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Spectrochimica Acta Part A 71 (2008) 529–536
SPECTROCHIMICA ACTA PART A
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New diorganotin(IV) derivatives of dipeptides: Synthesis and characteristic spectral studies

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Received 10 August 2007; accepted 4 January 2008

Abstract

Some new diorganotin(IV) derivatives of the formulae, R_2SnL, where R = Me, *n*-Bu, Ph, and *n*-Oct, and L is the dianion of histidinylalanine (H_2L-1) and histidinylleucine (H_2L-2) have been synthesized by the reaction of R_2SnCl_2 and the preformed sodium salt of the respective dipeptides. The bonding and coordination behaviour in these derivatives are discussed on the basis of FT-IR, multinuclear ^1H, ^{13}C and ^{119}Sn NMR and ^{119}Sn Mössbauer spectroscopic studies. These investigations suggest that dipeptides in R_2SnL act as dianionic tridentate coordinating through the COO^-, NH_2 and $N^-_{peptide}$ groups. The ^{119}Sn Mössbauer studies, together with the NMR data, suggest a trigonal bipyramidal geometry around tin in R_2SnL with the alkyl/aryl groups and $N_{peptide}$ in the equatorial positions, while a carboxylic oxygen and the amino nitrogen atom occupy the axial positions.

Keywords: Diorganotin(IV) complexes; Dipeptides; Multinuclear magnetic resonance; ^{119}Sn Mössbauer

1. Introduction

Organotins, important environmental pollutants widely used in agricultural and industrial applications, enter into the food chain and accumulate in the environment [1]. However, organotin(IV) compounds have emerged as potentially biologically active compounds among non-platinum chemotherapeutic metallopharmaceuticals in the last two decades [2,3]. Among the class of organotins, diorganotin compounds have attracted a great deal of attention not only because of their wide range of industrial and biological applications [4], but more because of their place among non-platinum chemotherapeutic compounds exhibiting good anti-tumour activity [2,3,5–15]. Due to the potential biological activity of diorganotin compounds, during the last decade considerable efforts have been directed to study the interaction of diorganotin(IV) moiety with amino acids [2,3,8,11,13,16–21] and peptides [2,3,8,12,17,20,22–25]. In view of this, the study of the interaction of diorganotin(IV) moiety with the dipeptides containing at least one essential amino acid residue is indispensable. Further, diorganotin(IV) derivatives of dipeptides [17,22,23] have been found to exhibit potent anti-inflammatory activity, thus such compounds may hold the potential to be placed in the class of nonsteroidal anti-inflammatory drugs (NSAIDs). Therefore, considerable efforts have been made to characterize model organotin compounds of the ligands having hetero donor atoms (O, N and/or S) [26(a–f)], and simultaneously several studies have been focused on structure–activity correlations [27(a, b)] during the last two decades.

In order to obtain a better insight into how the organotin species behave inside biological system, it is necessary to study their coordination behaviour with ligands that can occur in the biological medium, and hence to formulate structure activity correlations to devise new organotin derivatives with potential anti-tumour and anti-inflammatory activities. In view of this, here we report the synthesis and structural studies of some diorganotin(IV) derivatives of dipeptides containing at least one essential amino acid residue, *viz.*, histidinylalanine (H_2L-1) and histidinylleucine (H_2L-2).

2. Experimental

2.1. Materials

All of the reactions were carried out under an anhydrous nitrogen atmosphere. Specially dried methanol (99.95%, v/v) was

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doi:10.1016/j.saa.2008.01.006

dried by refluxing it with Mg metal and then distilled, and other solvents were dried and distilled before use. Dimethyltin(IV) dichloride, di-*n*-butyltin(IV) oxide, diphenyltin(IV) dichloride (E. Merck), di-*n*-octyltin(IV) oxide (Aldrich), histidinylalanine (His-Ala), and histidinylleucine (His-Leu) (Sigma) were used as-received.

2.1.1. Synthesis of dimethyltin/diphenyltin(IV) derivatives of dipeptides by sodium chloride method

The dipeptide (1.5 mmol) was dissolved in the minimum amount (20 ml) of specially dried methanol under dry nitrogen and added to sodium methoxide, prepared by reacting sodium (0.081 g, 3.5 mmol) with dry methanol (25 ml). The resulting mixture was first stirred at room temperature for half an hour and then refluxed giving a clear solution of Na_2L within half an hour. Refluxing was continued for another 4–6 h with constant stirring. A hot methanol solution (20 ml) of dimethyltin/diphenyltin(IV) dichloride (1.5 mmol) was added to the solution of the preformed sodium salt of the dipeptide. The resulting solution was further refluxed with constant stirring for another 14–16 h for the diphenyltin(IV) derivatives whereas only stirring was carried out at room temperature ($30 \pm 2\,^{\circ}C$) for the dimethyltin(IV) derivatives, under dry nitrogen atmosphere. It was then centrifuged and filtered in order to remove the sodium chloride formed. The excess of solvent was removed under reduced pressure and the solid product thus obtained was recrystallized from either methanol–hexane or methanol–petroleum ether (bp 40–60 °C) mixture (1:3, v/v).

2.1.2. Synthesis of di-n-butyltin/di-n-octyltin(IV) derivatives of dipeptides by the azeotropic removal of water method

The compounds were prepared under anhydrous nitrogen atmosphere by drop-wise addition of a dry, hot methanol solution of di-*n*-butyltin(IV) and di-*n*-octyltin(IV) oxide (1.5 mmol) to a hot methanol solution of the dipeptide (1.5 mmol). The reaction mixture obtained was refluxed with constant stirring for at least 14–16 h with azeotropic removal of water. The solution was filtered, and the excess of solvent was removed under reduced pressure and allowed to cool. The solid product thus obtained was recrystallized by either methanol–hexane or methanol–petroleum ether (bp 40–60 °C) mixture (1:3, v/v).

2.2. Measurements

The melting points of the synthesized compounds were determined on a Toshniwal capillary melting point apparatus and were uncorrected. Carbon, hydrogen and nitrogen analyses of these compounds were carried out on a VarioEL, CHNS-rapid elemental analyzer. The tin content in the synthesized compounds was determined gravimetrically as SnO_2 [12]. Infrared and far-infrared spectra of the solid compounds were recorded on a PerkinElmer 1600 series FT-IR spectrophotometer in the range 4000–400 cm^{-1} from KBr discs and 600–200 cm^{-1} from CsI discs. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 (300 MHz FT NMR) spectrometer at the Central Drug Research Institute, Luknow, India, using CD_3OD as solvent and TMS as the internal standard. ^{119}Sn NMR spectra were recorded on a Bruker DRX 500 (500 MHz FT NMR) spectrometer at the Institute Instrumentation Centre, IIT, Roorkee, India, using DMSO-d_6/CD_3OD as solvent and TMS as the internal standard. ^{119}Sn Mössbauer spectra were recorded on Mössbauer spectrometer model MS-900 according to the procedure reported previously [12], at the Department of Chemistry and Physics, University of The District of Columbia, Washington, D.C.

3. Results and discussion

The reactions of R_2SnCl_2 (R = Me and Ph) with the sodium salt of dipeptide ligand (formed according to Eq. (1)) in a 1:1 molar ratio led to the formation of the compounds according to Eq. (2). Di-*n*-butyltin/di-*n*-octyltin(IV) oxides react with the dipeptides in equimolar ratio in dry methanol to give the compounds under azeotropic removal of water (Eq. (3):

$$H_2L\text{-}1/H_2L\text{-}2 + 2NaOMe \xrightarrow{1:2 \text{ in sp. dried MeOH}} Na_2(L\text{-}1)/Na_2(L\text{-}2) + MeOH \quad (1)$$

$$R_2SnCl_2 + Na_2(L\text{-}1)/Na_2(L\text{-}2) \xrightarrow{1:1 \text{ in sp. dried MeOH}} R_2Sn(L\text{-}1)/R_2Sn(L\text{-}2) + 2NaCl \quad (2)$$

$$R'_2SnO + H_2L\text{-}1/H_2L\text{-}2 \xrightarrow{1:1 \text{ in sp. dried MeOH}} R'_2Sn(L\text{-}1/L\text{-}2) + H_2O \quad (3)$$

where R = Me and Ph; R′ = *n*-Bu and *n*-Oct; H_2L-1 = His-Ala and H_2L-2 = His-Leu.

The Me_2Sn(IV), *n*-Bu_2Sn(IV) and Ph_2Sn(IV) derivatives were synthesized within ~18–20 h of refluxing. Whereas, the reactions involving the synthesis of *n*-Oct_2Sn(IV) derivatives of H_2L-1 and H_2L-2 yielded a turbid solution after a prolonged heating, and the solid was obtained from the filtrate after removing the unreacted peptide/organotin oxide. The resulting solids were obtained in good yields (64–87%). All of the derivatives are found to be stable towards air and moisture. Most of the synthesized compounds are soluble in methanol, but sparingly soluble in chloroform and other solvents upon heating. The analytical data of the derivatives, as presented in Table 1, suggest that in every instance the resulting compounds crystallized with 1:1 stoichiometry regardless of the proportions of the organotin moiety and dipeptide used (Scheme 1).

3.1. Infrared spectral studies

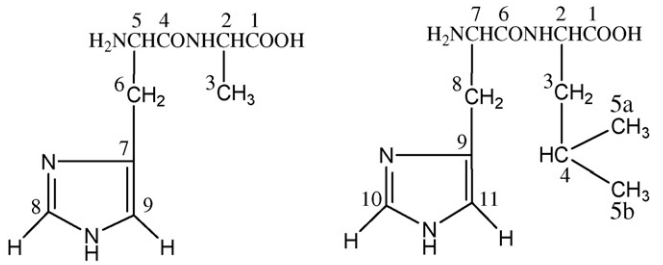
The characteristic infrared absorption frequencies (in cm^{-1}) and their assignments for the free dipeptides and their diorganotin(IV) derivatives are presented in Table 2.

3.1.1. Coordination by amino group

The infrared $-NH_2$ stretching frequencies were used to distinguish coordinated from non-coordinated amino groups of the dipeptides/amino acids. The position and intensity of

Table 1
Analytical data and physical characteristics of diorganotin(IV) derivatives of H_2L-1 (His-Ala) and H_2L-2 (His-Leu)

Complex number	Complex (empirical formula)	Method of preparation	Yield (%)	mp (°C)	Colour and physical state	Analysis (%): found (calculated)			
						Sn	N	C	H
1	$Ph_2Sn(L\text{-}1)$ ($C_{21}H_{22}N_4O_3Sn$)	Section 2.1.1	82	95–100 (decomp)	White solid	21.60 (22.01)	9.98 (10.40)	52.95 (53.46)	5.10 (5.23)
2	$Me_2Sn(L\text{-}1)$ ($C_{11}H_{18}N_4O_3Sn$)	Section 2.1.1	83	160–170 (decomp)	Creamish white solid	31.28 (31.83)	14.48 (15.02)	34.90 (35.42)	4.74 (4.86)
3	$n\text{-}Bu_2Sn(L\text{-}1)$ ($C_{17}H_{30}N_4O_3Sn$)	Section 2.1.2	79	110	Yellowish white solid	25.41 (25.96)	12.03 (12.26)	44.78 (44.66)	6.48 (6.61)
4	$n\text{-}Oct_2Sn(L\text{-}1)$ ($C_{25}H_{46}N_4O_3Sn$)	Section 2.1.2	69	205–210 (decomp)	White solid	20.35 (20.85)	9.30 (9.84)	52.42 (52.74)	8.24 (8.14)
5	$Ph_2Sn(L\text{-}2)$ ($C_{24}H_{28}N_4O_3Sn$)	Section 2.1.1	76	220–230 (decomp)	White solid	21.70 (22.01)	9.98 (10.40)	52.95 (53.46)	5.09 (5.23)
6	$Me_2Sn(L\text{-}2)$ ($C_{14}H_{24}N_4O_3Sn$)	Section 2.1.1	81	225 (decomp)	Creamish white solid	28.20 (28.60)	13.13 (13.50)	39.85 (40.50)	5.54 (5.83)
7	$n\text{-}Bu_2Sn(L\text{-}2)$ ($C_{20}H_{36}N_4O_3Sn$)	Section 2.1.2	87	185–195	Creamish white solid	23.47 (23.78)	10.83 (11.22)	48.58 (48.12)	7.48 (7.27)
8	$n\text{-}Oct_2Sn(L\text{-}2)$ ($C_{28}H_{52}N_4O_3Sn$)	Section 2.1.2	64	160–165 (decomp)	White solid	19.08 (19.40)	8.60 (9.15)	54.78 (54.95)	8.08 (8.56)



H_2L - 1 = His-Ala H_2L - 2 = His-Leu

Scheme 1.

ν(N–H) bands are influenced by hydrogen bonding, and by coordination of the nitrogen to tin [2,12]. In all of the studied diorganotin(IV) derivatives of dipeptides, very intense absorption bands in the range 2920–3397 cm^{-1} due to the $\nu(N\text{–}H)_{amino}$, undergo a substantial lowering in comparison to the non-coordinated dipeptides H_2L-1 (3464 cm^{-1}) and H_2L-2 (3421–3078 cm^{-1}), indicating coordination by the amino group to the central tin atom. Similar results have been reported for R_3SnAA (AA = amino acid anion) [2,13,16,18,19,21,28] and R_2SnL (H_2L = dipeptide) [12,17,22,23,29,30]. The appearance of a new band of medium intensity in the region ~409–500 cm^{-1} in all of the derivatives studied, which may be assigned to ν(Sn←N), further confirms the coordination of the amino nitrogen to the organotin(IV) moiety. Further, the $\nu(NH_2)$ absorption bands are broad, suggesting the presence of inter- and/or intramolecular hydrogen bonding [2,12,17,22,23,28].

3.1.2. Coordination by carboxylate group

Infrared O–C=O stretching frequencies have been utilized to distinguish coordinated from non-coordinated carboxyl groups, and also, to identify the nature of bonding of carboxylic group, *viz.*, monodentate or bridging. The carboxylate groups in the organotin(IV) derivatives generally adopt a bridged structure in the solid state unless the organic substituents at tin are bulky or unless the carboxylate group is branched at the α-carbon [29]. The infrared absorption spectra of all the diorganotin(IV) derivatives of the dipeptides indicate that ν_{as}(O–C=O) values shown by these amino-coordinated complexes get shifted to higher frequencies (1585–1635 cm^{-1}) in comparison to those of H_2L-1 (1566 cm^{-1}) and H_2L-2 (1565 cm^{-1}). Whereas, the corresponding ν_s(O–C=O) absorption frequencies (1381–1438 cm^{-1}) slightly moves either to lower or higher frequencies than in the non-coordinated dipeptides (H_2L-1 = 1400 cm^{-1}, H_2L-2 = 1390 cm^{-1}). The magnitude of the $(\nu_{as}-\nu_s)$(O–C=O) ($\Delta\nu$) separation, which has been found to be useful in identifying structural features [2], is larger in the amino-coordinated diorganotin(IV) derivatives of H_2L-1 ($\Delta\nu$ = 226–241 cm^{-1}) (except Ph_2Sn(L-1)) and H_2L-2 ($\Delta\nu$ = 174–193 cm^{-1}) than in the non-coordinated dipeptides, H_2L-1 $\Delta\nu$ = 166 cm^{-1} and H_2L-2 $\Delta\nu$ = 175 cm^{-1} (Table 2). Further, the magnitude of $\Delta\nu$ for all these studied derivatives of H_2L-1 have been found comparable to those obtained for R_3SnAA (AAH = amino acid) [2,13,16,18,19,21,28] and R_2SnL (H_2L = dipeptide) [12,17,22,23], indicating that the car-

Table 2
Characteristic IR frequencies[a] (in cm^{-1}) of diorganotin(IV) derivatives of H_2L-1 (His-Ala) and H_2L-2 (His-Leu)

Ligand/complex	ν(NH) amino/ν(NH) pep.	ν(CO) amide	ν_{as}(OCO)	ν_s(OCO)	Δν	ν_{as}(Sn–C); ν_s(Sn–C)	ν(Sn–O)	ν(Sn–N)/ν(Sn←N)
H_2L-1 (ligand)	3464 sbr	1677 sh 1634 s	1566 vs	1400 m	166	–	–	–
Ph_2Sn(L-1)	3383 s 3271 s	1633 s	1594 vs	1438 m	156	270 m 228 m	587 m	486 m; 447 m 417 w
Me_2Sn(L-1)	3367 s 3175 sh	1632 vs	1607 sh*	1381 m	226	616 w	566 m	494 sh
n-Bu_2Sn(L-1)	3207 s 3141 s 3033 s 2954 s	1681 s	1635 m	1394 m	241	625 m 597 m	566 m	499 w 414 m
n-Oct_2Sn(L-1)	3035 m 2954 s 2920 s	1680 s	1635 w	1394 m	241	625 m 602 m	560 m	500 m 409 w
H_2L-2 (ligand)	3421 mbr 3213 s 3078 s 2952 vs	1683 vs	1565 vs	1390 vs	175	–	–	–
Ph_2Sn(L-2)	3397 sbr 3343 s	1644 s	1585 vs	1399 s	186	206 m 228 m 247 m	565 m	448 m
Me_2Sn(L-2)	3395 sbr 3348 sh 3239 s	1643 vs 1678 sh	1587 s	1394 s	193	664 w 613 w	582 m	464 m 422 w
n-Bu_2Sn(L-2)	3210 s 3084 s 2957 s	1679 sh 1613 s	1568 sh*	1394 s	174	667 m 620 w	564 m	474 wsh 414 m
n-Oct_2Sn(L-2)	3212 m 3083 m 2922 s	1680 s	1613 sh 1589 m	1393 m	175	666 m 600 w	560 m	415 m 470 w

[a] Intensity of characteristic bands as: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad; *merge with ν(CO) amide.

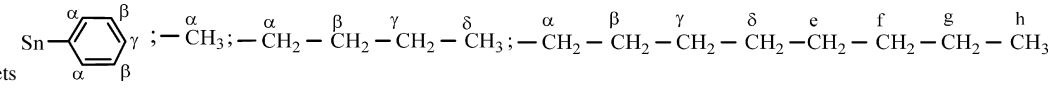
boxylate group acts as a monodentate ligand. The magnitude of the (ν_{as}–ν_s) (O–C=O) (Δν) separation in the diorganotin(IV) derivatives of H_2L-2 is <200 cm^{-1}, indicating that the carboxylate group is bidentate and bridging. Similar results are also reported for $R_2SnGlyGly$ (R = Me and *n*-Bu), *n*-$Bu_2SnGlyGly{\cdot}H_2O$ and $Me_2SnGlyAla$ [30]. Furthermore, the disappearance of a broad band in the spectra of all of the derivatives in the region 2750–2600 cm^{-1}, which was present in both the dipeptides as a weak intensity band (due to $\nu(O–H)_{carboxyl}$), suggests the deprotonation of the COOH group upon complexation [2]. The appearance of a medium intensity band in the IR spectra of all the compounds in the region 587–560 cm^{-1}, which may be assigned to ν(Sn–O), further supports the bonding of (O–C=O) group to the tin atom [2,12,16,17,21–23].

3.1.3. Coordination by peptide group

In the derivatives studied, apart from the carboxylic oxygen and amino nitrogen as potential coordinating sites to the tin atom, the amide group also exhibits strong tendency to coordinate with the organotin(IV) moiety. Two characteristic bands, *viz.*, amide I [essentially ν(C=O)] and amide II [δ(N–H) coupled with ν(C–N)], give the crucial information on the occurrence of metal coordination by the basic atoms of the amide group [12,31]. The intense bands of the amide I observed at 1677, 1634 cm^{-1} and 1683 cm^{-1} in H_2L-1 and H_2L-2, respectively, undergo a slight shift to a lower frequency (1681–1613 cm^{-1}) in the IR spectra of the diorganotin(IV) derivatives of H_2L-1 and H_2L-2 (except Bu_2Sn(L-1) and Oct_2Sn(L-1)) upon complexation. This is probably due to the involvement of the peptide nitrogen (because of the deprotonation that has taken place) in bonding with tin, which lowers the bond order of the $(C=O)_{amide}$ group due to the resonance stabilization. The possibility of the involvement of the $(C=O)_{amide}$ group in the intermolecular hydrogen bonding can not be excluded. Further, amide II band observed at 1557 cm^{-1} in H_2L-1 and at 1535 cm^{-1} in H_2L-2 gets shifted to lower frequency upon complexation in all of the diorganotin(IV) derivatives of dipeptides with respect to non-coordinated dipeptides, which suggests that the amide nitrogen is the third coordinating site due to the deprotonation of the amide nitrogen. The appearance of a pair of bands of medium intensity in the region (450 ± 40) cm^{-1} which may be assigned

Table 3
^{1}H NMR spectral data of the diorganotin(IV) derivatives of H_2L-1 (His-Ala) and H_2L-2 (His-Leu)

Complex number	Complex/ligand (solvent)	δ (ppm)[a]
H_2L-1	His-Ala (CD_3OD + DMSO-d_6 at 500 MHz)	H-2: 4.28 (q, 7.0, 7.5, 7.0 Hz, 1H); H-3: 1.45 (d, 7.0Hz, 3H); H-5: 4.09 (t, 5.2Hz, 1H); H-6: 3.27, 3.25 (dd, 5.5Hz, 2H) {10.0 Hz}[c]; H-8: 7.86 (s, 1H); H-9: 7.07 (s, 1H)
1	Ph_2Sn(L-1) (CD_3OD at 300 MHz)	H-2: 4.19 (q, 7.2 Hz, 1H); H-3: 1.34 (d, 7.2 Hz, 3H); H-5: 3.57 (t, 6.0 Hz, 1H); H-6: 2.96, 2.93 (dd, 5.7, 6.6 Hz, 2H) [38.7/37.8 Hz][b]; H-8: 7.54 (s, 1H); H-9: 6.82 (s, 1H); H-α: 7.77 (d, 7.2 Hz, 4H) [61.5/59.1 Hz][b]; H-β + H-γ: 7.45 (m, 6H)
2	Me_2Sn(L-1) (CD_3OD at 300 MHz)	H-2: 4.17 (q, 6.9, 6.6, 6.9 Hz, 1H); H-3: 1.28 (d, 6.9 Hz, 3H); H-5: 3.84, 3.82 (dd, 3.9, 4.2 Hz, 1H); H-6: 3.21, 2.12 (dd, 3.6, 7.5 Hz, 2H) [59.1/55.5 Hz][b]; H-8: 7.77 (s, 1H); H-9: 7.02 (s, 1H); Sn–CH_3: 0.75, 0.72 (s, 6H) [79.2/78.9 Hz][b]
3	*n*-Bu_2Sn(L-1) (CD_3OD at 300 MHz)	H-2: 4.13 (q, 6.9 Hz, 1H) [20.7 Hz]; H-3: 1.24 (d, 6.9 Hz, 3H); H-5: 3.75 (t, 5.0 Hz, 1H); H-6: 3.15, 3.09 (dd, 6.0, 4.2 Hz, 2H), {18.0 Hz}[c] [48.9/47.1][b]; H-8: 7.66 (s, 1H); H-9: 6.92 (s, 1H); H-α: 1.35 (t, 7.2 Hz, 4H); H-β: 1.53 (t, 6.3 Hz, 4H); H-γ: 1.44, 1.42 (m, 4H); H-δ: 0.91 (t, 6.3 Hz, 6H)
4	*n*-Oct_2Sn(L-1) (CD_3OD at 300 MHz)	H-2: 4.23 (q, 7.2 Hz) and 4.13 (q, 6.9 Hz, 1H); H-3: 1.39 (d, 7.2 Hz, 3H); H-5: 3.98 (t, 5.7 Hz) and 3.74 (t, 2.2 Hz, 1H); H-6: 3.18 (d, 5.7 Hz), 3.12 (d, 3.6 Hz) and 3.31 (s, 1H); H-8: 7.80, 7.65 (s, 1H); H-9: 7.01, 6.92 (s, 1H); H-octyl: 1.30, 0.93 (m)[d]
5	Ph_2Sn(L-2) (CD_3OD at 300 MHz)	H-2: 4.32, 4.28 (dd, 3.3, 3.9 Hz, 1H); H-3 + H-4: 1.68–1.56 (m, 3H); H-5a: 0.92 (d, 5.4 Hz, 3H); H-5b: 0.91 (d, 4.8 Hz, 3H); H-7: 3.59 (t, 1.9 Hz, 1H); H-8: 2.98 (d, 4.5 Hz, 2H); H-10: 7.54 (s, 1H); H-11: 6.82 (s, 1H); H-α: 7.78 (d, 6.3 Hz, 4H); H-β + H-γ: 7.74 (m, 6H)
6	Me_2Sn(L-2) (CD_3OD at 300 MHz)	H-2: 4.21 (t, 4.8, 6.0 Hz, 1H), 4.30 (d, 3.6 Hz) and 4.27 (d, 3.9 Hz, 1H); H-3 + H-4: 1.68–1.53 (m, 3H) (1.42–1.38 (m, 3H)); H-5a + H-5b: 0.91 (t, 5.2 Hz, 6H) (0.84 (d, 6.0 Hz, 6H); H-7: 3.59 (t, 5.7 Hz, 1H) (3.79, 3.77 (dd, 4.5, 4.5 Hz, 1H)); H-8: 2.97 (d, 5.4 Hz, 2H) (3.11 (t, 4.5, 6.5 Hz, 2H)); H-10: 7.56 (s, 1H); H-11: 6.84 (s, 1H); Sn–CH_3: 0.74, 0.69 (s, 6H) (0.56, 6H)
7	*n*-Bu_2Sn(L-2) (CD_3OD at 300 MHz)	H-2: 4.21 (t, 5.7 Hz, 1H) [37.5 Hz]; H-3 + H-4: 1.50–1.64 (m, 3H); H-5a + H-5b: 0.83 (d, 6.3 Hz, 6H); H-7: 3.74 (t, 4.8 Hz, 1H); H-8: 3.16, 3.21 (dd, 5.7, 5.7 Hz, 2H), 3.05, 3.00 (dd, 3.9, 4.2 Hz, 2H) [15.0 Hz]; H-10: 7.62 (s, 1H); H-11: 6.91 (s, 1H); H-α: 0.96 (d, 7.2 Hz, 4H); H-β + H-γ: 1.30–1.47 (m, 8H); H-δ: 0.90 (t, 7.2 Hz, 6H)
8	*n*-Oct_2Sn(L-2) (CD_3OD at 300 MHz)	H-2: 4.21 (t, 5.5 Hz, 1H); H-3 + H-4: 1.50–1.63 (m, 3H); H-5a + H-5b: 0.84 (t, 6.6 Hz, 6H); H-7: 3.74 (t, 4.9 Hz, 1H), 3.30 (t, 1.3 Hz, 1H); H-8: 3.19, 3.15 (dd, 6.0, 6.0 Hz, 2H), 3.05, 3.01 (dd, 4.2, 4.0 Hz, 2H); H-10: 7.61 (7.78) (s, 1H); H-11: 6.91 (7.0) (s, 1H); H-α to H-g: 1.50–1.15 (m, 28H); H-h; 0.89 (t, 3.3 Hz, 6H)

[a] Homonuclear proton–proton coupling multiplet abbreviations given in parentheses: s, singlet; d, doublet; t, triplet; q, quartet; dd, doubletdoublet; m, complex multiplet.
[b] $^2J/^nJ(^1H-^{117/119}Sn)$ coupling constants for the alkyl/phenyl groups are given between square brackets; small peak in parenthesis.
[c] Geminal coupling.
[d] Overlapping multiplets 

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to ν(Sn–N) and ν(Sn←N), further confirms the coordination of the amino nitrogen as well as the peptide nitrogen to the diorganotin(IV) moiety [2,12,17,22,23].

The ν_{as}(Sn–C) and ν_s(Sn–C) bands in all the dialkyltin(IV) derivatives are observed in the range 597–625 cm^{-1} for H_2L-1 and 613–667 cm^{-1} for H_2L-2, suggesting the existence of a bent C–Sn–C moiety [21,22], whereas in the diphenyltin(IV) derivatives, the corresponding ν_{as}(Sn–C) and ν_s(Sn–C) are observed at 270 ± 2 and 228 ± 2 cm^{-1}, respectively [21,22].

3.2. Solution NMR spectral studies

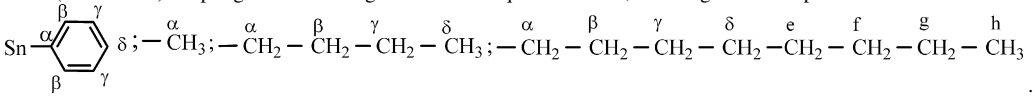
3.2.1. ^{1}H NMR spectral analysis

The characteristic resonance peaks in the ^{1}H NMR spectra of the studied derivatives, recorded in methanol-d_4, are presented in Table 3. The ^{1}H NMR spectral data of H_2L-1 are also included in Table 3 for comparison. In the ^{1}H NMR spectra of all of the derivatives studied, the CO(OH) resonance of the ligands (δ 12.0–13.0 ppm) is absent which suggests the replacement of the carboxylic proton by the organotin(IV) moiety. In all of the diorganotin(IV) derivatives, the –NH_2 resonances observed either as a broad weak signal or in conjugation with phenyl protons attached to the tin, are shifted towards low field in the ranges δ 7.45–7.78 ppm, when compared to those of the ligands (δ 5.0–8.0 ppm) [32]. This is probably due to the coordination of the amino group to the organotin(IV) moiety. As reported previously [2,13,17,19,21,22], upon complexation the magnetically non-equivalent alkyl protons of the ligands undergo the diamagnetic shielding due to the conformation adopted by the ligand molecules. The resonances due to the tin-alkyl protons in the studied Me_2Sn(IV), *n*-Bu_2Sn(IV) and *n*-Oct_2Sn(IV) derivatives are observed in the region δ 0.69–0.75, 0.90–1.53 and 0.89–1.50 ppm, respectively, whereas the tin-phenyl protons in the diphenyltin(IV) derivatives are observed in the regions δ

Table 4
^{13}C NMR spectral data of the diorganotin(IV) derivatives of H_2L-1 (His-Ala) and H_2L-2 (His-Leu)

Complex number	Complex/ligand (solvent)	δ (ppm)
H_2L-1	His-Ala (CD_3OD + DMSO-d_6 at 500 MHz)	C-1: 178.0; C-2: 48.4; C-3:16.0; C-4: 167.6; C-5: 55.5; C-6: 36.1; C-7: 111.0; C-8:134.6; C-9: 134.0
1	Ph_2Sn(L-1) (CD_3OD at 300 MHz)	C-1: 180.2; C-2: 51.8; C-3: 18.9; C-4: 175.6; C-5: 55.6; C-6: 32.9; C-7: 121.7; C-8: 136.7; C-9: 132.1; C-α: 141.2; C-β: 137.6 [37.4 Hz]; C-γ: 129.7 [60.4 Hz]; C-δ: 130.5
2	Me_2Sn(L-1) (CD_3OD at 300 MHz)	C-1: 181.2; C-2: 53.1; C-3: 20.0; C-4: 174.9; C-5: 55.9; C-6: 31.1; C-7: 117.8; C-8: 136.6; C-9: 134.9; C-α: 0.06, 0.00
3	Bu_2Sn(L-1) (CD_3OD at 300 MHz)	C-1: 181.3; C-2: 53.3; C-3: 19.7; C-4: 175.2; C-5: 56.2; C-6: 31.2; C-7: 117.3; C-8: 136.7; C-9: 135.4; C-α: 21.0, 20.7 [58.0 Hz][a]; C-β: 28.2 [38.0 Hz][a]; C-γ: 27.7, 27.5; C-δ: 13.9
4	Oct_2Sn(L-1) (CD_3OD at 300 MHz)	C-1: 181.5; C-2: 52.0 (51.7); C-3: 18.6, 19.7; C-4: 170.1; C-5: 56.2; C-6: 33.0; C-7: 121.1, 117.3; C-8: 137.1; C-9: 136.7; C-α: 26.1; C-β: 34.8, 34.5; C-γ: 31.3; C-δ: 30.3; C-e: 30.2; C-f: 23.7; C-g: 21.4, 21.1; C-h: 14.4
5	Ph_2Sn(L-2) (CD_3OD at 300 MHz)	C-1: 180.2; C-2 + C-7: 54.8; C-3: 42.9 (35.1); C-4: 23.8; C-5a + H-b: 22.0; C-6: 175.2; C-8: 26.2 (32.7); C-9: 136.6; C-10 + C-δ: 130.6; C-11 + C-γ: 129.7; C-α:153.2; C-β:137.6
6	Me_2Sn(L-2) (CD_3OD at 300 MHz)	C-1: 177.4; C-2: 52.7 (53.2); C-3: 40.0 (40.9); C-4: 23.2 (22.3); C-5a: 20.9 (21.2) C-5b: 19.1 (20.1); C-6: 172.9; C-7: 51.9 (53.1); C-8: 29.9 (28.1); C-9: 119.1 (114.3); C-10 + C-11: 133.7; C-α: −3.5
7	Bu_2Sn(L-2) (CD_3OD at 300 MHz)	C-1: 181.1; C-2: 56.6; C-3: 44.4; C-4: 25.4, 24.1; C-5a + C-5b: 21.2, 20.5; C-6: 175.0; C-7: 56.2; C-8: 31.1; C-9: 117.1; C-10 + C-11: 136.7 (136.2); C-α: 23.3; C-β: 28.4 [38.0 Hz]; C-γ: 27.9 (27.7); C-δ: 14.1
8	Oct_2Sn(L-2) (CD_3OD at 300 MHz)	C-1: 181.1; C-2: 56.6; C-3: 44.4; C-4: 24.2; C-5a + C-5b: 21.0, 21.5; C-6: 175.0; C-7: 56.3; C-8: 31.1; C-9: 117.1; C-10: 136.7; C-11: 124.4; C-α: 26.3; C-β: 35.0, 34.8; C-γ: 33.2 [88.5]; C-δ: 30.5, 30.4; C-e: 25.4; C-f: 23.9; C-g: 23.3; C-h: 14.6

[a] $^{n}J(^{13}C-^{119}Sn)$ coupling constants are given between square brackets; weak signals are in parenthesis



7.45–7.78 ppm [13,17,19,21,22]. The resonances due to all the magnetically non-equivalent protons in the complexes have been successfully identified, and the total numbers of protons calculated from the integration curve are in agreement with those calculated from the proposed molecular formula.

3.2.2. ^{13}C NMR spectral analysis

The characteristic resonance peaks in the ^{13}C NMR spectra of all of the studied derivatives, recorded in deuterodimethylsulfoxide/deuteromethanol, are presented in Table 4. The ^{13}C NMR spectral data of H_2L-1 are also included in Table 4. The ^{13}C NMR spectrum of the H_2L-2 could not be recorded because of its extremely low solubility in DMSO-d_6/$CDCl_3$/CD_3OD.

The spectra of the organotin(IV) derivatives of H_2L-1 and H_2L-2 are consistent with the following observations:

- The resonances of the carboxylic carbon (i.e. C-1) in all of the studied derivatives are observed at larger δ (δ 181.50–180.20 ppm) than in the ligand H_2L-1 (δ 178.00 ppm) except in the compound **6**, suggesting the coordination of the dipeptides, through the carboxylic oxygen to the organotin(IV) moiety [2,12,22].
- Various carbons of the ligand; especially C-2, undergo a downfield shift upon complexation as compared with that of H_2L-1, indicating the strong interactions of the O–C=O with tin.
- The carbons of phenyl (δ 129.70–153.20 ppm) and alkyl (δ −3.50 to 35.00 ppm) groups attached to tin are observed at positions comparable with other, similar compounds [2,12,16,17,22,23].

The resonances of the $CO_{peptide}$ also get substantial upfield shift (δ 170.10–175.60 ppm) in comparison to the ligand H_2L-1 (δ 167.60 ppm) due to the presence of the inter-/intra-molecular hydrogen bonding to the some extent. The observed downfield shifts in the magnetically non-equivalent alkyl carbons of the dipeptides upon complexation are due to: (i) the coordination of the COO^-, N_{amino} and $N^-_{peptide}$ to the dialky/diphenyltin(IV) moiety, (ii) the resonance in the –CONH– group, and (iii) the inter-/intra-molecular hydrogen bonding. The above observations are consistent with the infrared and ^{1}H NMR spectral data. Moreover, in Me_2Sn(IV) derivatives, doublets of some signals have been observed due to the presence of stereoisomers.

3.2.3. ^{119}Sn NMR spectral analysis

The characteristic resonance peaks in the ^{119}Sn NMR spectra of all of the studied derivatives except Ph_2Sn(L-2), recorded in deuteromethanol, are presented in Table 5. The ^{119}Sn chemical shifts of Me_2Sn(L-1/L-2), *n*-Bu_2Sn(L-1/L-2), Ph_2Sn(L-1), and Oct_2Sn(L-1/L-2) are observed in the range 100.00 to −188.20 ppm which are characteristic of the five-coordinated dialkyl- and diphenyl-tin derivatives [2,12,16,17,22]. Further,

Table 5
^{119}Sn NMR spectral data of the diorganotin(IV) derivatives of H_2L-1 (His-Ala) and H_2L-2 (His-Leu)

Complex number	Complex	δ (ppm)
1	Ph_2Sn(L-1)	−188.2
2	Me_2Sn(L-1)	−120.0, −142.0
3	Bu_2Sn(L-1)	−145.5
4	Oct_2Sn(L-1)	100.0
6	Me_2Sn(L-2)	−170.50
7	Bu_2Sn(L-2)	−142.60
8	Oct_2Sn(L-2)	−143.15

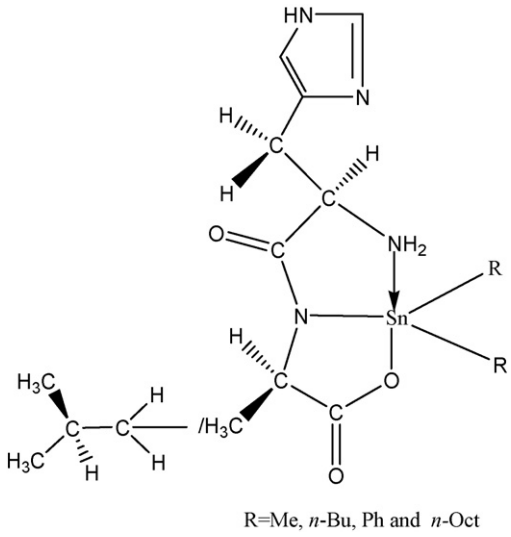
^{119}Sn NMR spectra of Me_2Sn(L-1) gave additional peak at −141.86 ppm indicating the presence of stereoisomers.

3.3. ^{119}Sn Mössbauer spectral studies

The ^{119}Sn Mössbauer parameters have been utilized as a diagnostic tool for proposing the structure that a particular compound can adopt in the solid state. These parameters point out whether, the coordination of the amino group nitrogen atom, bonding of the $N^-_{peptide}$ and the carboxylic oxygen to tin lead to chelation or polymerization. The ^{119}Sn Mössbauer spectral data of all of the studied compounds are presented in Table 6. The narrowness of the linewidths, τ, except the diphenyltin(IV) derivatives, implies the general occurrence of single tin sites in each compound, as well as of multiple coordination sites with corresponding environment [30]. The experimental nuclear quadrupole splitting (Q.S.) values of the solid-state R_2Sn(IV) derivatives (R = Me, *n*-Bu, Ph and *n*-Oct), presented in Table 6, describe two classes of compounds:

(i) Those having a doublet centered in the region 0.40–0.60 mm s^{-1}; quadrupole splitting (Q.S.) in the region 1.00–1.54 mm s^{-1} for Ph_2Sn(L-1) and Ph_2Sn(L-2).
(ii) Those having a doublet centered in the region 0.90–1.16 mm s^{-1}; quadrupole splitting (Q.S.) in the region 1.97–3.03 mm s^{-1} for R_2Sn(L-1) and R_2Sn(L-2) (R = Me, *n*-Bu and *n*-Oct).

These observations indicate that on going from class (i) to class (ii) compounds, both I.S. (isomer shift) and Q.S. (quadrupole splitting) values increase due to an increase in s-



R=Me, *n*-Bu, Ph and *n*-Oct

Fig. 1. Proposed structure of diorganotin(IV) hitidinylalaninates/histidinylleucinates.

electron density as well as the large asymmetry of the electron distribution around the tin atom [29,30]. This is probably due to stronger bonding of the ligands to the dialkyltin(IV) than to the diphenyltin(IV) moiety, and partly due to the strain developed in the ligand. It has been reported that the replacement of an alkyl group by a phenyl group lowers the isomer shift in the organotin(IV) derivatives of the dipeptides/amino acids [12,16,17,22,30,33]. Similar trend is also observed in I.S. and Q.S. values of the diphenyltin(IV) complexes studied (Table 6).

I.S. and Q.S. values observed in R_2Sn(IV) derivatives of the peptides are slightly lower than those of previously reported complexes [12,17,22,30]. The spectroscopic and crystallographic studies reported a distorted trigonal bipyramidal configuration for R_2Sn(L) (where H_2L = dipeptide), where the organic groups of the organotin(IV) moiety and peptide nitrogen are lying in equatorial position, and the amino nitrogen and carboxylic oxygen atoms are axial [2,12,17,22,30]. Thus, the tin atom configuration as shown in Fig. 1 can be again proposed for R_2Sn(L-1)/(L-2), which would then be [histidinylalaninato/histidinylleucinato-*O*,*N*,*N*-(2-)diorganotin(IV)], mainly on the basis of the above mentioned similarity between the observed and reported Q.S. values [2,12,17,22,30], taking also into account the symmetry as

Table 6
^{119}Sn Mössbauer data (80 K) of the diorganotin(IV) derivatives of H_2L-1 (His-Ala) and H_2L-2 (His-Leu)

Complex number[a]	Complex	Q.S. (mm s^{-1})	I.S. (mm s^{-1})	ρ (Q.S/I.S.)	τ_1(L)	τ_2(R)
1	Ph_2Sn(L-1)	1.00	0.40	2.50	1.20	2.00
2	Me_2Sn(L-1)	2.90	1.16	2.50	1.15	1.26
3	*n*-Bu_2Sn(L-1)	3.03	1.03	3.00	3.50	4.00
4	*n*-Oct_2Sn(L-1)	2.12	1.00	2.12	1.03	1.13
5	Ph_2Sn(L-2)	1.54	0.60	2.56	1.28	1.81
6	Me_2Sn(L-2)	2.17	0.90	2.41	1.02	1.13
7	*n*-Bu_2Sn(L-2)	1.97	0.95	2.07	2.65	2.68
8	*n*-Oct_2Sn(L-2)	2.33	1.03	2.26	1.12	1.46

[a] Q.S., quadrupole splitting; I.S., isomeric shift relative to $BaSnO_3$ and tin foil (splitting: 2.52 mm s^{-1}); τ_1(L): half line-width left doublet component; τ_2(R): half line-width right doublet component (mm s^{-1}).

well as the chelation constraints of the coordinated ligands [20].

Further it has been reported that the equatorial nitrogen, i.e. $N_{peptide}$ would release more negative charge into the neighborhood of tin than the axial nitrogen (N_{amino}) atom [34,35] in diorganotin glycylglycinates. The bond length Sn–$N_{peptide}$ is quite short [34], which is indicative of a consistent s-character in that bond as well as its involvement into the π-delocalization of the peptide group [34]. The latter feature would concentrate negative charge in the trigonal plane in the proximity of the tin nucleus, so that $\{N\}^{tbe}$ would not be very much different from $\{R\}^{tbe}$ [34,35]. The lower values of I.S. and Q.S. in all the diorganotin(IV) derivatives of dipeptides may be due to the almost symmetrical distribution of charge in the plane containing O, N, N donor atoms even though considerable s-character in the Sn–$N_{peptide}$ bond makes $N_{peptide}$ similar to $\{R\}^{tbe}$, R = Me, *n*-Bu, *n*-Oct and Ph. This suggest that considerable electron withdrawal from equatorial plane occurs due to the involvement of axial groups in bonding with neighboring molecules, thereby, giving a polymeric structure (as evident from low solubility of the compounds in common organic solvents, and from IR data). Further, the Mössbauer data (Table 6) indicate a pronounced line intensity asymmetry (Goldanskii–Karyagin effect) in all the studied diorganotin(IV) derivatives (not much pronounced in dimethyltin(IV) derivatives), which reflects a lattice dynamic anisotropy in the recoil-free fraction arising in the diorganotin(IV) derivatives possessing intermolecular association along particular axes in the solid state [28]. Further, the intermolecular hydrogen bonding between amino and carbonyl oxygen taking place in Ph_2Sn(Gly-Gly) [34,35] is also present to the some extent in all of these derivatives studied, which is responsible for the low solubility of the compounds in common organic solvents.

Acknowledgements

Thanks are due to the DST, New Delhi (India) for sanctioning the research project to Prof. Mala Nath (grant no. SP/S1/F07/2000) sponsored by DST, New Delhi, India. H. Singh is grateful to DST, New Delhi, India, for awarding JRF under the same project. G. Eng and X. Song thank the National Institute of Health Minority Biomedical Research, U.S.A. for the financial support for Mössbauer work.

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