_2$	2.95	2.10
(9) $Cl_2Sn[SCH_2CH(NH_2)CO_2Me]_2$	0.85	1.34
(10) $Cl_2Sn[SCH_2CH(NH_2)CO_2Et]_2$	0.79	1.27
(11) $Sn[SCH_2CH(NH_3^+Cl^-)C(O)O]_2\cdot 2H_2O$	0.72	0.99
(12) $ClSn[SCH_2CH(NH_2)CO_2H]$	3.50	1.30
(13) $Sn[SCH_2CH(NH_2)CO_2Me]_2$	3.18	1.95
(14) $Sn[SCH_2CH(NH_3^+Cl^-)C(O)O]_2$	0.71	0.91
(15) $SnCl_2$	4.17 [a]	0.00 [a]
(16) $Sn(SC_7H_{15})_2$	3.06 [b]	1.69 [b]
(17) $Sn(SCH_2CH_2O)$	3.08 [c]	1.58 [c]
(18) $Sn(O_2CCH_2NH_2)_2$	3.06 [d]	1.88 [d]
(19) $Cl_2Sn(SC_5H_4N\text{-}2)_2$ [e]	0.80	0.68

[a] S. R. A. Bird, J. D. Donaldson, and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1972, 1950. [b] Ref. 18. [c] Ref. 22. [d] Ref. 6. [e] F. P. Mullins, *J. Inorg. Nucl. Chem.*, 1979, **41**, 463, reports δ = 0.81 mm s^{-1} and Δ = 0.93 mm s^{-1}.

cyclic tin(II) esters (2) and (3) of L-cysteine and DL-penicillamine show ν_{asym}(C=O) bands at 1 639 and 1 587 cm^{-1} respectively and $\nu(NH_2)$ doublets in the region 3 077—3 205 cm^{-1}. These may be weakly associated by intermolecular bridging carbonyl groups (Figure 1), as demonstrated crystallographically for the lead(II) analogue, $Pb[SCMe_2CH(NH_2)C(O)O]$, for which ν_{asym}(C=O) is 1 587 cm^{-1}. The lead compound also contains an intramolecularly co-ordinated $-NH_2$ group [19] and shows $\nu(NH_2)$ at 3 077 and 3 155 cm^{-1}.



R = H or Me

FIGURE 1 Proposed structure of the cyclic tin(II) derivatives (2) and (3)

The asymmetric carbonyl stretching band in the cyclic penicillamine derivative is lower than that in the cysteine complex, indicating a higher degree of association, possibly due to a greater inductive effect of the electron-donating methyl groups in the former compound. A strong band at 573 cm^{-1} in the cysteine derivative (and at 552 cm^{-1} in the penicillamine analogue) is assigned to ν(Sn–O) [*cf.* $Sn(OMe)_2$, which shows [20] ν(Sn–O) at 570 cm^{-1}].

The monochlorotin(II) compound (1) shows a low carbonyl stretching frequency (1 587 cm^{-1}), which may be due to weak intermolecular bridging, and a $\nu(NH_2)$ band in the co-ordinated amino-region which is broadened, presumably due to extensive hydrogen bonding. Hydrogen bonding involving a co-ordinated amino-group has also been observed in glycylglycinatodiphenyltin(IV).[5] The alternative formulations of compound (1) as $Sn[SCH_2CH(NH_3^+Cl^-)C(O)O]\cdot H_2O$, the hydrochloride, or as the zwitterion $ClSn[SCH_2CH(NH_3^+)C(O)O^-]\cdot H_2O$, are considered unlikely because of the insolubility of the product in water.

An interesting feature of the ^{119}Sn Mössbauer data (Table 2) is the effect of replacement of one or more Cl ligands in $SnCl_2$ by amino-acid groups which results in a large drop in the values of chemical isomer shifts. This drop means that the tin uses more of its *s* electron density in bonding to the amino-acid residues than to chlorine atoms. Presumably, replacement of one of the Cl atoms in $SnCl_2$ by a cysteine ligand results in the replacement of two short Sn–Cl bonds in the tin(II) environment [21] in tin(II) chloride by an Sn–S bond and an N→Sn interaction. The greater asymmetry of the tin environment in the cysteine derivative (1) compared with that in $SnCl_2$ is reflected in the appearance of a resolvable quadrupole splitting in its Mössbauer spectrum. The ^{119}Sn Mössbauer data for the anhydrous compound $ClSn[SCH_2CH(NH_2)CO_2H]$ (12) are identical, within experimental error, to those obtained for the hydrated material, suggesting that the water of hydration present does not enter the co-ordination sphere of the tin.

The cyclic tin(II) derivatives, containing one Sn–S bond, one Sn–O bond, and an N→Sn interaction, have similar Mössbauer chemical isomer shifts to that of $Sn(SCH_2CH_2O)$ (17). However, the value for the pencillamine complex (3) is significantly lower than that for the cysteine analogue (2). This is presumably due to a greater degree of association in the penicillamine derivative resulting in a greater tendency towards pyramidal four-co-ordination and a reduction of *s* electron density about the tin nucleus. This tendency also gives rise to further distortion of the tin(II) environment so that the penicillamine derivative shows a much larger value of Δ than the cysteine complex.

Attempts to prepare an analogous cyclic tin(II) ester of DL-homocysteine, $HS(CH_2)_2CH(NH_2)CO_2H$, were unsuccessful, possibly due to instability of the seven-membered tin(II) heterocycle. It was also found that the cyclic tin(II) derivatives of 3-mercaptopropionic acid, $HSCH_2CH_2CO_2H$, and 2-mercaptoacetic acid, $HSCH_2CO_2H$, could not be synthesised, which suggests that the compounds (2) and (3) may be stabilised by the presence of the intramolecularly co-ordinating amino-group. In line with this, Harrison and Stobart [18] found that $Sn(SCH_2CH_2O)$ was not formed in the reaction between 2-mercaptoethanol and bis(η^5-methylcyclopentadienyl)tin(II) in benzene, although tin(II) heterocycles containing exclusively Sn–S bonds could be prepared by a similar route. Honnick and Zuckerman [22] have, however, recently prepared $Sn(SCH_2CH_2O)$ from $Sn(OMe)_2$ and 2-mercaptoethanol.

Infrared spectra of the tin(II) derivatives of the L-

TABLE 3

Infrared data for the inorganic tin derivatives [a]

Compound	$\nu(NH_2)$	$\nu(C{=}O)$	$\delta(NH_2)$	$\nu(Sn{-}O)$	$\nu(Sn{-}S)$	$\nu(Sn{-}Cl)$
(1) $ClSn[SCH_2CH(NH_2)CO_2H]\cdot H_2O$ [b]	3 175—3 012	1 587	1 538		373	365
(2) $Sn[SCH_2CH(NH_2)C(O)O]$	3 205 3 115	1 639	1 587	573	376 345	
(3) $Sn[SCMe_2CH(NH_2)C(O)O]$	3 145 3 077	1 587	1 538	552	365 340	
(4) $Sn[SCH_2CH(NH_2)CO_2Me]_2\cdot 2H_2O$ [b]	3 155 3 077	1 709	1 600 1 563		368	
(5) $Sn[SCH_2CH(NH_2)CO_2Et]_2\cdot 2H_2O$ [b]	3 155 3 086	1 709	1 613 1 563		350	
(6) $Sn[O_2CCH(NH_2)CHMe_2]_2$	3 125—3 012	1 587	1 613 1 563	541		
(7) $Sn[O_2CCH(NH_2)CH_2CHMe_2]_2$	3 125—3 030	1 587	1 613	531		
(8) $Sn[O_2CCH(NH_2)CH_2Ph]_2$	3 077—3 012	1 550	1 613	522		
(9) $Cl_2Sn[SCH_2CH(NH_2)CO_2Me]_2$	3 145 3 067	1 724	1 563		370 356	303
(10) $Cl_2Sn[SCH_2CH(NH_2)CO_2Et]_2$	3 175 3 096	1 724	1 563		365 346	303
(11) $Sn[SCH_2CH(NH_3{}^+Cl^-)C(O)O]_2\cdot 2H_2O$ [b]	3 257—3 030	1 587	1 613 1 538	526	368	

[a] Data given in cm^{-1}. [b] Broad band observed at *ca.* 3 450 cm^{-1} due to $\nu(O{-}H)$.

cysteine esters (4) and (5) show a free ester carbonyl vibration (at 1 709 cm^{-1}) and a doublet in the range 3 077—3 155 cm^{-1} attributable to co-ordinated amino-residues. The Mössbauer isomer shifts for these derivatives are similar to the value quoted for the compound $Sn(SC_7H_{15})_2$ (16), the environment of the tin presumably being dominated by the two directly bound sulphur atoms in each case. The anhydrous compound $Sn[SCH_2CH(NH_2)CO_2Me]_2$ (13) shows similar Mössbauer parameters to the hydrated derivative (4), indicating that the water molecules present do not co-ordinate to the tin atom.

The tin(II)–sulphur bonded derivatives are found to be relatively stable to oxidation and hydrolysis in air. In particular, the cyclic tin(II) esters (2) and (3) are found to be stable to atmospheric oxidation, as shown by the absence of a tin(IV) resonance in the Mössbauer spectra of samples which are several months old. In line with this observation, several heterocyclic tin(II) compounds containing Sn–O bonds have also been found to possess a high degree of stability.[22]

Tin Derivatives of Non-sulphur-containing Amino-acids.—The inorganic tin(II) and tin(IV) derivatives of non-sulphur-containing amino-acids could not be prepared from $SnCl_2$, SnO, or $SnCl_4$ in aqueous or methanolic media. Hall and Zuckerman [6] have, however, reported the synthesis of bis(glycinato)tin(II) from tin(II) chloride and glycine in methanol, although they were unable to prepare derivatives of higher amino-acids by the same route. Similarly, our attempts to prepare 1 : 1 or 1 : 2 adducts of $SnCl_2$ or $SnCl_4$ with glycine ethyl ester hydrochloride or L-histidine methyl ester dihydrochloride in methanol were unsuccessful, although Sumarokova *et al.*[7,8] claim to have synthesised several tin(IV) and tin(II) adducts of simple amino-acids, in which the organic ligand was co-ordinated to tin *via* the carbonyl group. We now report the successful syntheses of tin(II) derivatives of L-valine, compound (6), L-leucine, compound (7), and L-β-phenylalanine, compound (8), by an exchange reaction between $SnCl_2$ and the corresponding tributylstannyl ester. Similar reactions of $SnCl_2$ with di- and tri-organotin(IV) compounds have been reported.[23,24] Attempts to prepare the inorganic tin(IV) analogues by this route were unsuccessful, however.

The i.r. spectra of compounds (6)—(8) all show a strong band in the range 522—541 cm^{-1} that can be assigned to $\nu(Sn{-}O)$, low carbonyl stretching frequencies (1 550—1 587 cm^{-1}), which may be due to weak intermolecular bridging, and $\nu(NH_2)$ bands in the co-ordinated amino-region, which are broadened due to extensive hydrogen bonding. ^{119}Sn Mössbauer parameters of the new tin(II) derivatives (6)—(8) are similar to those for bis(glycinato)tin(II) (18). The low values of δ imply extensive use of *s* electron density in the bonding of the tin to the amino-acid ligands and the large values of Δ are indicative of highly asymmetric tin(II) environments. The appearance of a tin(IV) peak in the Mössbauer spectra of all but freshly prepared samples shows that the compounds oxidise fairly rapidly in air.

The direction of the principal component of the electric field gradient, V_{zz}, in all of the new tin(II) derivatives, compounds (1)—(8), (12), and (13), could lie either along the lone-pair direction or, if the N→Sn interaction is weak, along the direction of that interaction.

Tin(IV) Derivatives of Sulphur-containing Amino-acids.—Three tin(IV) derivatives of L-cysteine and its esters are prepared in this work from $SnCl_2$. The dichlorotin(IV) compounds (9) and (10) were previously thought to be formed [13] by oxidative addition of the tin(II) chloride to the disulphide bond in L-cystine dialkyl ester dihydrochloride (which may be formed by oxidation of the cysteine ester). However, no product is obtained from a methanolic mixture of $SnCl_2$ and L-cystine dimethyl ester dihydrochloride and, further-

more, $SnCl_2$ does not add to the disulphide bond in DL-α-lipoic acid, $\overline{SSCH_2CH_2}CH(CH_2)_4CO_2H$, although tin(II) compounds have previously been found to react with diaryl disulphides to give tin(IV) products.[17,25]

An alternative mechanism for the formation of compounds (9) and (10) can be proposed because $Cl_2Sn(acac)_2$ is known [17] to react with 2-pyridinethiol to form dichlorobis(2-pyridinethiolato)tin(IV), $Cl_2Sn(SC_5H_4N\text{-}2)_2$, and, similarly, in this work we found it to react with L-cysteine methyl ester hydrochloride in methanol to

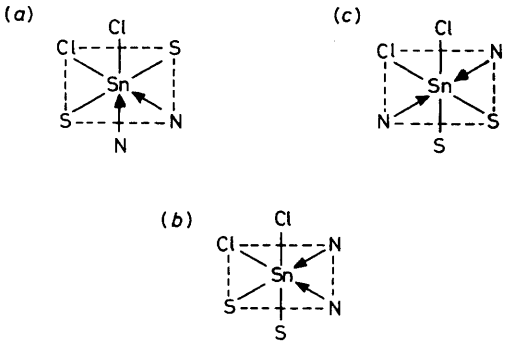


FIGURE 2 The three possible arrangements of the ligands about tin, assuming *cis* chlorines, for the tin(IV) derivatives (9) and (10)

form $Cl_2Sn[SCH_2CH(NH_2)CO_2Me]_2$ in 40% yield. Aged solutions of $SnCl_2$ in methanol are likely to contain tin(IV) oxo-species of the type $[Cl_3Sn(OH)(H_2O)]_2\cdot 4H_2O$ [26] or $SnOCl_2$ [27] and these could react in a similar manner to form the tin(IV) product. This would account for the low yields obtained from the reactions of $SnCl_2$ with the L-cysteine ester hydrochlorides in methanol. In addition to Sn–S stretching modes in the region 346—370 cm^{-1}, i.r. spectra of the dichlorotin(IV) complexes (9) and (10) show a broad single band at 303 cm^{-1}, attributable to ν(Sn–Cl) [*cf.* $Cl_2Sn(SC_5H_4N\text{-}2)_2$, which shows [17] bands at 300 and 310 cm^{-1}]. It is likely that the broad single band observed is an unresolved doublet resulting from the overlap of the symmetric and asymmetric Sn–Cl stretching modes, as in $Cl_2Sn(acac)_2$, in which the halogen atoms are known from *X*-ray crystallography [28] to be in *cis* positions and which shows [15] a single band at 344 cm^{-1}. Further strong bands observed in the far-i.r. spectra of (9) and (10), at 277 and 282 cm^{-1} respectively, are unlikely to be Sn–Cl vibrational modes.[17] In the near-i.r. region, these complexes show a doublet in the range 3 067—3 175 cm^{-1}, indicative of a co-ordinated $-NH_2$ residue, and a single band at 1 724 cm^{-1}, due to a free ester carbonyl group {*cf.* $Me_2ClSn[SCH_2CH(NH_2)CO_2Et]$, which is known [2] to contain a chelating amino-group and a free carbonyl moiety, and which shows [3] ν(NH_2) at 3 243 and 3 309 cm^{-1} and ν_{asym}(C=O) at 1 733 cm^{-1}}.

^{119}Sn Mössbauer chemical isomer shifts of the dichlorotin(IV) derivatives are similar to the value obtained for $Cl_2Sn(SC_5H_4N\text{-}2)_2$ (19), which contains [29] an octahedrally co-ordinated tin atom, with a *cis* Cl_2Sn unit, *trans* S atoms and *cis* N atoms [Figure 2(*a*)]. The larger values of Δ, however, suggest that the compounds (9) and (10) have different conformations to $Cl_2Sn(SC_5H_4N\text{-}2)_2$. The larger crystal fields would arise if there was a *trans* distribution of these weaker N→Sn interactions [Figure 2(*c*)].

The mechanism of formation of the water-soluble tin(IV) compound (11) is unclear but it is likely to involve an initial oxidation of the $SnCl_2$ to a tin(IV) oxo-species. An attempt to prepare the analogous DL-homocysteine derivative by a similar route was unsuccessful, presumably due to the instability of the seven-membered ring system, as found for the tin(II) case. Additionally, a neutral tin(IV)–cysteine derivative could not be prepared by neutralisation of an aqueous mixture of $SnCl_4$ and L-cysteine, using aqueous sodium bicarbonate. The near-i.r. spectrum of compound (11) shows a low carbonyl stretching frequency and a broad ν(NH_3^+) band, the former due to weak intermolecular bridging and the latter to extensive hydrogen bonding; ν(Sn–O) and ν(Sn–S) can be clearly discerned at lower frequencies. ^{119}Sn Mössbauer data for the anhydrous tin(IV) derivative (14) are similar to those obtained for the hydrated compound, indicating non-co-ordination of the water molecules to the tin.

The ^1H n.m.r. spectrum of compound (11) in D_2O solution shows a large downfield shift of the CH_2 ($\Delta\tau$ = −0.43 p.p.m.) and CH ($\Delta\tau$ = −0.42 p.p.m.) protons, relative to free L-cysteine, with the signals existing as a very broad singlet and a broad triplet respectively. A similar downfield shift has been observed previously by Carty [30] for the H^γ protons in $MeHg[S(CH_2)_2CH(NH_3^+)\text{-}C(O)O^-]$. The NH_3^+ protons in (11) ($\Delta\tau$ = −0.12 p.p.m.) are seen as a sharp singlet, which is only slightly shifted from that in L-cysteine.

This work indicates that, as with inorganic lead(II),[19] organolead(IV),[30] and organotin(IV),[2,5,31] inorganic tin(II) and tin(IV) appear to favour binding to a combination of S, O, and N sites in amino-acids.

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