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Synthesis and spectroscopic characterization of dimethyl-, di-n-butyl-, di-t-butyl- and diphenyl-tin(IV) derivatives of dipeptides: Crystal and molecular structure of di-n-butyltin(IV) glycylvalinate*

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The dipeptide complexes R_2SnL listed below have been synthesized: (a) Me_2SnL; H_2L = glycylalanine (H_2GlyAla), glycylvaline (H_2GlyVal), glycylmethionine (H_2GlyMet), glycyltryptophan (H_2GlyTrp), glycyltyrosine (H_2GlyTyr); (b) nBu_2SnL; H_2L = H_2GlyAla, H_2GlyVal; (c) $nBu_2SnL \cdot H_2O$; H_2L = glycylglycine (H_2GlyGly), H_2GlyAla; (d) tBu_2SnL; H_2L = H_2GlyAla, H_2GlyVal; (e) tBu_2SnGlyGly·H_2O; (f) Ph_2SnL; H_2L = H_2GlyAla, H_2GlyVal, H_2GlyTyr, H_2GlyTrp; (g) $Ph_2Sn(HGlyVal)_2$. The crystal and molecular structures of nBu_2SnGlyVal have been determined by single-crystal X-ray diffraction. The polyhedron around tin is a distorted trigonal bipyramid, analogous to that of Et_2SnGlyTyr (see Vornefeld *et al.*, Appl. Organomet. Chem., 1992, 6: 75). According to infrared and ^{119}Sn (ΔE parameters) Mössbauer spectroscopic data the R_2SnL derivatives can be classified by their solid-state structure into two types which are distinguished by the nature of the axial carboxylate [(i) monodentate, as in nBu_2SnGlyVal; (ii) bidentate]. Bonding in $R_2SnL \cdot H_2O$ and $Ph_2Sn(HGlyVal)_2$ has been discussed on the basis of vibrational data. Rationalization of the ^{119}Sn Mössbauer parameters has been attempted by 'literal' point-charge model calculations of ΔE in the structural context described above. According to ^{13}C NMR spectra, compounds Me_2SnL are undissociated in methanol solutions, whilst dissociation is inferred for aqueous solutions, probably concerning the carboxyl and amino groups only. Five-coordination in methanol and aqueous solutions has been assumed for Me_2SnL from ^{119}Sn NMR chemical shifts. Values of coupling constants $|^2J(^{119}Sn, ^1H)|$, determined from ^{1}H NMR spectra, gave estimates of C–Sn–C angles in Me_2SnL in the range 128–136 ° in methanol and aqueous solutions, which correspond to values from ^{119}Sn Mössbauer ΔE parameters (129.6–133.8 °). The structural relationship of R_2SnL molecules in the solid state and in solution phase has been discussed.

Keywords: Organotin, dipeptides, structures, X-ray diffraction, NMR, Mössbauer, infrared

INTRODUCTION

In a preceding paper,[1] it has been shown that the complex Et_2SnGlyTyr assumes a distorted trigonal bipyramidal structure in the solid state, with a rather large C–Sn–C angle (131.4 °). The order of magnitude of the Mössbauer nuclear quadrupole splitting parameters ΔE for the series of solid complexes Et_2SnL (L = dianion of dipeptide), indicated the occurrence of two classes of compounds characterized by different ranges of ΔE_{exp} values, and these have been tentatively attributed to two sets of C–Sn–C angles occurring in these compounds.[1] However, no structural effects of the nature of the dipeptide ligands [i.e. of the eventual steric hindrance due to the bulkiness of the groups bound to C(2); see Fig. 1 of Ref. 1] have been detected for the assumed variations of C–Sn–C angles. Moreover, in methanol solution any difference between individual complexes disappears, C–Sn–C angles being around the solid-state value detected for Et_2SnGlyTyr,[1] and analogous to data reported for Me_2SnGlyGly.[2]

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In order to clarify the trends detected in Et_2SnL, the work reported in the present paper was planned. Complexes R_2SnL have been synthesized, where R are alkyl groups with increasing bulkiness (Me, nBu, tBu), as well as phenyl (Ph) radicals; moreover, dipeptides H_2L have been selected which are characterized by increasing molecular volumes (i.e. $H_2L = H_2GlyGly$, $H_2GlyAla$, $H_2GlyVal$, $H_2GlyTrp$, $H_2GlyTyr$, $H_2GlyMet$; for abbreviations, see the abstract above). The crystal and molecular structures of a member of the series, $nBu_2SnGlyVal$, have been determined by single-crystal X-ray diffraction. The nature of the carboxylate and carbonyl groups bound to tin, in the solids, has been investigated by vibrational spectroscopy, and solid-state C–Sn–C angles have been estimated by ^{119}Sn Mössbauer spectroscopic ΔE parameters. The species present in solution phases (methanol and water) have been studied essentially by ^{13}C, ^{1}H and ^{119}Sn NMR.

EXPERIMENTAL

Me_2SnCl_2, tBu_2SnCl_2 and Ph_2SnCl_2 were prepared by published methods;[3-5] nBu_2SnO was obtained by hydrolysis of nBu_2SnCl_2[6] dissolved in methanol with 15 % aqueous potassium hydroxide (KOH) solution. Dipeptides were commercial products. The solvents were dried by standard methods; the preparations were carried out under exclusion of moisture.

The derivatives R_2SnL, $R_2SnL \cdot H_2O$ and $R_2Sn(HL)_2$ were synthesized by the following methods.

(a) Alkoxide method

The alkoxides $R_2Sn(OMe)_2$ were synthesized under nitrogen from 20 mmol sodium methoxide and 10 mmol R_2SnCl_2, each dissolved in 30 cm^3 methanol. After stirring at room temperature for 0.5 h the precipitated NaCl was filtered off. To the solution of $R_2Sn(OMe)_2$ 10 mmol dipeptide was added and the mixture was refluxed for 2–3 h.

(b) Sodium chloride method

The sodium salts of the dipeptides were prepared by stirring 20 mmol sodium methoxide and 10 mmol dipeptide in 70 cm^3 methanol at room temperature until the mixture became clear. Then 10 mmol R_2SnCl_2 was added and the solution was refluxed for 2–3 h.

(b_1) $Ph_2SnGlyTyr$ was prepared in the same way in ethanol at room temperature.

(b_2) $Ph_2Sn(HGlyVal)_2$ was obtained by reaction of 2 mmol sodium methoxide and 2 mmol dipeptide in methanol; 1 mmol Ph_2SnCl_2 was added to the clear solution, which then was refluxed.

(c) Neutralization method

The compounds were synthesized by refluxing 5 mmol nBu_2SnO and 5 mmol dipeptide in the presence of 2 cm^3 2,2-dimethoxypropane in 50 cm^3 methanol for 3 h.

The products were isolated as follows. $Me_2SnGlyAla$ precipitated from the hot solution after 10 min; $Me_2SnGlyTrp$ and $R_2SnGlyTyr$ (R = Me, Ph) precipitated while cooling. The compounds were filtered off, and recrystallized from methanol in order to be purified from NaCl. The solutions of the other derivatives were concentrated to about 10 cm^3 and diethyl ether was added if no product had precipitated. The solids were filtered off and, except in the case of the di-n-butyltin(IV) compounds, were recrystallized from ethanol. The nBu_2Sn derivatives were dried *in vacuo* at 80 °C on a waterbath.

Some of the dibutyltin(IV) compounds contain one molecule of water per molecule of dipeptide. The n-butyltin derivatives of glycylglycine and glycylalanine loose the water molecule on drying at 80 °C so that the water-free compounds are obtained. This process is reversible; the hydrates $nBu_2SnL \cdot H_2O$ (L = GlyGly, GlyAla) are regained when the anhydrous compounds are stored in the laboratory in the open atmosphere. In the case of $tBu_2SnGlyGly \cdot H_2O$ under the same drying conditions, the water molecule is not removed. DTA measurements showed that the n-butyltin compounds loose water at about 50 °C, and $tBu_2SnGlyGly \cdot H_2O$ at 90 °C (Table 1). The preparation of compounds of the type $R_2Sn(HL)_2$ was successful only in the case of $Ph_2Sn(HGlyVal)_2$. Reactions of Me_2Sn, nBu_2Sn, tBu_2Sn or Ph_2Sn educts with glycylglycine and glycylalanine, as well as the reactions of Me_2Sn, nBu_2Sn or tBu_2Sn educts with glycylvaline, always lead to free dipeptide (H_2L) and to R_2SnL. All the products obtained are colourless.

The results of the elemental analyses are reported in Table 1, together with the estimated

Table 1 Analytical data for diorganotin(IV) derivatives of dipeptides[a]

Compound	Method of preparation	Yield (%)	Mp (°C)	Microanalytical data: Found (Calcd) (%) N	C	H	Molecular weight: found in methanol, DMSO$^+$ (Calcd)
$Me_2SnGlyAla$	(a)	79.4	231 (dec)	9.5 (9.6)	28.8 (28.8)	4.9 (4.8)	308$^+$ (292)
$Me_2SnGlyVal$[b]	(b)	81.8	248 (dec)	8.1 (8.7)	31.3 (33.6)	5.3 (5.6)	306 (321)
$Me_2SnGlyMet$	(a)	75.4	247 (dec)	7.9 (7.9)	30.7 (30.7)	5.3 (5.1)	361 (352)
$Me_2SnGlyTrp$	(b)	87.9	248 (dec)	10.1 (10.3)	43.3 (44.2)	4.5 (4.7)	192 (407)
$Me_2SnGlyTyr$	(a)	79.3	250 (dec)	7.3 (7.3)	41.0 (40.6)	4.4 (4.7)	377 (384)
$nBu_2SnGlyGly \cdot H_2O$	(c)	76.7	51,[c] 222 (dec)	7.0 (7.0)	36.2 (36.0)	7.0 (6.8)	394 (399)
$nBu_2SnGlyAla$	(c)	61.7	237 (dec)	7.4 (7.4)	41.2 (41.5)	6.9 (6.9)	381 (376)
$nBu_2SnGlyAla \cdot H_2O$	(c)	73.6	49,[c] 235	7.0 (7.1)	39.3 (39.6)	6.9 (7.6)	376 (394)
$nBu_2SnGlyVal$	(c)	75.5	267 (dec)	6.7 (6.9)	44.1 (44.5)	7.2 (7.4)	395 (406)
$tBu_2SnGlyGly \cdot H_2O$	(b)	59.4	90,[c] 279 (dec)	7.2 (7.4)	37.2 (37.9)	6.8 (6.6)	205 (380)
$tBu_2SnGlyAla$	(b)	56.3	275 (dec)	6.9 (7.4)	39.5 (41.5)	6.5 (6.9)	354 (376)
$tBu_2SnGlyVal$	(b)	62.6	247 (dec)	6.6 (6.9)	43.1 (44.5)	7.3 (7.4)	387 (405)
$Ph_2SnGlyAla$	(b)	58.6	147; 211 (dec)	6.2 (6.7)	48.5 (49.0)	3.9 (4.3)	404 (416)
$Ph_2SnGlyVal$[d]	(a)	69.1	189; 217 (dec)	6.0 (6.3)	47.2 (51.2)	4.7 (4.9)	434 (445)
$Ph_2SnGlyTrp$	(b)	67.4	226 (dec)	7.6 (7.9)	55.4 (56.5)	4.0 (4.3)	280 (531)
$Ph_2SnGlyTyr$	(b_1)	61.8	224 (dec)	5.2 (5.5)	54.3 (54.3)	4.0 (4.3)	437 (451)
$Ph_2SnGlyMet$	(c)	62.5	143–145	5.6 (5.9)	47.4 (47.8)	4.4 (4.6)	—[e] —
$Ph_2Sn(HGlyVal)_2$	(b_2)	75.4	211 (dec)	8.9 (9.0)	50.2 (50.3)	5.7 (5.8)	—[e] —

[a] $H_2GlyGly$, glycylglycine; $H_2GlyAla$, glycylalanine; $H_2GlyVal$, glycylvaline; $H_2GlyMet$, glycylmethionine; $H_2GlyTrp$, glycyltryptophan; $H_2GlyTyr$, glycyltyrosine. [b] Contains 7% NaCl. [c] According to DTA/TG: liberation of 1 mol H_2O per 1 mol of compound. [d] Contains 7.7% NaCl. [e] Not determined due to low solubility.

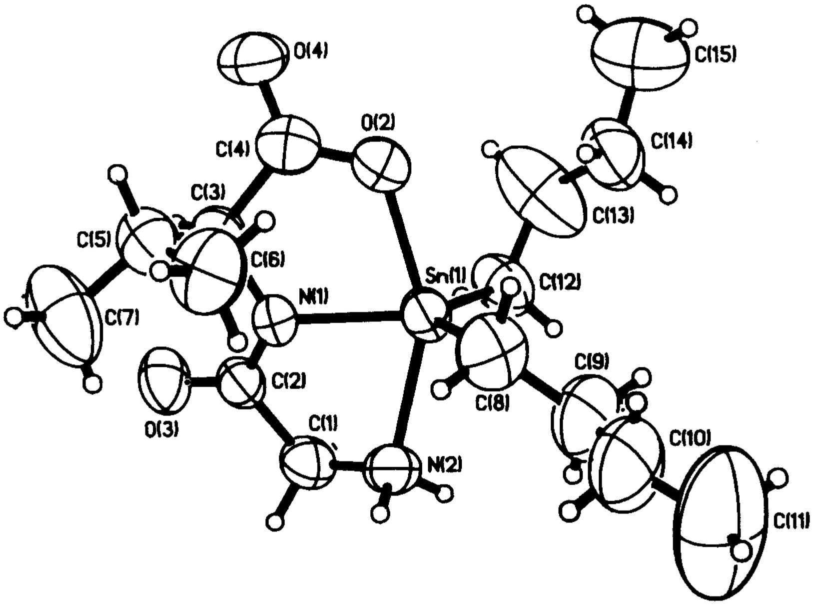


Figure 1 Molecular structure of $nBu_2SnGlyVal$: view of molecule showing atom numbering scheme.

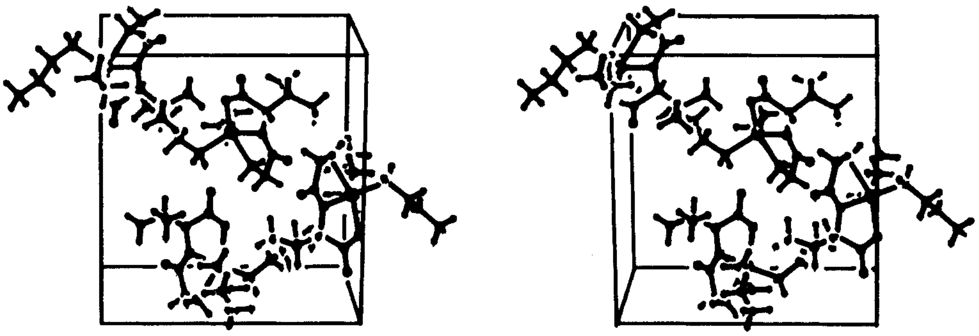


Figure 2 Structure of $nBu_2SnGlyVal$: stereoscopic view of the unit cell.

molecular weights, and melting and decomposition points. $Me_2SnGlyGly$, $nBu_2SnGlyGly$ and $Ph_2SnGlyGly$ have been prepared by literature methods.[7, 8]

Single crystals of $nBu_2SnGlyVal$ were obtained by recrystallization from methanolic solution after addition of diethyl ether. Crystal data: $C_{15}H_{30}N_2O_3Sn$, $M_r = 405.10$, orthorhombic, space group $P2_12_12_1$, $a = 980.4(9)$, $b = 1360.2(12)$, $c = 1413.6(14)$ pm, $V = 1885(3) \times 10^6$ pm^3, $Z = 4$, $D_x = 1.427$ Mgm^{-3}, $F(000) = 8320$, graphite-monochromated MoKα radiation, $\lambda = 71.073$ pm, $\mu = 1.37$ mm^{-1}, $T = 291(1)$ K, crystal size ≈ 0.51 mm $\times$ 0.29 mm $\times$ 0.38 mm, $\omega/2\theta$ scan, scan speed 5.0–14.6 ° min^{-1} in θ, Nicolet R3m/V diffractometer, graphite-monochromated MoKα; lattice parameters from least-squares fit with 20 reflections up to $2\theta = 35.1$ °; six standard reflections recorded every 2.5 h, only random deviations; 3751 reflections measured $1.5° \leq \theta \leq 25.0°$, $-12 \leq h \leq 12$, $0 \leq k \leq 17$, $0 \leq l \leq 17$; after averaging ($R_{int.} = 0.027$): 3343 unique reflections, 2929 with $F \geq 3.0\,\sigma(F)$; Lorenz-polarization correction, no absorption correction; systematic absences ($h00$) $h = 2n + 1$, ($0k0$) $k = 2n + 1$, ($00l$) $l = 2n + 1$ conform to space group $P2_12_12_1$; structure solution via Patterson function, ΔF syntheses and full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H atoms, which were placed in geometrically calculated positions (C–H 0.95 Å); refinement of F with 2929 reflections and 191 refined parameters; $w = 1.0/[\sigma^2(F) + 0.0005\,F^2]$; $S = 1.20$, final $R = 0.038$, $wR = 0.037$, $(\Delta/\sigma)_{max} = 0.08$, refinement of the enantiomorph gave a higher R and S, no extinction correction; largest peak in final ΔF map $\pm 0.8(3)$ e Å^{-3}, atomic scattering factors for neutral atoms and real and imaginary dispersion terms from *International Tables for X-ray Crystallography*;[9] programs: SHELXTL PLUS[10] and PARST.[11] A molecule is shown in Fig. 1, together with the related numbering scheme, and a stereoview of the unit cell in Fig. 2. Positional parameters, and the equivalent values of the anisotropic temperature factors for the non-H atoms, are given in Table 2. Bond lengths and angles are reported in Table 3.

Table 2 Atomic coordinates of $nBu_2SnGlyVal$, and equivalent isotropic thermal parameters (A$^2 \times 10^4$) $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$

	x	y	z	U_{eq}
Sn(1)	0.81083 (4)	0.97776 (3)	0.07532 (3)	555
N(1)	0.6787 (5)	0.8579 (3)	0.0930 (3)	499
N(2)	0.8237 (5)	0.8904 (3)	−0.0614 (3)	642
O(2)	0.7288 (4)	1.0013 (3)	0.2137 (3)	693
O(3)	0.5217 (5)	0.7636 (3)	0.0164 (3)	777
O(4)	0.5794 (5)	0.9480 (4)	0.3199 (3)	858
C(1)	0.6905 (7)	0.8422 (4)	−0.0754 (4)	688
C(2)	0.6229 (6)	0.8171 (4)	0.0189 (4)	548
C(3)	0.6204 (6)	0.8442 (4)	0.1869 (4)	563
C(4)	0.6423 (7)	0.9379 (5)	0.2449 (5)	678
C(5)	0.6777 (9)	0.7569 (5)	0.2439 (4)	763
C(6)	0.8329 (8)	0.7645 (6)	0.2569 (5)	981
C(7)	0.642 (1)	0.6609 (6)	0.2012 (7)	1373
C(8)	1.0182 (7)	0.9616 (6)	0.1146 (5)	854
C(9)	1.1197 (7)	1.0052 (7)	0.0476 (7)	1156
C(10)	1.2658 (8)	0.9730 (9)	0.0723 (8)	1374
C(11)	1.368 (1)	1.013 (1)	0.020 (1)	2438
C(12)	0.7243 (8)	1.1050 (5)	0.0087 (5)	827
C(13)	0.693 (1)	1.1886 (6)	0.0694 (7)	1399
C(14)	0.806 (1)	1.2334 (6)	0.1243 (6)	1016
C(15)	0.754 (1)	1.3149 (9)	0.1853 (7)	1436

IR spectra (KBr pellets) were recorded on a Perkin–Elmer grating spectrometer PE 580 B. The melting and decomposition points were determined by DTA. ^{1}H NMR spectra have been

Table 3 Bond distances (Å), bond angles (°), least-squares planes, dihedral angles (°) and possible hydrogen bonds

Sn(1)-N(1)	2.097 (5)	C(1)-C(2)	1.528 (8)
Sn(1)-N(2)	2.272 (5)	C(3)-C(4)	1.530 (9)
Sn(1)-O(2)	2.140 (4)	C(3)-C(5)	1.541 (9)
Sn(1)-C(8)	2.119 (7)	C(5)-C(6)	1.54 (1)
Sn(1)-C(12)	2.146 (7)	C(5)-C(7)	1.48 (1)
N(1)-C(2)	1.305 (7)	C(8)-C(9)	1.50 (1)
N(1)-C(3)	1.456 (7)	C(9)-C(10)	1.54 (1)
N(2)-C(1)	1.474 (8)	C(10)-C(11)	1.35 (2)
0(2)-C(4)	1.287 (8)	C(12)-C(13)	1.46 (1)
O(3)-C(2)	1.230 (7)	C(13)-C(14)	1.49 (1)
O(4)-C(4)	1.233 (8)	C(14)-C(15)	1.50 (1)
C(8)-Sn(1)-C(12)	125.3 (3)	N(1)-C(2)-C(1)	115.0 (5)
O(2)-Sn(1)-C(12)	97.6 (2)	N(1)-C(2)-O(3)	127.8 (6)
O(2)-Sn(1)-C(8)	97.8 (2)	N(1)-C(3)-C(5)	115.6 (5)
N(2)-Sn(1)-C(12)	94.0 (2)	N(1)-C(3)-C(4)	109.1 (5)
N(2)-Sn(1)-C(8)	96.6 (2)	C(4)-C(3)-C(5)	108.1 (5)
N(2)-Sn(1)-O(2)	151.3 (2)	O(4)-C(4)-C(3)	118.9 (6)
N(1)-Sn(1)-C(12)	115.8 (3)	O(2)-C(4)-C(3)	117.8 (6)
N(1)-Sn(1)-C(8)	118.7 (3)	O(2)-C(4)-O(4)	123.3 (6)
N(1)-Sn(1)-O(2)	77.0 (2)	C(3)-C(5)-C(7)	112.4 (6)
N(1)-Sn(1)-N(2)	74.3 (2)	C(3)-C(5)-C(6)	111.8 (6)
Sn(1)-N(1)-C(3)	116.7 (4)	C(6)-C(5)-C(7)	109.9 (7)
Sn(1)-N(1)-C(2)	119.6 (4)	Sn(1)-C(8)-C(9)	115.5 (5)
C(2)-N(1)-C(3)	120.8 (5)	C(8)-C(9)-C(10)	111.2 (8)
Sn(1)-N(2)-C(1)	107.3 (4)	C(9)-C(10)-C(11)	116.9 (10)
Sn(1)-O(2)-C(4)	117.4 (4)	Sn(1)-C(12)-C(13)	117.0 (6)
N(2)-C(1)-C(2)	111.5 (5)	C(12)-C(13)-C(14)	118.0 (8)
O(3)-C(2)-C(1)	117.2 (5)	C(13)-C(14)-C(15)	110.3 (8)

No.	Plane through atoms	Equation of the plane	χ^2
1	N(1), C(8), C(12), Sn(1)	$-0.233x+0.352y+0.906z=3.76$ Å	0.0
2	Sn(1), O(2), N(1), C(3), C(4)	$-0.7680x+0.507y-0.391z=0.23$ Å	568.7
3	Sn(1), N(1), N(2), C(1), C(2)	$-0.698x+0.650y-0.300z=2.74$ Å	6838.7

Dihedral angles: 1,2, 89.8(2); 1,3, 83.2(2); 2,3, 10.5(1).

Possible hydrogen bond

N(2)···O(3) (1)	H(21)n···O3 (1)	N(2)-H(21)n···O3(1)
2.962 (7)	1.985 (7)	166.2 (6)

Symmetry codes: (O) x, y, z; (1) $+x+1/2, -y+1/2+1, -z$.

obtained with a Perkin–Elmer R32 90 MHz instrument and ^{119}Sn and ^{13}C spectra by a Bruker AM300 spectrometer. Molecular weights were determined osmometrically. The Mössbauer spectra were measured with the apparatus and techniques described in the preceding paper,[1] as well as in a previous publication.[12] The results are reported in Tables 4–8.

RESULTS AND DISCUSSION

R$_2$Sn–dipeptide complexes in the solid state

The molecular structure of nBu$_2$SnGlyVal

In nBu$_2$SnGlyVal, as well as in the diorganotin(IV) dipeptides Et$_2$SnGlyTyr,[1] Ph$_2$SnGlyGly,[8]

Table 4 Characteristic infrared vibrations (cm^{-1})[a, b]

Compound	$\nu(NH_2)$	$\nu(CO_{pept})$	$\nu_{as}(COO)$	$\nu_{sym}(COO)$	$\Delta\nu$
$Me_2SnGlyGly$	3270 m, b 3160 m,b	1675 vs	1605 vs	1410 m	195
$Me_2SnGlyAla$	3240 vs 3110 vs	1625 vs, b	1595 vs, b	1405 vs	190
$Me_2SnGlyVal$	3240 s 3190 s 3120 s	1660 vs	1635 vs	1385 vs	250
$Me_2SnGlyMet$	3140 vs 3070 vs	1645 vs	1615 vs	1395 vs	220
$Me_2SnGlyTrp$	3600 m[c] 3240 vs 3120 s	1650 s, sh	1620 vs	1395 vs	225
$Me_2SnGlyTyr$	3330 s, sh[d] 3320 vs 3110 vs	1650 s, sh	1625 vs	1405 s	220
$nBu_2SnGlyGly$	3290 vs 3240 vs 3140 vs	1625 vs	1595 vs	1410 vs	185
$nBu_2SnGlyGly \cdot H_2O$	3430 s, b[e] 3260 s 3150 s	1625 vs, b	1610 vs	1410 vs	200
$nBu_2SnGlyAla$	3230 vs 3130 vs	1620 vs, b		1395 vs	225
$nBu_2SnGlyAla \cdot H_2O$	3420 s[e] 3230 vs 3140 vs	1630 vs	1615 vs	1395 vs	220
$nBu_2SnGlyVal$	3220 s 3130 s	1650 vs	1620 vs	1390 vs	230
$tBu_2SnGlyGly \cdot H_2O$	3490 s[e] 3370 s[e] 3170 vs 3090 vs	1620 vs, b		1410 s	210
$tBu_2SnGlyAla$	3230 m 3080 m	1640 vs	1625 vs	1400 s	225
$tBu_2SnGlyVal$	3220 s 3130 s	1650 vs	1625 vs	1395 s	230
$Ph_2SnGlyGly$	3200 m	1655 s	1625 vs	1410	215
$Ph_2SnGlyAla$	3220 s, b	1660 vs, sh	1630 vs	1400 s	230
$Ph_2SnGlyVal$	3240 s, b	1655 s, sh	1630 vs	1395 s	235
$Ph_2SnGlyMet$	3211 s 3094 s	1620 s, b		1397 s	223
$Ph_2SnGlyTrp$	3440[c] 3220 s, b 3130 m	1655 vs, sh	1635 vs	1395 vs	240
$Ph_2SnGlyTyr$	3450 s, b[d] 3220 s 3140 s	1655 vs, sh	1635 vs	1400 s	235
$Ph_2Sn(HGlyVal)_2$	3340 vs, b 3250 vs, b	1665 vs	1590 vs	1420 vs	170

[a] KBr pellets; [b] vs, very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder. [c] NH (indole). [d] OH (Tyr). [e] $OH(H_2O)$.

Table 5 ^{119}Sn Mössbauer parameters of R_2Sn dipeptides in the solid state ($T \approx 77$ K)

Compound[a]	δ^b (mm s^{-1})	ΔE^c (mm s^{-1})	Γ_1^d (mm s^{-1})	Γ_2^d (mm s^{-1})
(I)				
$Me_2SnGlyAla$	1.20	3.27	0.81	0.83
$nBu_2SnGlyGly \cdot H_2O$	1.37	3.23	0.83	0.82
$nBu_2SnGlyAla$	1.34	3.27	0.90	0.81
$nBu_2SnGlyAla \cdot H_2O$	1.29	3.00	0.96	0.85
(II)				
$Me_2SnGlyVal$	1.12	2.59	0.85	0.87
$Me_2SnGlyMet$	1.11	2.53	0.83	0.82
$Me_2SnGlyTyr$	1.15	2.74	0.84	0.86
$nBu_2SnGlyVal$	1.23	2.65	0.83	0.82
$tBu_2SnGlyGly \cdot H_2O$	1.37	2.65	0.87	0.91
$tBu_2SnGlyAla$	1.39	2.70	0.86	0.87
$tBu_2SnGlyVal$	1.36	2.56	0.80	0.79
(III)				
$Ph_2SnGlyAla$	1.05	2.21	0.82	0.88
$Ph_2SnGlyVal$	1.02	2.29	1.08	0.93
$Ph_2SnGlyMet$	1.06	2.39	0.91	0.89
$Ph_2SnGlyTrp$	1.03	2.30	0.99	0.86

[a] Sample thickness was in the range 0.50–0.65 mg ^{119}Sn cm^{-2}. (I)–(III): see discussion in the text. [b] Isomer shift with respect to $Ca^{119}SnO_3$. [c] Nuclear quadrupole splitting. [d] Full width at half-height of the resonant peaks, at greater and lesser velocity than the spectrum centroid respectively.

$Me_2SnGlyMet$[13] and $tBu_2SnGlyGly \cdot H_2O$,[14] the polyhedron around the tin atom is a distorted trigonal bipyramid formed by the two organic groups and the tridentate dipeptide ligand, the latter having on the whole a planar skeleton (see Figs 1 and 2, Table 3, and Refs 1, 8, 11, 13, 14). The dihedral angle formed by the two chelate rings of the SnGlyVal skeleton (planes 2 and 3, Table 3) has a value of 10.5°. It is noticeably larger than the appropriate angle in other diorganotin dipeptides, e.g. 1.8° in $Ph_2SnGlyGly$,[8] and 2.8 ° in $tBu_2SnGlyGly$.[14] The ligand is axially bonded via the oxygen of the unidentate carboxylate group and the nitrogen of the terminal NH_2 group (bond angles O–Sn–N between 149.6 ° in $tBu_2SnGlyGly \cdot H_2O$[14] and 153.5 ° in $Ph_2SnGlyGly$[8]) and via peptide nitrogen occupying one of the equatorial positions. The latter bond is very short, being in the range found in other dipeptides R_2SnL (between 2.071 pm in $Me_2SnGlyMet$[13] and 2.097 pm in $nBu_2SnGlyVal$). While the other molecules R_2SnL are linked by hydrogen bonds between the NH_2 group and the carboxyl and carbonyl oxygen atoms of two neighbouring units, the molecules of $nBu_2SnGlyVal$ are only connected by a hydrogen bond between the NH_2 group N(2) and carbonyl oxygen O(3) (Table 3). In $tBu_2SnGlyGly \cdot H_2O$[14] the water molecule is fixed in the crystal packing by hydrogen bonds involving both hydrogen atoms of H_2O and the NH_2 group and the carboxyl and carbonyl oxygen.

Vibrational spectra

The data $\nu_{as}(COO)$, and $\Delta\nu = \nu_{as} - \nu_{sym}$, reported in Table 4, would suggest the following structural details:

(1) $Me_2SnglyGly$, $Me_2SnGlyAla$, $nBu_2SnGlyGly$, $nBu_2SnGlyGly \cdot H_2O$: $\nu_{as}(COO) =$ 1595–1610 cm^{-1}, $\Delta\nu = 185$–200 cm^{-1}; the carboxylate groups are bidentate and bridging.[15] For the other compounds R_2SnL listed in Table 4; $\nu_{as}(COO) =$ 1615–1635 cm^{-1}, $\Delta\nu = 210$–240 cm^{-1}; the carboxylate groups are monodentate.[15]

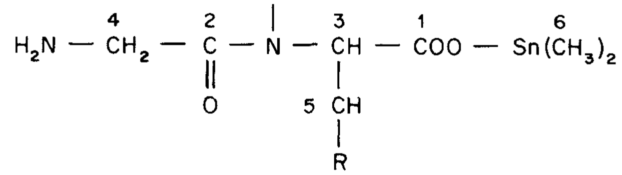
(2) $Me_2SnGlyAla$, $nBu_2SnGlyGly$, $nBu_2SnGlyGly \cdot H_2O$, $nBu_2SnGlyAla$, $nBu_2SnGlyAla \cdot H_2O$: $\nu(CO_{pept}) < 1630$ cm^{-1}. For the other compounds R_2SnL in Table 4: $\nu(CO_{pept}) \geq 1655$ cm^{-1}. CO_{pept} is involved in bonding in the five complexes listed above.

From these observations it may be inferred that bulky substituent groups bound to tin, as well as to the carbon atom C(2) of the ligand (Fig. 1), favour the formation of monomeric complexes, with monodentate carboxyls and non-coordinating peptide carbonyl, whilst the reverse would occur with sterically less hindering substituents. On the other hand, these assumptions would be at variance with respect to Et_2SnL, where carboxyl groups appear to be always monodentate, irrespective of the bulkiness of substituent groups at ligands.[1]

The IR spectra, Table 4, of the water-containing di-n-butyltin(IV) compounds $nBu_2SnGlyGly \cdot H_2O$ and $nBu_2SnGlyAla \cdot H_2O$ show one broad and intensive ν(OH) band at 3430 cm^{-1} and 3420 cm^{-1}, respectively. In the case of $tBu_2SnGlyGly \cdot H_2O$ this ν(OH) absorption is split into two bands, at 3490 and 3370 cm^{-1}. This should indicate differences in the mode of interaction of the water molecules and the Bu_2SnL moieties. In this context it should be remembered that $nBu_2SnL \cdot H_2O$ loses water at lower temperatures (50 °C; Table 1) than $tBu_2SnGlyGly \cdot H_2O$ (90 °C). The water molecule in the latter complex is not bound to tin but is fixed by hydrogen bonds.[14] From the results of Mössbauer measurements of the di-n-butyltin compounds (*vide infra*), and the IR data on carboxylate- and carbonyl-oxygen coordination to tin, we generally exclude a coordination between tin and water in these compounds. Probably the mode of interaction between water and carboxyl/carbonyl oxygen and amino nitrogen is different in $tBu_2SnGlyGly \cdot H_2O$ and in the di-n-butyltin dipeptides containing water.

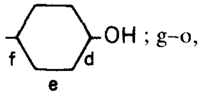
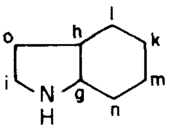
The IR spectra of $Ph_2Sn(HGlyVal)_2$ (Table 4) are characterized by a low value of $\nu_{as}(COO)$ as well as of Δν, which strongly suggests the occurrence of bidentate carboxyl (*vide supra*). Moreover, $\nu(NH_2)$ does not differ substantially from the value of the alkali-metal salts of dipeptides (3410, 3350 cm^{-1}), and $\nu(CO_{pept})$ would indicate that O_{pept} is not coordinating. A polymeric structure, with bridging carboxyl groups, may then be advanced in the present context. It is

Table 6 ^{13}C NMR data of dimethyltin(IV) dipeptides: δ(ppm)



$$\overset{4}{H_2N-CH_2}-\overset{2}{\underset{\underset{O}{\|}}{C}}-\overset{|}{N}-\overset{3}{\underset{\underset{\underset{R}{|}}{5\;CH}}{\overset{}{CH}}}-\overset{1}{COO}-\overset{6}{Sn(CH_3)_2}$$

Compound	Solvent	1+2	3	4	5	6	R*			
$Me_2SnGlyVal$	CD_3OD	178.60; 173.63	61.96	44.40	33.39	0.08; −0.74	19.97^a	18.64^a		
$Me_2SnGlyMet$	CD_3OD	179.36; 173.75	56.62	44.37	32.97	0.41; −0.37	30.45^b	15.29^c		
$Me_2SnGlyAla$	D_2O	184.16; 182.90	54.73	45.99	21.76	3.72; −3.15				
		176.48; 169.17	54.11	43.42	20.09					
$Me_2SnGlyVal$	D_2O	181.75; 181.21	63.84	45.83	34.81	3.07; −2.08	21.60^a	20.30^a		
		176.40; 169.44	63.78	43.24	32.87		19.89			
$Me_2SnGlyMet$	D_2O	182.35; 181.10	58.15	45.82	33.77	3.54; −2.72	32.56^b	17.08^c		
		176.70; 169.37	57.30	43.33	33.62		31.38	16.98		
$Me_2SnGlyTyr$	D_2O	180.56; 179.21	58.54	44.18	38.01	0.93; −0.31	155.81^d	132.47^e	131.78^e	116.91^f
		174.88; 167.45	58.09	41.68	36.08		155.45	130.85	129.56	116.64
$Me_2SnGlyTrp$	D_2O	181.10; 174.86	58.98	44.22	27.10	0.92; −1.21	137.28^g	129.63^h	125.41^i	122.93^k
							120.52^l	119.33^m	113.32^n	110.43^c

* Assigned as follows:
a, CH_3, b, CH_2; c, CH_3; d, e, f,  ; g–o, 

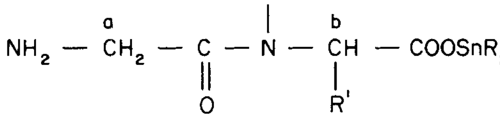
worth noting that this type of bonding has been found only in this Ph_2Sn derivative of dipeptides having a bulky group at C(2), and is actually the only $R_2Sn(HL)_2$ species obtained so far.[1]

^{119}Sn Mössbauer spectra

The isomer shift (δ) data in Tables 5 and 8 are typical of diorganotin derivatives;[16, 17] moreover, the narrowness of the linewidths, Γ, implies the general occurrence of single tin sites in each compound, as well as of multiple sites with corresponding environments. The experimental nuclear quadrupole splitting parameters, ΔE, reported in Table 5 describe three classes of compounds:

(I) Table 5, $\Delta E = 3.00-3.27$ mm s^{-1}; Alk_2Sn-GlyGly, Alk = Me, nBu, nOct, $\Delta E = 3.32–3.43$ mm s^{-1};[2, 7, 18] Et_2Sn-GlyAla, –AlaAla and –GlyTyr, $\Delta E = 2.87–3.14$ mm s^{-1};[1]

Table 7 ^1H and ^{119}Sn NMR data of dialkyltin(IV) dipeptides, and free dipeptides; δ (ppm); $|^2J(^{119}Sn, ^1H)|$ and $|^3J(^{119}Sn, ^1H)|$ (Hz)



$$\overset{a}{NH_2-CH_2}-\underset{\underset{O}{\|}}{C}-\overset{|}{N}-\underset{\underset{R'}{|}}{\overset{b}{CH}}-COOSnR_2$$

Compound	Solvent	R	a	b	c	d	e	$^2J/^3J$	^{119}Sn
$H_2GlyGly$	D_2O		3.84	3.90					
(R' = H)									
$nBu_2SnGlyGly$	CD_3OD	0.77–1.67	3.42	3.80					
$tBu_2SnGlyGly$	CD_3OD	1.37	3.51	3.84				102	
$H_2GlyAla$	D_2O		3.76	4.08	1.29				
$(R' = \underset{c}{CH_3})$									
$Me_2SnGlyAla$	DMSO-d6	0.59	—[a]	3.80	1.09			82	
		0.66						84	
	D_2O (1)[b]	0.71	3.33	4.11	1.24			84	
		0.78						82	
	(2)[b]	0.71	3.46	4.07	1.25			82	−93.8
		0.80	3.73					82	
$nBu_2SnGlyAla$	CD_3OD	0.78–1.69	3.36	4.14	1.34				
$tBu_2SnGlyAla$	CD_3OD	1.37	3.41	4.18	1.35			102	
		1.30						101	
$H_2GlyVal$	D_2O		3.78	4.00	2.02	0.89			
$(R' = \underset{c}{CH}(\underset{d}{CH_3})_2$						0.83			
$Me_2SnGlyVal$	DMSO-d6	0.51	—[a]	3.84	1.98	0.91		78	
		0.67				0.73		80	
	CD_3OD	0.71	3.51	4.23	2.22	1.07		78	−89.4
		0.84				0.88		78	
	D_2O (1)[b]	0.78	3.39	3.59	2.21	1.05		80	
		0.95				0.90		82	
	(2)[b]	0.69	3.33	3.62	2.04	0.88		80	−94.4
		0.78	3.86	4.07		0.85		80	
		0.86							
		0.98							
$nBu_2SnGlyVal$	CD_3OD	0.71–1.69	3.34	4.14	2.13	1.02			
						0.84			
$tBu_2SnGlyVal$	CD_3OD	1.36	3.27	4.22	2.22	1.17		105	
		1.51				1.03		98	
$H_2GlyMet$	D_2O		3.85	4.20	2.50	1.96	2.03		
$(R' = \underset{c}{CH_2}-\underset{d}{CH_2}-S-\underset{e}{CH_3})$									

Table 7 *continued*

Compound	Solvent	R	a	b	c	d	e	$^2J/^3J$	^{119}Sn
$Me_2SnGlyMet$	DMSO-d6	0.60	—[a]	3.94	2.20	2.20	2.00	82	
		0.67						82	
	CD_3OD	0.74	3.44	4.27	3.39	2.24	2.06	84	−93.8
		0.86						82	
	D_2O (1)[b]	0.78	3.52	4.33	2.40	2.40	2.04	80	
		0.87						80	
	(2)[b]	0.77	3.51	4.26	2.19	2.19	2.04	80	−97.1
		0.88	3.84				2.07	80	
$H_3GlyTyr$ $(R' = \underset{c}{CH_2}\text{—}\underset{d}{Ph}\text{—}OH)$	D_2O		3.97	4.64	3.01	7.28			
$Me_2SnGlyTyr$	DMSO-D6	−0.14	—[a]	4.04	3.20	6.57		80	
		0.64						78	
	$D_2O(1,2)$[b]	−0.02	3.48	—[a]	—[c]	7.00		80	
		0.64	3.66					78	
$Me_2SnGlyTrp$	DMSO-d6	−0.49	3.38	4.16	3.22	7.18		79	
$(R' = \underset{c}{CH_2}\text{—}\underset{d}{Trp})$		−0.44						77	
	$D_2O(1,2)$[b]	−0.50	3.52	—[a]	—[c]			80	
		0.58						78	

[a] Superimposed by signals of non-deuterated solvent molecules.

[b] D_2O: (1) measurement made immediately after dissolution; (2) measurement after six weeks.

[c] Assignment not possible.

Table 8 ^{119}Sn Mössbauer parameters of representative compounds of the R_2Sn dipeptide series, in frozen solutions (T≈77 K)

Compound[a]	δ^b (mm s^{-1})	ΔE^c (mm s^{-1})	$\Gamma_1{}^d$ (mm s^{-1})	$\Gamma_2{}^d$ (mm s^{-1})
Solutions in methanol[e]				
$Me_2SnGlyVal$	1.21	3.09	0.90	0.81
$Me_2SnGlyMet$	1.22	3.13	0.93	0.80
$Me_2SnGlyGly$[f]	1.23	3.23	1.02	0.87
Solutions in water[e, g]				
$Me_2SnGlyVal$	1.19	2.98	0.88	0.80
$Me_2SnGlyMet$	1.19	2.99	1.07	0.93
$Me_2SnGlyGly$[h]	1.24	3.27	0.99	0.84

[a] The spectra have been measured on absorber samples from freshly prepared solutions; see Ref. 12.

[b–d] See footnotes b–d to Table 5.

[e] The concentration was in the range 36–65 mmol dm^{-3} for $Me_2SnGlyVal$. A saturated solution was employed for $Me_2SnGlyMet$ (<36 mmol dm^{-3}).

[f] Ref. 2.

[g] The concentration was in the range 36–100 mmol dm^{-3}. The parameters reported here are average values measured in (frozen) solutions in redistilled water, as well as in 0.3% (w/v) of an aqueous solution of the surfactant 2-hydroxypropylcellulose, and in Klucel (0.3% 2-hydroxypropylcellulose, 0.9% NaCl, by wt). See Ref. 2.

[h] Ref. 2 and this paper, average values.

(II) Table 5, $\Delta E = 2.53\text{–}2.74$ mm s^{-1}; Et_2Sn-GlyGly, −GlyVal, −ValVal and −GlyMet, $\Delta E = 2.46\text{–}2.69$ mm s^{-1};[1]

(III) Table 5, $\Delta E = 2.21\text{–}2.39$ mm s^{-1}; Ph_2Sn GlyGly, $\Delta E = 2.39$ mm s^{-1} (average value, this work and Ref. 18).

These data reflect the trend observed for infrared group vibrations referred to in the preceding text, in the sense that a definite influence neither of steric factors, nor of the occurrence of donor atoms in side chains, must be considered in order to rationalize the whole set of ΔE data. However, we have tried here to apply the point-charge model in order to find confirmation for the structural proposal advanced on the basis of infrared spectroscopy which implies carboxylate groups axially coordinating tin to produce trigonal bipyramidal geometries (according to the X-ray diffraction structure). Calculations have been effected as described in the preceding paper,[1] according to literature reports;[16, 17, 19, 20] partial nuclear quadrupole splittings employed in the calculations are from the literature[16, 17, 19–21] (see Ref. 1; moreover, $\{Ph\}^{tbe} = -0.98$ mm s^{-1}).

We have established that ΔE values in Et_2SnL may be related to the magnitude of the angles C–Sn–C;[1] here we correlate the variations of ΔE

with the nature of axially bonded carboxylate groups. In fact, the following ΔE_{calcd} values are obtained, for regular trigonal bipyramidal structures, using the 'literal' version of the point-charge model:

(i) Alk_2SnL: employing the partial nuclear quadrupole splitting (pqs) value $\{COO\}^{tba} = +0.075\ mm\ s^{-1}$,[18,20] indicative of bridging (bidentate) behaviour, the value $\Delta E_{\text{calcd}} = -3.09\ mm\ s^{-1}$ is obtained,[18] which would correspond to ΔE_{exp} of class (I) as listed above.

(ii) Alk_2SnL: employing the pqs value $\{O{=}C{-}O\}^{tba} = -0.10\ mm\ s^{-1}$,[21] i.e. the value for monodentate carboxyl, $\Delta E_{\text{calcd}} = +2.78\ mm\ s^{-1}$ results, which would agree with ΔE_{exp} for group (II) above.

(iii) Ph_2SnL: with $\{COO\}^{tba} = +0.075\ mm\ s^{-1}$, $\Delta E_{\text{calcd}} = -2.70\ mm\ s^{-1}$[18] is obtained, while with $\{O{=}C{-}O\}^{tba} = -0.10\ mm\ s^{-1}$, $\Delta E_{\text{calcd}} = -2.39\ mm\ s^{-1}$. The latter value exactly corresponds to ΔE_{exp} for group (III) above.

In conclusion, these calculations would indicate that the X-ray molecular structure of $nBu_2SnGlyVal$ is reflected by the other members of the R_2SnL series of dipeptide complexes investigated here, also in accordance with previous work. Infrared and Mössbauer spectroscopic data have been employed in order to state and interpret fine structural details, such as the nature of ligand groups and the angles in coordinated R_2Sn moieties (although in some cases the data from the two techniques are contrasting). Moreover, these fine effects apparently cannot be safely interpreted by a simple rationale based upon stereochemical effects.

R_2Sn–dipeptide complexes in the solution phase: ^{13}C, ^{1}H, ^{119}Sn NMR spectra, and ^{119}Sn Mössbauer spectra

The ^{13}C NMR data for Me_2SnL (Table 6) give the following information:

(1) in CD_3OD solution, chemical shifts (δ) for COO and CO_{pept}, as well as δ for peptide CH_2 and CH, consist of individual values, which suggest the occurrence of a single species, presumably the coordinated ligand, having a structure corresponding to that of the solid-state complexes.[1,2]

(2) in D_2O solution, the above-mentioned δ signals are generally doubled, which would be consistent with the partial dissociation of the dipeptide complex.[2]

These ^{13}C data strictly correspond to findings concerning $Me_2SnGlyGly$ in CD_3OD and D_2O solutions;[2] accordingly, the partial dissociation of the dipeptide assumed for $Me_2SnGlyGly$ in D_2O, where only the $Sn{-}N_{\text{pept}}$ bond would be maintained, may be advanced also for the Me_2SnL complexes investigated here.

The ^{1}H NMR spectra (Table 7) give essentially analogous information on the bonding of the dipeptide to tin centres in CD_3OD and D_2O solutions.[2] Moreover, the application of Lockhart's relationship between C–Sn–C bond angles and coupling constants $|^2J(^{119}Sn, ^1H)|$[22] gives the following results:

(1) Me_2SnL (in CD_3OD and D_2O): $|^2J| = 78$–84 Hz (Table 7); C–Sn–C = 128–136°.

(2) tBu_2SnL (in CD_3OD): $|^2J| = 102$–105 Hz (Table 7); C–Sn–C = 166–172 °.

Angles as for (1) may be attributed also to $Me_2SnGlyGly$ through the reported $|^2J|$ data.[2] It then appears that, in CH_3OH solution, monomeric species Me_2SnL occur (from osmometry, Table 1), where L are coordinated tridentate ligands (from ^{13}C NMR, *vide supra*) and tin atoms assume the coordination number five (from $\delta(^{119}Sn)$,[23] Table 7 and Ref. 2).

The C–Sn–C angles of tBu_2SnL in CD_3OD, reported in (2) above, seem to be overestimated by Lockhart's correlation. In fact, the latter has been established for Me_2Sn compounds,[22] although employed also for a Bu_2Sn derivative;[24] moreover, a similar relationship has been proposed for n-butyltin compounds.[23,25]

The C–Sn–C angles of Me_2SnL in methanol have been estimated also from the ^{119}Sn Mössbauer parameters ΔE in the frozen solutions (Table 8), by the 'literal' version of the point-charge model employed in the preceding paper.[1] The range of values C–Sn–C = 129.6–133.8° has been calculated, which corresponds to the data extracted from $|^2J(^{119}Sn,^1H)|$ (*vide supra*). According to the ΔE values in Table 8, C–Sn–C angles for Me_2SnL in aqueous solution would strictly correspond to data in methanol. To this purpose, it must be recalled that ^{1}H NMR spectra in aqueous solutions evidence the occurrence of two distinct tin-containing species, characterized by coincident $|^2J(^{119}Sn,^1H)|$ coupling constants, which are in turn quite similar to $|^2J|$ values measured in methanol solutions (Table 7). This circumstance, in conjunction with the narrowness of the Mössbauer resonance linewidths (Table 8), enables us to assess that all Me_2SnL species in the various solution phases are strictly correlated, as far as the C–Sn–C bond angle is concerned.

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