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Synthesis and spectroscopic characterization of diethyltin(IV) derivatives of dipeptides: Crystal and molecular structure of diethyltin glycyltyrosinate‡

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Dipeptide complexes of the diethyltin(IV) moiety, Et_2SnL, have been synthesized, H_2L being glycylglycine ($H_2GlyGly$), glycylalanine ($H_2GlyAla$), alanylalanine ($H_2AlaAla$), glycylvaline ($H_2GlyVal$), valylvaline ($H_2ValVal$), glycylmethionine ($H_2GlyMet$), glycyltyrosine ($H_2GlyTyr$). The crystal and molecular structure of the complex $Et_2SnGlyTyr$ has been determined by single-crystal X-ray diffraction. It consists of monomeric units, with the tin atom having a considerably distorted trigonal bipyramidal environment. The dipeptide acts as a tridentate ligand bonding the tin of the C_2Sn fragment (equatorial carbon atoms) with the peptide nitrogen atom (equatorial) and axial (monodentate) carboxyl oxygen and amino nitrogen atoms, into a monomeric unit. Bond lengths and angles are reported. Infrared spectroscopic data show the occurrence of monodentate carboxyl in all solid compounds, as well as in methanol solutions of some representative complexes. ^{119}Sn Mössbauer spectroscopic data, and their rationalization through point-charge model (literal version) calculations of the parameter nuclear quadrupole splitting (ΔE) confirm the general occurrence of trigonal bipyramidal structures of the $Et_2SnGlyTyr$ type, in the solid state, and give evidence of variations of the C–Sn–C angle in the individual Et_2SnL species. Monomers occur in CH_3OH solution as suggested by osmometric measurements. ^{13}C and ^{119}Sn NMR spectroscopic data in CD_3OD show the persistence of the solid-state structures also in the solution phase, where the order of magnitude of the C–Sn–C angles, as estimated from the coupling constants $|^1J(^{119}Sn,^{13}C)|$, corresponds to that shown by $Et_2SnGlyTyr$ in the solid state. ^{119}Sn Mössbauer parameters of $Et_2SnGlyGly$ in frozen CH_3OH solution are consistent with the assumptions from the NMR studies.

Keywords: Diorganotin dipeptides, X-ray structure determination, ^{13}C and ^{119}Sn NMR, IR, Mössbauer

INTRODUCTION

A series of diorganotin derivatives of dipeptides (R_2SnL where H_2L = dipeptide) have been found to exhibit antileukemic activity.[1-3] The molecular structure of a number of these compounds, as determined by X-ray diffraction methods, is generally characterized by tridentate bis-chelating ligands L^{2-} with two carbon atoms (of the R_2Sn moiety) and $N_{peptide}$ in the equatorial plane, and $O_{carboxylate}$ and N_{amino} in the apical positions, of a distorted trigonal bipyramidal polyhedron around tin.[4-7] Only in $(Et_2SnGlyHis)_2 \cdot MeOH$ has one of the two tin sites been found to be hexacoordinated.[8] In order to extend knowledge on these structure–biological activity relationships, it seemed worthwhile to study diethyltin compounds Et_2SnL, which show appreciable antileukemic activity.[9, 10] In this paper we report on the synthesis and structure of diethyltin derivatives of various types of dipeptides.

EXPERIMENTAL

The dipeptides were a gift from Degussa, Frankfurt, Germany. Et_2SnO was prepared from Et_2SnBr_2 and KOH in methanol; the product was

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* Further X-ray structure determination data is available from the authors.

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separated by centrifuging and was dried in vacuum after washing with MeOH. Solvents were commercial products and were dried as usual.

The new compounds listed in Table 1 were synthesized as follows.

Method I

Et_2SnO (2 mmol) and 2 mmol of the appropriate dipeptide H_2L in 30–50 cm^3 of dry methanol were reacted under reflux for 4 h; 2,2-dimethoxypropane was added to the reaction mixture to remove water of neutralization. The products, after reducing the volume of the clear reaction mixture *in vacuo* to about 5 cm^3, were precipitated as white solids by adding petroleum ether (40–60 °C) and diethyl ether 1:1 v/v.

Method II

Et_2SnCl_2 (2 mmol) was added to a solution obtained from 2 mmol of H_2L and 4 mmol of NaOMe in 30 cm^3 of methanol. After stirring for 0.5 h at room temperature, refluxing for 2 h, and separation of NaCl, the product was precipitated as in Method I, washed with diethyl ether and recrystallized several times from ethanol to remove NaCl.

Elemental analyses were carried out with an Elemental analyzer 1106 Carlo Erba, Milano (Italy). Melting points were measured in open capillaries and are uncorrected. Molecular weights were determined osmometrically in anhydrous methanol. The IR spectra were recorded on a Perkin–Elmer grating spectrometer PE 580B in KBr and CD_3OD. ^{13}C and ^{119}Sn NMR spectra were recorded in CD_3OD on a Bruker AM300 and chemical shifts were measured in ppm downfield from internal TMS and external Me_4Sn references, respectively. ^{119}Sn Mössbauer spectra were recorded by a Mössbauer spectrometer consisting of: (1) a 4096-channel analyzer (Master 4000, Laben, Milano); (2) function generator, driving unit and related electronics (Takes, Ponteranica, Bergamo); (3) linear velocity transducer (Halder, München); (4) scintillation and proportional counters (Harshaw, De Meern, The Netherlands, and Reuter–Stokes, Cleveland, respectively); (5) Mössbauer sources, $Ca^{119}SnO_3$ and $^{57}Fe(^{57}Co)$, 10–1 mCi (Radiochemical Centre, Amersham, UK).

Velocity calibration has been effected periodically by means of six-line spectra of iron metal; zero-point calibration has been obtained from room-temperature $CaSnO_3$–$CaSnO_3$ spectra. The source, at room temperature, was moving with linear velocity, constant acceleration, in a triangular waveform. The spectra of solid-state organotin complexes were taken at 77.3 K in liquid-nitrogen cryostats (AERE Harwell, Didcot, UK). The measurements on frozen solutions were carried out on 1.0–2.0 cm^3 of 36–100 mmol dm^{-3} solutions in polythene holders, according to a procedure described elsewhere.[11] Data reduction was effected conventionally by fitting the experimental data points with Laurentzian lineshapes.[11] Single crystals of Et_2SnGlyTyr were obtained by crystallization from methanol after addition of Et_2O and petroleum ether (40–60 °C). A crystal of dimensions 0.22 mm × 0.26 mm × 0.22 mm mounted on a glass fibre was used to obtain cell data, and subsequently for intensity measurements. Crystal data were as follows: $M_r = 413.04$, $a = 11.492(6)$, $b = 11.618(6)$, $c = 12.786(10)$ Å, $V = 1707(2)$ Å^3, $Z = 4$, $D_x = 1.607$ Mg m^{-3}, space group = $P2_12_12_1$. The intensities of 6550 ($1.5° \leq \theta \leq 25.0°$; $0 \leq h \leq 13$; $-13 \leq k \leq 13$; $-15 \leq l \leq 15$) reflections were measured on a Nonius CAD-4 diffractometer, with graphite-monochromated MoKα radiation, $\lambda = 0.71073$ Å, $\mu = 1.52$ mm^{-1}, $T = 291(1)$ K; $F(000) = 832$, $\omega/2\theta$ scans, scan speed 1.5–5.0 ° min^{-1} in θ. Lattice parameters are taken from a symmetry-constrained least-squares fit with 25 reflections up to $2\theta = 25.1$. The data were corrected for Lorentz polarization effects and absorption effects via ψ scans. After averaging equivalent reflections, 3008 unique reflections ($R_{int} = 0.016$) remained from which 2806 reflections with $F \geq 4.0\,\sigma(F)$ were used for the structure determination via a Patterson function, ΔF syntheses and full-matrix least-squares refinements with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for hydrogen atoms, which were placed in geometrically calculated positions (C–H 0.96 Å). Complex neutral atom scattering factors were taken from Ref. 12, refinement on F with 2806 reflections and 201 refined parameters converged at $R = 0.019$; $w = 1.0/[\sigma^2(F) + (0.0005\,F^2]$; $S = 0.89$, $wR = 0.021$, $(\Delta/\sigma)_{max} = 0.01$; there was no extinction correction. An η-refinement[13] [$\eta = 1.06(5)$] confirmed the proposed chirality. The largest peak in the final ΔF map was $\pm 0.4(2)$ e Å^{-3}. The following programs were used: Enraf–Nonius Structure Determination Package,[14] PARST,[15] SHELXTL PLUS[16] and PCK83.[17]

RESULTS AND DISCUSSION

The diethyltin derivatives of the dipeptides (Et_2SnL; **1**, **4**, **6** and **7**) listed in Table 1 were prepared by reaction of Et_2SnO with the appropriate dipeptides H_2L ($=H_2GlyVal$, $H_2GlyGly$) in methanol in a 1:1 molar ratio. The other compounds, and **1** and **4** as well, were obtained from Et_2SnCl_2 and Na_2L under similar conditions. Attempts to prepare 1:2 compounds $[Et_2Sn(HL)_2]$ by reaction of Et_2SnO and H_2L or by reaction of Et_2SnCl_2 and NaHL failed. In both cases the 1:1 compounds **1** and **4**, respectively, were obtained; the latter reaction proceeds according to Eqn [1].

$$Et_2SnCl_2 + 2\,NaHL = Et_2SnL + H_2L + 2\,NaCl \quad [1]$$

Compounds **1–7** are soluble in methanol, ethanol and DMSO but insoluble in diethyl ether, acetone and chloroform. According to molecular weight measurements the complexes are monomeric in methanol (Table 1).

In the IR spectra of the compounds (Table 2), vibrations associated with $\nu(NH_3^+)$ of the H_2L are missing, which implies the bonding of the Et_2Sn moiety to the carboxylate group. The values of $\Delta\nu = \nu_{as}(COO) - \nu_{sym}(COO)$ are in the range 200–230 cm^{-1} (Table 2), indicating that the carboxylate groups act as monodentate; bridging COO groups, which would afford a $\Delta\nu$ value <200 cm^{-1},[18] are thereby excluded. The comparison of $\nu(NH_{amino})$ of the sodium salts (3315–3410 cm^{-1}) or of matrix isolated amino acids (HGly: 3414 cm^{-1})[19] with those of the solid compounds **1–7** (3120–3260 cm^{-1}; Table 2) shows a distinct shift to lower frequencies for the latter compounds, indicating the coordination of the amino group to the central tin atom.[20] The strong band $\nu(NH_{pept})$ present in the IR spectra of the acids H_2L (3240–3320 cm^{-1}) is missing in the spectra of the complexes **1–7**, suggesting that the Et_2Sn moiety is bonded to $N_{peptide}$. This corresponds to the shift of $\nu(CO_{pept})$ of **1** and **4–7** with respect to the corresponding disodium salts (1665–1690 cm^{-1}) to lower frequencies in the range 1642–1650 cm^{-1} (Table 2). In **2** and **3**, $\nu(CO_{pept})$ is shifted, in comparison with **1** and **4–7**, markedly to lower frequencies (1632–1625 cm^{-1}; Table 2), indicating additional $CO_{pept} \rightarrow Sn$ coordination in the solid state.

Table 1 Analytical data for diethyltin derivatives of dipeptides Et_2SnL

Compound[a]	Method of synthesis[b]	Yield (%)	Analysis (%): Found (Calcd) N	C	H	M.p. (°C)	Mol. wt[c] Found (Calcd)
1 $Et_2SnGlyGly$	I	65	8.9	30.2	5.2	113	306
							(307)
	II	92	9.1	31.3	5.3		
			(9.1)	(31.3)	(5.2)		
2 $Et_2SnGlyAla$	II	89	8.7	34.0	5.9	127	322
			(8.7)	(33.7)	(5.7)		(343)
3 $Et_2SnAlaAla$	II	87	7.8	35.5	6.2	98	336
			(8.4)	(35.8)	(6.0)		(335)
4 $Et_2SnGlyVal$	I	58	8.0	38.4	6.3	102	350
							(348)
	II	95	8.0	37.5	6.4		
			(8.0)	(37.9)	(6.3)		
5 $Et_2SnValVal$	II	70	6.9	42.3	6.9	75	392
			(7.2)	(43.0)	(7.2)		(395)
6 $Et_2SnGlyMet$	I	84	7.0	33.2	6.2	60[d]	378
			(7.3)	(34.7)	(5.8)		(381)
7 $Et_2SnGlyTyr$	I	94	6.4	43.9	5.2	178	410
			(6.8)	(43.6)	(5.4)		(413)

[a] Abbreviations: HGly, NH_2CH_2COOH; HAla, $CH_3CH(NH_2)COOH$; HVal, $(CH_3)_2CHCH(NH_2)COOH$; HMet, $CH_3SCH_2CH_2CH(NH_2)COOH$; HTyr, $HOC_6H_4CH_2CH(NH_2)COOH$. [b] See the Experimental section. [c] Molecular weight in methanol. [d] Decomposition.

Table 2 Characteristic IR vibrations of Et2SnL[a] (cm^{-1})

Compound	$\nu(NH_{amino})$	$\nu(CO_{pept})$	$\nu_{as}(COO)$	$\nu_{sym}(COO)$	$\Delta\nu$[b]
1 $Et_2SnGlyGly$	3120 br 3240 s, br 3280 sh	1645 s	1625 vs	1396 vs	229
In CD_3OD	-	1669 s, br	1628 s, br	1400 s, br	228
2 $Et_2SnGlyAla$	3125 s, br 3230 s, br	1632 s, br	1610 sh	1400 vs	210
In CD_3OD	—	1665 s, br	1622 s, br	1400 s, br	222
3 $Et_2SnAlaAla$	3120 s, br 3210 s, br	1625 s, br	1610 vs	1400 vs	210
In CD_3OD	—	1672 vs	1615 s, br	1405 s, br	210
4 $Et_2SnGlyVal$	3200 s, br 3180 sh	1650 sh	1630 s, br	1400 vs	230
5 $Et_2SnValVal$	3200 s, br 3260 sh	1643 vs	1602 vs	1390 vs	212
6 $Et_2SnGlyMet$	3120 s, br 3200 s, br	1648 vs	1610 s, br	1408 vs	202
7 $Et_2SnGlyTyr$	3145 s, br 3220 s, br 3360 br, sh[c]	1642 sh	1626 s, br	1396 vs	230
In CD_3OD	—	1675 vs	1622 s, br	1400 vs	222

[a] In the solid state, or in solution in CD_3OD where indicated. [b] $\Delta\nu = \nu_{as}(COO) - \nu_{sym}(COO)$. [c] Including $\nu(OH)$.

The molecular structure of $Et_2SnGlyTyr$ is shown in Fig. 1 and a stereoscopic view of the unit cell in Fig. 2. Atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table 3 and bond lengths and angles in Table 4. Full listings of atomic coordinates are available upon request from the authors and are lodged at the Cambridge Data Base, UK.

$Et_2SnGlyTyr$ crystallizes in the space group $P2_12_12_1$. The atoms bound to tin form a distorted trigonal bipyramid with $N_{peptide}$ and two ethyl-C(α) atoms occupying the equatorial positions whereas N_{amino} and $O_{carboxylate}$ are in the apical positions. The bond distances and angles within the two chelate rings are in the same range as in the isostructural compound $Me_2SnGlyMet$.[5] The equatorial angle C(6)–Sn–C(8) in $Et_2SnGlyTyr$, 131.4(2) °, is larger than in other pentacoordinated diorganotin dipeptides [e.g. 123.8(2) ° in $Me_2SnGlyMet$,[5] and 117.5(3) ° in $Ph_2SnGlyGly$[4]]; however, intermolecular coordination to tin, e.g. by carboxylate or peptide oxygen, as the cause of the enlargement of the C–Sn–C angle, can be excluded since Sn–O contacts smaller then 3.5 Å are not observed. The distortion of the molecule is evident from the axial angle O(1)–Sn–N(1) of 152.2(1) °. From short N . . . O distances the presence of hydrogen bonds is inferred. Thus, intermolecular distances N(1) . . . O(3) = 2.809(5) Å and O(2) . . . O(4) = 2.678 Å are markedly shorter than the sum of the van der Waals radii (3.11 Å).[21]

The ^{13C} and ^{119}Sn NMR spectra of the compounds **1–7** have been recorded in CD_3OD and are given in Table 5. The number of signals in the ^{13}C NMR spectra corresponds to the number of magnetically non-equivalent carbon atoms. The doublet of α-C atoms of the Et_2Sn group in the spectra of the compounds **2–7** correlates with the different shielding due to the α-C dipeptide ligand, whilst in the spectrum of **1** only one signal for the appropriate carbon atoms can be distinguished.

The occurrence of unique ^{13}C signals for δ(CO) and δ(CHR) for the coordinated ligands (Table 5) suggests that the solid-state species exists also in CH_3OH solution in the form of undissociated monomers (*vide supra*), analogous to methanolic $Me_2SnGlyGly$.[3]

The coupling constant $|^1J(^{119}Sn, ^{13}C)|$ values (608–632 Hz, Table 5) are in the expected range for pentacoordinated[22] or hexacoordinated diorganotin chelate complexes (632–977 Hz);[23] tetracoordination would afford lower values (e.g. 365–402 Hz, as found in various dibutyltin(IV) complexes[24]) and can be safely excluded. The

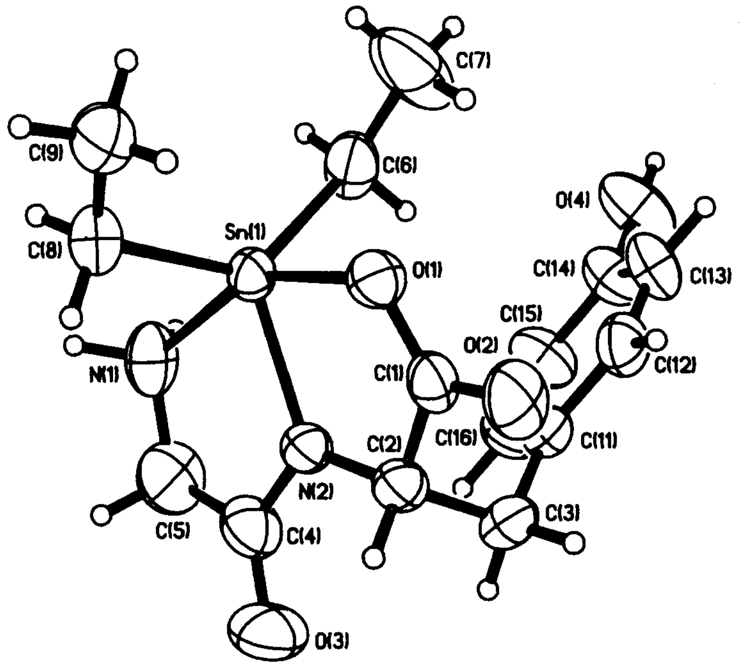


Figure 1 Molecular structure of $Et_2SnGlyTyr$: view of molecule showing atom numbering scheme.

chemical shift values (^{119}Sn) of **1–6**, ranging from −122.21 to −128.06 ppm, at 37 °C (Table 5) are characteristic of pentacoordinated tin.[25] The orders of magnitude of the angles C–Sn–C of the Et_2Sn moieties reported in Table 5, estimated from the coupling constants $|^1J(^{119}Sn,^{13}C)|$, employing the correlations advanced previously for methyltin derivatives,[26,27] are practically coincident, and correspond to the solid-state C–Sn–C value found for the $Et_2SnGlyTyr$ complex (*vide supra*).

The ^{119}Sn Mössbauer parameters of solid-state Et_2SnL complexes (Table 6) seem to indicate the occurrence of two classes of compounds: (i) **1**, **4**, **5**, **6**, $\delta = 1.18–1.20\ mm\ s^{-1}$, $\Delta E = 2.46–2.69\ mm\ s^{-1}$; (ii) **2**, **3**, **7**, $\delta = 1.26–1.32\ mm\ s^{-1}$, $\Delta E = 2.87–3.14\ mm\ s^{-1}$. These data suggest an increase of *s* electron density at the tin nuclei (δ), as well as a larger asymmetry of the electron distribution around tin atoms (ΔE), from class (i) to class (ii).[28] Inasmuch as the narrow linewidths (Γ; Table 6) obtained for the

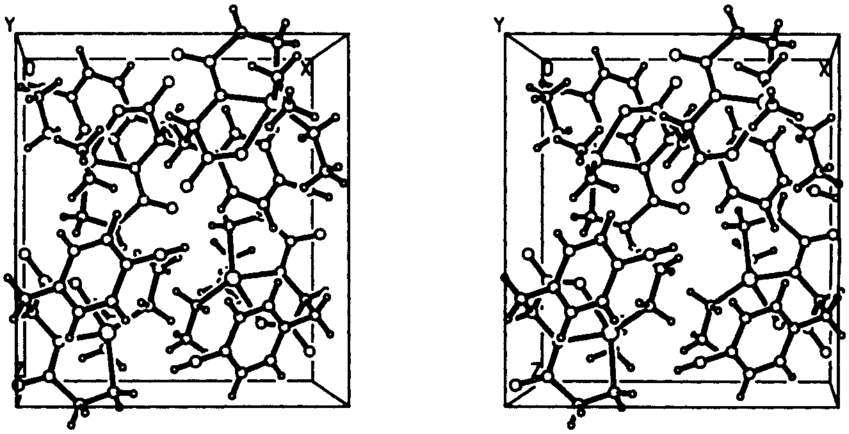


Figure 2 Structure of $Et_2SnGlyTyr$: stereoscopic view of the unit cell.

Table 3 Atomic coordinates and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$) in Et_2SnGlyTyr
$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$

	x	y	z	U_{eq}
Sn(1)	0.28103(2)	0.56678(2)	0.82150(2)	37
N(1)	0.2995(3)	0.6412(3)	0.9863(2)	57
N(2)	0.1251(2)	0.6538(2)	0.8440(2)	39
O(1)	0.1797(2)	0.5275(2)	0.6808(2)	44
O(2)	0.0167(2)	0.5626(3)	0.5951(2)	59
O(3)	−0.0016(3)	0.7309(3)	0.9604(3)	80
O(4)	0.4344(3)	1.0064(3)	0.5905(2)	78
C(1)	0.0808(3)	0.5767(3)	0.6716(2)	40
C(2)	0.0410(3)	0.6555(3)	0.7593(3)	42
C(3)	0.0214(3)	0.7799(3)	0.7174(3)	50
C(4)	0.0947(4)	0.6934(3)	0.9381(3)	56
C(5)	0.1913(4)	0.6947(4)	1.0175(3)	76
C(6)	0.4111(3)	0.6584(4)	0.7411(3)	60
C(7)	0.4436(5)	0.6073(6)	0.6366(4)	106
C(8)	0.2763(4)	0.3952(3)	0.8784(3)	50
C(9)	0.3003(4)	0.3019(4)	0.7998(3)	67
C(11)	0.1299(3)	0.8405(3)	0.6831(3)	44
C(12)	0.1752(3)	0.8261(3)	0.5827(3)	52
C(13)	0.2766(4)	0.8803(3)	0.5505(3)	55
C(14)	0.3338(4)	0.9523(3)	0.6179(3)	54
C(15)	0.2891(4)	0.9691(3)	0.7180(3)	61
C(16)	0.1890(3)	0.9134(3)	0.7489(3)	54

complexes indicate the presence of only one type of tin atom in the structures, the above trends may be rationalized in terms of point-charge model calculations of quadrupole splittings ΔE.[28] [For this purpose, the 'literal' point-change model is employed, which accounts for all valence electrons in the tin environment;[29] regular trigonal bipyramidal structures are considered (except SnC_2 fragments in the trigonal plane where C–Sn–C angles are allowed to vary, and these are taken as the structural factor dictating the magnitude of ΔE)]. The values of partial nuclear quadrupole splitting (pqs) employed in the calculations are taken from the literature;[30-33] for apical monodentate carboxylate, to correspond with the IR study deduced above, a pqs value of $-0.10\ \text{mm s}^{-1}$ has been employed:[33] ($\{\text{Alk}\}^{\text{tbe}} = -1.13\ \text{mm s}^{-1}$; $\{N_{\text{pept}}\}^{\text{tbe}} = -0.30\ \text{mm s}^{-1}$; $\{NH_2\}^{\text{tba}} = +0.01\ \text{mm s}^{-1}$).

The results of the calculations are as follows: for class (i), C–Sn–C = 107 ° (Et_2SnGlyVal) 117 ° (Et_2SnGlyGly); and for class (ii), C–Sn–C = 124 ° (Et_2SnGlyTyr) −131 ° (Et_2SnGlyAla).

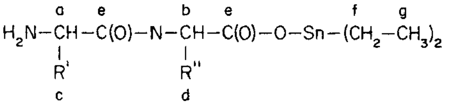
The increase of the C–Sn–C angles from (i) to (ii) would provoke a parallel increase of the percentage *s* character in the Sn–C bonds, which are then assumed to dictate the *s* electron density at the tin nuclei as inferred from the magnitude of the Mössbauer parameters δ.[28]

It is observed that the bond angles deduced for compounds in class (ii) complexes agree reasonably with the X-ray diffractometry value for C–Sn–C of 131.4 ° in Et_2SnGlyTyr; the agreement for class (i) complexes is consistently lower. These effects bear no relationship to any steric effects of substituents at C(2) in the amino-acid residues (Fig. 1), nor to the occurrence of potentially coordinating atoms in these substituent groups; the latter circumstance is in line with the lack of tin bonding by the peptide carbonyl in

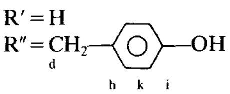
Table 4 Bond distances (Å) and angles (°) in Et_2SnGlyTyr

Sn(1)–N(1)	2.288(3)	C(6)–Sn(1)–C(8)	131.4(2)
Sn(1)–N(2)	2.077(3)	O(1)–Sn(1)–C(8)	94.1(1)
Sn(1)–O(1)	2.191(3)	O(1)–Sn(1)–C(6)	94.7(1)
Sn(1)–C(6)	2.104(4)	N(2)–Sn(1)–C(8)	112.8(1)
Sn(1)–C(8)	2.123(3)	N(2)–Sn(1)–C(6)	115.7(1)
N(1)–C(5)	1.446(6)	N(2)–Sn(1)–O(1)	75.9(1)
N(2)–C(2)	1.452(4)	N(1)–Sn(1)–C(8)	92.4(1)
N(2)–C(4)	1.335(4)	N(1)–Sn(1)–C(6)	101.1(2)
O(1)–C(1)	1.278(4)	N(1)–Sn(1)–O(1)	152.2(1)
O(2)–C(1)	1.236(4)	N(1)–Sn(1)–N(2)	76.6(1)
O(3)–C(4)	1.224(5)	Sn(1)–N(1)–C(5)	109.7(3)
O(4)–C(14)	1.361(5)	Sn(1)–N(2)–C(4)	121.3(2)
C(1)–C(2)	1.518(5)	Sn(1)–N(2)–C(2)	118.5(2)
C(2)–C(3)	1.558(5)	C(2)–N(2)–C(4)	119.6(3)
C(3)–C(11)	1.497(5)	Sn(1)–O(1)–C(1)	117.1(2)
C(4)–C(5)	1.505(6)	O(1)–C(1)–O(2)	123.0(3)
C(6)–C(7)	1.509(7)	O(2)–C(1)–C(2)	119.0(3)
C(8)–C(9)	1.504(5)	O(1)–C(1)–C(2)	118.0(3)
C(11)–C(12)	1.396(5)	N(2)–C(2)–C(1)	110.0(3)
C(11)–C(16)	1.374(5)	C(1)–C(2)–C(3)	110.4(3)
C(12)–C(13)	1.387(6)	N(2)–C(2)–C(3)	111.4(3)
C(13)–C(14)	1.369(5)	C(2)–C(3)–C(11)	114.6(3)
C(14)–C(15)	1.393(5)	N(2)–C(4)–O(3)	124.8(4)
C(15)–C(16)	1.378(6)	O(3)–C(4)–C(5)	120.4(4)
		N(2)–C(4)–C(5)	114.7(4)
		N(1)–C(5)–C(4)	116.4(4)
		Sn(1)–C(6)–C(7)	114.2(3)
		Sn(1)–C(8)–C(9)	116.3(2)
		C(3)–C(11)–C(16)	121.5(3)
		C(3)–C(11)–C(12)	121.6(3)
		C(12)–C(11)–C(16)	116.9(3)
		C(11)–C(12)–C(13)	122.2(3)
		C(12)–C(13)–C(14)	119.6(4)
		O(4)–C(14)–C(13)	121.9(4)
		C(13)–C(14)–C(15)	119.1(4)
		O(4)–C(14)–C(15)	119.0(4)
		C(14)–C(15)–C(16)	120.4(4)
		C(11)–C(16)–C(15)	121.8(3)

Table 5 ^{13}C and ^{119}Sn NMR spectral data for diethyltin derivatives of dipeptides Et_2SnL in CD_3OD



$\underset{}{H_2N}-\underset{\underset{c}{R'}}{\overset{a}{C}H}-\overset{e}{C}(O)-N-\underset{\underset{d}{R''}}{\overset{b}{C}H}-\overset{e}{C}(O)-O-Sn-(\overset{f}{C}H_2-\overset{g}{C}H_3)_2$

Compound	a (ppm)	b (ppm)	c(d′) (ppm)	d (ppm)	e (ppm)	f (ppm)	g (ppm)	$\lvert ^1J(^{119}Sn,^{13}C)\rvert$ (Hz)	Angle C–Sn–C[a] (°)	$\delta(^{119}Sn)$ (ppm)
1 R′ = R″ = H	44.69	47.21	—	—	177.75 174.26	14.07	9.61 9.69	632.84	132.4	−128.06
2 R′ = H, R″ = Me	44.80	53.27	—	19.64	174.04 181.18	13.38 13.44	9.87 9.66	623.04	131.4	−126.24
3 R′ = R″ = Me	52.17	53.34	19.69	19.48	175.74 179.06	9.89 9.69	12.89 12.76	605.00	129.8	n.m.[c]
4 R′ = H, R″ = CH(Me)$_2$ (Me: d′)	44.79	62.27	18.55 (20.03)	33.49	173.80 178.78	12.05 13.34	9.69 9.80	607.80	130.2	−126.17
5[b] R′ = R″ = CH(Me)$_2$ (Me: h)	61.45	62.44	15.67	18.65	177.30 181.41	9.94 9.69	11.83 13.02	n.o.[c]		n.m.[c]
6[b] R′ = H R″ = $\underset{d}{CH_2}-\underset{h}{CH_2}-S-\underset{i}{Me}$	44.59	59.69	—	33.44	174.08 179.65	12.71 13.66	9.65 9.87	612.32	130.5	−123.44
7[b] R′ = H 	44.63	58.85	—	36.31	173.77 174.08	12.33 12.38	9.60 9.69	616.32	130.9	−122.21

[a] From $\lvert ^1J(^{119}Sn,\ ^{13}C)\rvert$, according to Ref. 25. See text.

[b] Additional data, chemical shift values (ppm) for C atoms: **5**, h: 19.65, 19.90; **6**, h: 30.75, i: 15.33; **7**, h: 128.81, i: 157.42, k: 116.16, 132.04.

[c] n.m. = not measured; n.o. = not observed

Table 6 ^{119}Sn Mössbauer parameters of diethyltin derivatives of dipeptides Et_2SnL[a]

Compound	δ[b] (mm s^{-1})	ΔE[c] (mm s^{-1})	Γ_1[d] (mm s^{-1})	Γ_2[d] (mm s^{-1})
1 $Et_2SnGlyGly$	1.18	2.69	0.88	0.88
(in CH_3OH)	1.33[e]	3.49[e]	0.87[e]	0.84[e]
2 $Et_2SnGlyAla$	1.32	3.14	0.87	0.86
3 $Et_2SnAlaAla$	1.29	2.96	0.93	0.83
4 $Et_2SnGlyVal$	1.17	2.46	0.85	0.84
5 $Et_2SnValVal$	1.19	2.54	0.86	0.87
6 $Et_2SnGlyMet$	1.20	2.58	0.88	0.85
7 $Et_2SnGlyTyr$	1.26	2.87	0.83	0.80

[a] In the solid state, unless otherwise stated. $T = 77$ K. Absorber thickness 0.51–0.55 mg ^{119}Sn cm^{-2}. [b] Isomer shift with respect to room-temperature $Ca^{119}SnO_3$. [c] Nuclear quadrupole splitting. [d] Full width at half height of the resonant peaks, at lower and higher velocity than the spectrum centroid, respectively. [e] 1 cm^3 of $Et_2SnGlyGly$ solution (0.13 mol dm^{-3}) in CH_3OH, frozen by immersion in liquid nitrogen.[11]

$Et_2SnGlyTyr$ as shown by X-ray diffractometry, as well as with the present vibrational investigations.

In methanol solution, the point-charge model C–Sn–C angle of $Et_2SnGlyGly$ increases to 141.7 °, as estimated from ΔE_{exp} (Table 6), being now of the same order as the data obtained from $\lvert ^1J(^{119}Sn,^{13}C)\rvert$ in CD_3OD (Table 5). Unexpectedly, $Et_2SnGlyGly$ behaves in quite a different way compared with $Me_2SnGlyGly$.[3]

In conclusion, we think that the present investigation establishes the occurrence of trigonal bipyramidal structures for the Et_2Sn–dipeptide complexes investigated here. Monomeric species occur, in both solid-state and methanol solutions, where terminal carboxylate groups of the dipeptides act as monodentate axial ligands; the C–Sn–C angles of the Et_2Sn moieties are generally larger in the solution phase compared to the solid-state species.

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