APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 385–391 (1991)

Synthesis and spectroscopic characterization of organotin derivatives of *N*-benzoylglycylglycine

Giuseppe Ruisi and Maria Teresa Lo Giudice
Dipartimento di Chimica Inorganica, Università di Palermo, 26 via Archirafi, I-90123 Palermo, Italy

Di- and tri-organotin derivatives of *N*-benzoylglycylglycine (HBzGlyGly) were synthesized and characterized by infrared, ^{1}H, ^{13}C NMR and ^{119}Sn Mössbauer spectroscopy. Diorganotin derivatives appear to be dimer distannoxanes ($[R_2SnBzGlyGly]_2O)_2$ (R = CH_3, n-C_4H_9, n-C_8H_{17}) with a ladder-type structure where tin atoms are five-coordinated and N-benzoylglycylglycine alternatively acts as a unidentate or bridging bidentate ligand through the carboxylate group. For triorganotin derivatives $R_3SnBzGlyGly$ (R = CH_3, n-C_4H_8) we propose a polymeric structure where *N*-benzoylglycylglycine bridges planar SnC_3 units through the carboxylate group.

Keywords: Organotin compounds, *N*-benzoylglycylglycine

INTRODUCTION

Di- and tri-organotin derivatives of *N*-protected dipeptides were recently investigated.[1–5] In all cases the triorganotin derivatives[1–4] seem to have the same structure, with the carboxylate group unidentately bound to the Alk_3Sn moiety and an intermolecular NHCO · · · $SnAlk_3$ bond. In diorganotin derivatives[5] an Sn—O—Sn bond is present and the ligand (*N*-benzoyl-DL-alanylglycine) binds the tin atoms through the chelating carboxylate group, or through the carboxylate group (unidentate) and the peptide C=O group. We synthesized di- and tri-organotin derivatives of *N*-benzoylglycylglycine (only the former are new products) and propose, on the basis of spectroscopic data, quite different structures.

EXPERIMENTAL

Products and solvents, unless otherwise stated, were obtained from C. Erba, Milano, Italy, and used as received. *N*-Benzoylglycylglycine ($C_6H_5CONHCH_2CONHCH_2COOH$, abbreviated to HBzGlyGly) was prepared following published procedures;[6] glycylglycine ($H_2NCH_2CONHCH_2COOH$) was from Behring Corp., San Diego, USA. The complexes were synthesized from organotin oxides R_2SnO (R = CH_3, n-C_4H_9, n-C_8H_{17}) and hydroxides R_3SnOH (R = CH_3, n-C_4H_9) freshly prepared from the respective organotin chlorides, obtained from Schering AG, Bergkamen (FRG): *N*-benzoylglycylglycine and the organotin oxide or hydroxide were refluxed in a 1:1 molar ratio for 1–2 h in methanol or absolute ethanol giving a clear solution. The crystallization of the products was obtained by concentration *in vacuo* or by addition of ether. In the case of the tri-n-butyltin complex it was necessary to evaporate to dryness. The dimethyl derivative is also moderately soluble in water, whilst it decomposes in dimethyl sulphoxide (DMSO). In chloroform ($CH Cl_3$), acetone and benzene all diorganotin derivatives are insoluble. Trialkyltin complexes are soluble in methanol, ethanol, DMSO and $CHCl_3$; $Me_3SnBzGlyGly$ is also slightly soluble in water. Tin was estimated gravimetrically as SnO_2; carbon, hydrogen and nitrogen assays were carried out by the Dipartimento di Chimica Organica e Industriale, University of Milan. Infrared spectra were recorded on a Perkin–Elmer 580B spectrophotometer from Nujol and hexachlorobutadiene mulls in CsI discs. NMR spectra were recorded on a Bruker W80 instrument, operating at 80.1 MHz for ^{1}H spectra (trimethylsilane (TMS) or 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt (DSS) internal standard) and 20.15 MHz for ^{13}C spectra (TMS internal standard). ^{13}C spectra, like ^{1}H NMR spectra in D_2O, were restricted to

0268-2605/91/050385-07$05.00

Received 12 February 1991
Revised 25 May 1991

Table 1 Analytical data

Compound	M.p. (°C)	C(%) (calcd)	H(%) (calcd)	N(%) (calcd)	Sn(%) (calcd)
$[Me_2SnBzGlyGly]_2O$	191–192	40.55 (39.83)	4.29 (4.37)	7.17 (7.15)	30.01 (30.28)
$[Bu^n_2SnBzGlyGly]_2O$	160–162	48.31 (47.93)	5.82 (6.14)	5.85 (5.88)	24.78 (24.93)
$[Oct^n_2SnBzGlyGly]_2O$	137–140	55.86 (55.12)	7.51 (7.71)	4.81 (4.76)	20.66 (20.17)
$Me_3SnBzGlyGly$	80–85	42.31 (42.14)	4.95 (5.05)	7.03 (7.02)	29.40 (29.75)
$Bu^n_3SnBzGlyGly$	91–92	52.01 (52.59)	7.13 (7.29)	5.17 (5.33)	22.39 (22.60)

dimethyltin derivatives, which are the more soluble and/or more representative terms. The Mössbauer spectrometer employed in the present investigations consists of a Master 4000 multichannel analyser (Laben, Milan), equipped with function generator, driving unit, scintillation and proportional counters, and related instrumental units. The velocity transducer (Halder, Munich, FRG) moved at linear velocity, constant acceleration, in a triangular waveform. The Mössbauer sources were $Ca^{119}SnO_3$ and ^{57}Fe, 5 mCi, from the Radiochemical Centre, Amersham, UK. The latter was employed for the velocity calibration of the spectrometer using natural iron foil absorbers. The absorber samples were held at 77.3 K in a liquid N_2 cryostat (AERE Harwell, UK). The solution samples of di- and trimethyltin complexes, the only ones soluble enough in the solvents employed, were *ca* 0.05 mol dm^{-3}.

RESULTS AND DISCUSSION

Dialkyltin derivatives

Glycylglycine,[7,8] like glycylmethionine,[9] is known to coordinate diorganotin moieties tridentately by O(carboxylate), N(peptide) and N(amino) donor atoms. The polyhedron around tin is a distorted trigonal bipyramid formed by the two organic groups and the tridentate dipeptide ligand, the latter having a nearly planar skeleton. Acylation of the dipeptide prevents this type of coordination, the terminal amino group being converted to a substituted amide group which is not able to coordinate the metal: the N(amide) atom binds a metal only when the process is accompanied by the dissociation of the amide proton; the O(amide) atom is only weakly basic, metal-binding is weak, and when it occurs it is often stabilized by the closure of a chelate ring.[10] *N*-Benzoylglycylglycine reacts, however, with diorganotin oxides very easily; elemental analyses (Table 1) fit well for 1:1 complexes, whilst ^{119}Sn Mössbauer and ^1H NMR spectra (Tables 2 and 3) clearly indicate a trigonal-bipyramidal arrangement around tin. This may suggest, at first, a tridentate coordination of the ligand, as in the dipeptide complexes, with amide groups coordinating the organotin moiety, possibly, by the oxygen atom. However, amide oxygen atoms have very poor donor character and its coordination should require the formation of a not particularly stable hepta-atomic ring. A thorough examination of spectroscopic data strongly suggests that the neutralization of the diorganotin oxide is incomplete and a Sn—O bond is retained, the

Table 2 ^{119}Sn Mössbauer parameters, at 77 K, for $[R_2SnBzGlyGly]_2O$ and $R_3SnBzGlyGly$ compounds

Compound	IS[a] (mm s^{-1})	QS[b] (mm s^{-1})	$\Gamma\pm$[c] (mm s^{-1})
$[Me_2SnBzGlyGly]_2O$	1.17	3.33	0.88
Sol. in MeOH[d]	1.18	3.32	0.94
Sol. in H_2O[d]	1.19	3.27	0.89
$[Bu^n_2SnBzGlyGly]_2O$	1.28	3.31	0.85
$[Oct^n_2SnBzGlyGly]_2O$	1.28	3.32	0.83
$Me_3SnBzGlyGly$	1.29	3.38	0.84
Sol. in MeOH[d]	1.30	3.42	0.76
Sol. in H_2O[d]	1.30	3.48	0.79
$Bu^n_3SnBzGlyGly$	1.52	3.64	0.84

[a] Isomer shift relative to RT $CaSnO_3$. [b] Nuclear quadrupole splitting. [c] Full width at half height of the resonant peaks, average. [d] Solutions frozen by immersion in liquid N_2 soon after their preparation.

Table 3 ^{1}H NMR spectral data for *N*-benzoylglycylglycine (C_6H_5—CO—NH^{β}—CH_2^{β}—CO—NH^{α}—CH_2^{α}—COOH), its sodium salt and organotin complexes.

Compound	$\delta(CH_2)^{\alpha}$ (ppm)	$\delta(CH_2)^{\beta}$ (ppm)	$\delta(C_6H_5)$ (ppm)	δ(R—Sn) (ppm)	$\lvert^2J(^1H-^{119}Sn)\rvert$ (Hz)	$\delta(NH)^{\alpha}$ (ppm)	$\delta(NH)^{\beta}$ (ppm)	δ(OH) (ppm)
CD_3OD[a]								
HBzGlyGly	3.95	4.11	7.44–7.53 7.83–7.95					
NaBzGlyGly	3.78	4.09	7.44–7.53 7.84–7.94					
$[Me_2SnBzGlyGly]_2O$	3.86	4.09	7.44–7.53 7.84–7.94	0.76	86.0			
$[Bu^n_2SnBzGlyGly]_2O$	3.86	4.10	7.43–7.52 7.83–7.95	0.93–1.58				
$[Oct^n_2SnBzGlyGly]_2O$	3.86	4.10	7.44–7.53 7.83–7.95	0.83–1.61				
$Me_3SnBzGlyGly$	3.80	4.08	7.44–7.53 7.83–7.95	0.46	68.0			
$Bu^n_3SnBzGlyGly$	3.84	4.09	7.43–7.55 7.83–7.95	0.81–1.76				
D_2O[b]								
HBzGlyGly	3.94	4.16	7.52–7.60 7.79–7.89					
NaBzGlyGly	3.81	4.15	7.52–7.62 7.78–7.90					
$[Me_2SnBzGlyGly]_2O$	3.84	4.15	7.52–7.60 7.79–7.89	0.85	89.8			
$Me_3SnBzGlyGly$	3.81	4.15	7.52–7.60 7.78–7.91	0.53	68.2			
DMSO-d_6[a]								
HBzGlyGly	3.77	3.91	7.43–7.52 7.83–7.95			8.16	8.72	12.48
NaBzGlyGly	3.31	3.86	7.44–7.53 7.83–7.96			7.30	8.88	
$Me_3SnBzGlyGly$	3.55	3.88	7.44–7.53 7.83–7.95	0.39	70.6	7.66	8.68	
$Bu^n_3SnBzGlyGly$	3.58	3.90	7.43–7.52 7.83–7.95	0.76–1.68		7.68	8.68	

[a] Chemical shifts downfield from internal TMS. [b] Chemical shifts downfield from internal DSS.

products being tetraorganodistannoxanes $[R_2SnBzGlyGly]_2O$: the ligand should coordinate the metal centres only by carboxylic groups. Many distannoxanes containing carboxylate groups of the type $[R_2SnOOCR']_2O$ are known.[11,12] These compounds are characterized by dimeric structures, based on a four-membered $(Sn—O)_2$ ring, in which the carboxylate groups act alternatively as unidentate or bridging bidentate ligands and tin atoms are five- or six-coordinated (Fig. 1). The expansion of the coordination number of tin from five to six should be due to the interaction with unidentate carboxylate groups. In the infrared spectra of the complexes (Table 4) the vibrations associated with the COOH group of the free *N*-benzoylglycylglycine

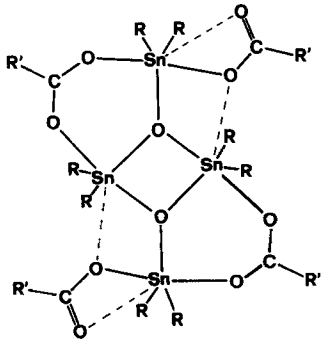

Figure 1 The structure of dicarboxylatotetraorganodistannoxanes.

Table 4 Relevant infrared frequencies (cm^{-1}) of *N*-benzoylglycylglycine, its sodium salt and organotin complexes

		$[R_2SnBzGlyGly]_2O$			$R_3SnBzGlyGly$		
HBzGlyGly	NaBzGlyGly	R = Me	R = Bu^n	R = Oct^n	R = Me	R = Bu^n	Assignments
1720s	—	—	—	—	—	—	C=O str. (COOH)
1667 s	1677 m	1677 m	1689 m	1687 m	1664 s	1655 sh	Amide I (peptide group)
1626 vs	1636 s	1642 s	1647 s	1642 s	1642 s	1639 vs	Amide I (amide group)
—	1587 s	1590 s	1586 vs	1597 s	1592 s	1604 s	CO_2 asym. str.
1573 s	1580 sh	1580 sh	1577 sh	1578 m	1574 m	1578 m	Amide II (peptide group)
1554 s	1535 s	1554 m	1550 m	1539 m	1531 m	1552 m	Amide II (amide group)
—	1400 m	1401 m	1396 m	1396 m	1401 m	1389 m	CO_2 sym. str.
		1344 m	1344 m	1336 m			CO_2 sym. str.
		652 s	634 s	634 s			SnO str. and
637 m	616 m	637 sh					CO_2 out-of-plane bend.[a]
		499 s	469 s	475 s			SnO ring and
491 m	513 m		490 m				CO_2 rock[b]

Abbreviations: s = strong; m = medium; sh = shoulder. [a] Refs 10, 11, 32. [b] Refs. 10, 11.

have disappeared, so that it can be concluded that the R_2Sn moieties are bound through the carboxylic group to the *N*-benzoylglycylglycine. On the other hand, comparison between peptide and amide group stretching frequencies in the ligand, its sodium salt and diorganotin complexes do not reveal any participation of these groups in the binding to the metal. According to the literature,[13] coordination by oxygen of the amido group to a metal atom causes an increase in the frequency of the Amide I absorption band and a decrease in that of Amide II. The opposite effect is observed on coordination by nitrogen atoms. The shifts in the frequencies of Amide I and Amide II bands observed in the spectra of our complexes do not follow such patterns and are probably due to interactions such as hydrogen bonding. The type of bonding of the carboxylic group may be deduced from the frequencies of $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$.[14] The spectra of the complexes are characterized by a broad band at 1586–1597 cm^{-1}, clearly attributable to $\nu_{asym}(COO)$, and two bands, at 1396–1401 and at 1336–1344 cm^{-1} respectively, which we attribute to symmetric stretching vibrations of the carboxylate. These assignments support the proposed structure. In fact, while for the bridging carboxylate we must expect stretching frequencies similar to those in the sodium salt ($\nu_{asym}(COO)$ = 1578 cm^{-1}; $\nu_{sym}(COO)$ = 1400 cm^{-1}), the bidentate coordination keeping the equivalence of the C—O bonds, unidentate carboxylate should be characterized by a greater separation between symmetric and asymmetric stretching frequencies.[14] So, the band at 1336–1344 cm^{-1} is assigned to $\nu_{sym}(COO)$ of unidentate carboxylate, the corresponding asymmetric vibration being probably included in the broad band at 1642–1647 cm^{-1} attributed to Amide I stretching of the peptide group. At low energies two intense bands are present in the spectra of the complexes, at 634–652 cm^{-1} and 475–499 cm^{-1}, which are characteristic of dimer distannoxanes.[15,16]

Other information on the environment of tin atoms may be deduced from Mössbauer spectra in Table 2. It is well known that the quadrupole splitting in R_2SnX_3 compounds is largely determined by the C—Sn—C bond angle, being the electric field gradient dominated by the highly covalent Sn—C bonds. Reasonably good point-charge calculations can be made, in effect, by ignoring the contribution of the ligands X. Under these approximations the symmetrization method gives:[17]

$$QS = -4[R][1 - \tfrac{3}{4}\sin^2\theta]^{1/2}$$

where θ is the C—Sn—C bond angle; QS is the nuclear quadrupole splitting; $[R]$ is the partial quadrupole splitting of alkyl group. In dicarboxylatotetraorganodistannoxanes so far investigated by X-ray diffraction studies,[11,12] the C—Sn—C bond angles in the four Alk_2Sn units of the dimer are sometimes very similar,[12] but usually they differ somewhat and differences of *ca* 15° are common. On this basis the Mössbauer spectra would be expected to show generally two quadrupole split doublets of differing separations, or one pair of broadened peaks. In the dimer

$[n\text{-}(C_4H_9)_2Sn(O_2CC_6H_4NH_2\text{-}o)_2]_2$, characterized by Narula *et al.*[18], one molecule has one six-coordinated and one five-coordinated tin atom while the other has two six-coordinated tin atoms. The C—Sn—C bond angles are 137°, 140°, 149° for six-coordinated tin atoms and 136° for the five-coordinated one; the Mössbauer spectrum is characterized by a doublet with a quadrupole splitting of 3.50 mm s^{-1} which closely corresponds to the average of the QS values calculated for each tin atom with Parish's equation.[18] The quadrupole splitting parameter is related then to the mean C—Sn—C bond angle in the dimer. The spectra of all *N*-benzoylglycylglycine complexes in the solid state consist of a symmetric unbroadened doublet with quadrupole splitting values of 3.31–3.33 mm s^{-1}. Similar values were reported for $[n\text{-}Bu_2SnOCOMe]_2O$,[19] which was assumed to have the structure in Fig. 1 with five-coordinated tin atoms, whilst the quadrupole splittings for the compounds $Me_2SnCl_3^-$ and $Me_2SnBr_2.Et_4N$, which are known by X-ray crystallography[20,21] to possess trigonal-bipyramidal geometry with two equatorial alkyl groups, are 3.30 mm s^{-1} (Ref. 22) and 3.39 mm s^{-1} (Ref. 21) respectively. The C—Sn—C bond angle calculated for *N*-benzoylglycylglycinates is 128–129° and is consistent with the five-coordination, although the C—Sn—C angles in isolation cannot be used, in principle, to predict the geometry of each tin atom in the dimer.[18] The spectra of frozen solutions of dimethyltin derivatives in methanol and in water (see Table 2) are slightly asymmetric, but QS and linewidth values are comparable to those of the solid, showing that the organotin moiety maintains in these solvents the configuration (essentially the C—Sn—C bond angle) of the solid.

^1H NMR spectral data are reported in Table 3. Following the notation of Sheinblatt,[23] the peptide/amide and methylene groups of *N*-benzoylglycylglycine are labelled as follows:

$$C_6H_5\text{—}CO\text{—}NH\text{—}\underset{\beta}{CH_2}\text{—}CO\text{—}NH\text{—}\underset{\alpha}{CH_2}\text{—}COOH$$

Resonances for the α- and β-methylene protons are assigned on the basis of the shift they undergo owing to the ionization of the carboxylic group (sodium salt spectrum), the α-methylene protons being more shifted than the β-methylene ones.[24] The spectra of the complexes in methanol (water) are characterized by an analogous shift, from 3.95 (3.94) to 3.86 (3.84) ppm, in the resonance of α-methylene protons, whilst the β-methylene ones are practically unaffected by coordination. Only the carboxylic group appears then to be involved in the bonding of the *N*-benzoylglycylglycine to the $Alk_2Sn(IV)$ moiety. The coupling constant $|^2J(^1H\text{–}^{119}Sn)|$, which characterizes the resonance of the methyl protons in Me_2Sn derivative (86.0 Hz in CD_3OD and 89.8 Hz in D_2O), agrees with the trigonal-bipyramidal configuration around tin in the dimer corresponding, according to Holmes and Kaesz,[25] to a 40–41% *s* character in the Sn—C bonds.

Trialkyltin derivatives

The absence of the ν(C=O) in the IR spectra of the complexes points out the coordination of the carboxylic group. Taking as an example $Me_3SnBzGlyGly$, ν_{asym}(COO) and ν_{sym}(COO) frequencies, at 1592 and 1401 cm^{-1}, are practically coincident with the corresponding frequencies in the spectrum of the sodium salt (at 1587 and 1400 cm^{-1}): the equivalence of the C—O bonds of the carboxylate is maintained in the complex and then the carboxylate acts as a bridging bidentate ligand.[14] Chelation would require a greater separation between symmetric and asymmetric (COO) stretching and it is ruled out, in any case, by tin–carbon stretching modes which occur in the 500–550 cm^{-1} region. A trigonal-planar SnC_3 structure (local D_{3h} symmetry) will give rise to the infrared-active ν_{asym}(Sn—C) mode; the ν_{sym}(Sn—C) mode, Raman-active, will appear in the infrared spectrum if there is significant deviation from planarity (local C_{3v} symmetry).[26] In the spectrum of $Me_3SnBzGlyGly$ only one band is present, at 551 cm^{-1}, which is attributable to the $\nu_{asym}(SnC_3)$; hence the $Sn(CH_3)_3$ moiety has presumably a planar or nearly planar structure. The analysis of IR spectra shows, at last, that peptide and amide groups are, once again, not involved in bonding to the organotin moiety. The infrared spectrum of the tributyltin derivative may clearly be interpreted in the same way. Roge *et al.*[27] gave the same interpretation of the IR spectra of $Me_3SnBzGly$, where $BzGly^-$ is the anion of the *N*-benzoylglycine. ^{119}Sn Mössbauer parameters (Table 2) support the above assignments, QS values are in fact very similar to those obtained for trimethyltin acetate and trimethyltin formate (3.58 and 3.59 mm s^{-1}, respectively[28]) which is known[29,30] to be polymeric with tin atoms linked

Table 5 ^{13}C NMR spectral data[a] for *N*-benzoylglycylglycine (C_6H_5—CO^{β}—NH—CH_2^{β}—CO^{α}—NH—CH_2^{α}—COOH), its sodium salt and $Me_3SnBzGlyGly$

Compound	$\delta(C_6H_5)$[b] (ppm)	$d(C{=}O)^{\beta}$ (ppm)	$\delta(CH_2)^{\beta}$ (ppm)	$\delta(C{=}O)^{\alpha}$ (ppm)	$\delta(CH_2)^{\alpha}$ (ppm)	δ(COOH) (ppm)	$\lvert J(^{13}C-^{119}Sn)\rvert$ (Hz)
HBzGlyGly	135.06^{i} 128.49^{o} 129.58^{m} 132.94^{p}	170.46	43.93	172.21	41.85	172.98	
NaBzGlyGly	135.09^{i} 128.49^{o} 129.51^{m} 132.87^{p}	170.39	44.22	171.33	44.47	176.30	
$Me_3SnBzGlyGly$[c]	134.95^{i} 128.45^{o} 129.51^{m} 132.86^{p}	170.24	43.44	171.63	44.04	175.57	500

[a] In CD_3OD, chemical shifts downfield from internal TMS. [b] *i*, *ipso*, *o*, *ortho*; *m*, *meta*; *p*, *para*. [c] $\delta(CH_3Sn) = -2.20$ ppm.

by carboxylate bridges, the tin atoms being in five-fold trigonal-bipyramidal coordination with alkyl groups in the basal plane and oxygen atoms at the apices. $Me_3SnBzGly$, mentioned above, has a QS of 3.63 mm s^{-1}. It is noteworthy that the parameters relative to frozen solutions of $Me_3SnBzGlyGly$ are very similar to those which characterize the solid, and then the complexes maintain in solution the configuration they assume in solid, at least as far as the geometry of the R_3Sn group is concerned. Such a hypothesis is proved by NMR data. Proton resonances, in CD_3OD, D_2O and DMSO-d_6, are in Table 3. Resonances for the peptide/amide protons of *N*-benzoylglycylglycine in DMSO-d_6 occur at 8.16 and 8.72 ppm; their assignment is still based on the effect that the ionization of the ligand has on the chemical shifts: the 8.16 ppm resonance is shifted upfield (at 7.30 ppm) in the spectrum of the sodium salt, and then it is assigned to the α-NH (peptide) group, whilst the 8.72 ppm resonance is almost unaffected by ionization and may be therefore associated with β-NH. The ionization of the ligand also produces an upfield shift of the α-methylene resonance[24] (from 3.77 to 3.31 ppm). The OH resonance is at 12.48 ppm. The spectra of the complexes are characterized by analogous shifts in the resonances of α-NH and α-methylene groups, showing that the carboxylic group is coordinated to the triorganotin moiety. The same changes are observed, as far as the methylene groups are concerned, in the other solvents employed. The $\lvert^2J(^1H-^{119}Sn)\rvert$ coupling constant is practically the same (68.0–70.6 Hz) in all the solvents; the corresponding *s*-character of tin atomic orbitals in Sn—C bonds[25] is 32–33%, in excellent agreement with the other structural information in the solid and in the solution phase. Carbon-13 resonances, in CD_3OD, are shown in Table 5. Assignments are proposed tentatively and in any case the uncertainty in some of them does not invalidate the structural hypotheses. It is evident, in fact, that the changes due to complexing (shift of the methylene and carbonyl resonances) are similar to those produced by ionization of *N*-benzoylglycylglycine, confirming that the carboxylic group alone is involved in the bonding to the trialkyltin moiety. The coupling constant $\lvert J(^{13}C-^{119}Sn)\rvert$ (500 Hz) is characteristic of five-coordinated trialkyltin compounds with the Sn—Alk_3 moiety on the trigonal plane.[31] The adduct $Me_3SnCl \cdot Py$, for example, is characterized by a coupling constant of 472 Hz.

CONCLUSIONS

N-Benzoylglycylglycine binds di-and tri-organotin moieties through the carboxylic group only, giving, respectively, dimer tetraorganodistannoxanes and polymers with planar $SnAlk_3$ units linked by carboxylate groups.

Acknowledgements

The support of the Ministero dell' Università e della Ricerca Scientifica e Tecnologica, Rome, is gratefully acknowledged.

REFERENCES

1. Sandhu, G K, Kaur, G, Holecek, J and Lycka, A *J. Organomet. Chem.*, 1987, 332: 75
2. Sandhu, G K, Kaur, G, Holecek, J and Lycka, A *J. Organomet. Chem.*, 1988, 345: 51
3. Sandhu, G K, Kaur, G, Holecek, J and Lycka, A *J. Organomet. Chem.*, 1989, 365: 215
4. Sandhu, G K and Kaur, G *J. Organomet. Chem.*, 1990, 388: 63
5. Sandhu, G K, Gupta, R, Sandhu, S S, Moore, L S and Parish, R V *J. Organomet. Chem.*, 1986, 311: 281
6. William, M W and Young, G T *J. Chem. Soc.*, 1963, 881
7. Huber, F, Haupt, H J, Preut, H, Barbieri, R and Lo Giudice, M T *Z. Anorg. Allg. Chem.*, 1977, 432: 51
8. Preut, H, Mundus, B, Huber, F and Barbieri, R *Acta Cryst.*, 1989, C45: 728
9. Preut, H, Mundus, B, Huber, F and Barbieri, R *Acta Cryst.*, 1986, C42: 536
10. Freeman, H C Metal complexes of amino acids and peptides. In: *Inorganic Biochemistry*, Eichorn, L (ed), Elsevier Scientific Publishing Company, Amsterdam, vol 1, 1973, pp 121–166
11. Parulekar, C S, Jain, V K, Das, T K Gupta, A R, Hoskins, B F and Tiekink, E R T *J. Organomet. Chem.*, 1989, 372: 193 and references therein
12. Chandrasekhar, V, Day, R O, Holmes, J M and Holmes R R *Inorg. Chem.*, 1988, 27: 958
13. Roge, G, Huber, F, Preut, H, Silvestri, A and Barbieri, R *J. Chem. Soc., Dalton Trans.*, 1983, 595 and references therein
14. Deacon, G B and Phillips, R J *Coord. Chem. Rev.*, 1980, 33: 227; Deacon, G B, Huber, F and Phillips, R *Inorg. Chim. Acta*, 1985, 104: 41
15. Wang, C S-C and Shreeve, M *J. Organomet. Chem.*, 1972, 46: 271 and references therein
16. Maeda, Y and Okawara, R *J. Organomet. Chem.*, 1967, 10: 247
17. Parish, R V Structure and bonding in tin compounds. In: *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Long, G J (ed), Plenum Press, New York, vol 1, 1984, pp 527–575
18. Narula, S P, Bharadwaj, S K, Sharma, H K, Mairesse, G, Barbier, P and Nowogrowcki, G *J. Chem. Soc., Dalton Trans.*, 1988, 1719
19. Davies, A G, Smith, L, Smith, P J and McFarlane, W *J. Organomet. Chem.*, 1971, 29: 245
20. Einstein, F W B and Penfold, B R *J. Chem. Soc. (A)*, 1968, 3019
21. Parish, R V and Johnson, C E *J. Chem. Soc. (A)*, 1971, 1906
22. Ali, K M, Cunningham, D, Frazer, M J, Donaldson, J D and Senior, B J *J. Chem. Soc. (A)*, 1969, 2836
23. Sheinblatt, M *J. Am. Chem. Soc.*, 1966, 88: 2123
24. Rabenstein, D L and Libich, S *Inorg. Chem.*, 1972, 11: 2960
25. Holmes, J R and Kaesz, H D *J Am. Chem. Soc.*, 1961, 83: 3903
26. Ho, B Y K and Zuckerman, J J *Inorg. Chem.*, 1973, 12: 1552
27. Roge, G, Huber, F, Silvestri, A and Barbieri, R *Z. Naturforsch.*, 1982, 37b: 1456
28. Molloy, K C, Quill, K and Nowell, I W *J. Chem. Soc., Dalton Trans.*, 1987, 101
29. Chih, H and Penfold, B R *J. Cryst. Mol. Struct.*, 1973, 3: 285
30. Ho, B Y K and Zuckerman, J J *J. Organomet. Chem.*, 1973, 49: 1
31. Mitchell, T N, *J. Organomet. Chem.*, 1973, 59: 189
32. Alcock, N W, Tracy, V M and Waddington, T C *J. Chem. Soc., Dalton Trans* 1976, 2243