Journal of Organometallic Chemistry, 365 (1989) 111–121
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09493

Triorganotin and triorganolead derivatives of glutamic and aspartic acid. Crystal structure of trimethyltin glutamate *

F. Huber, B. Mundus-Glowacki and H. Preut
Fachbereich Chemie, Universität Dortmund, Postfach 500 500, D-4600 Dortmund 50 (F.R.G.)

(Received July 27th, 1988)

Abstract

Triorganotin and triorganolead derivatives of glutamic acid (H_2Glu) and aspartic acid (H_2Asp) $(R_3M)_2Glu$ (M = Sn, R = Me, Ph; M = Pb, R = Ph) and R_3SnHL (L = Glu, R = Me, n-Bu; L = Asp, R = Me) have been prepared from R_3MOH or $(n\text{-}Bu_3Sn)_2O$ and the amino acid. Methanolysis of $(R_3Sn)_2L$ also produces R_3SnHL. The crystal structure of trimethyltin glutamate $Me_3SnHGlu$ has been determined by single crystal X-ray diffraction. Tin is in a slightly distorted trigonal bipyramidal environment with Me in equatorial positions. The axial positions are occupied by oxygen atoms of the monodentate carboxylate groups (O–Sn–O 174.8(2)°; Sn–O 2.222(3), 2.301(3) Å) such as to form a helical chain. Hydrogen bonds link the NH_3^+ group to the four carboxylate oxygen atoms (N ··· O 2.601(4) to 2.797(6) Å). The intramolecular hydrogen bonds appear to stabilize the helical structure, the helices being associated by the intermolecular hydrogen bonds. From IR data analogous molecular structures are inferred for the other R_3SnHL derivatives. $(Ph_3Sn)_2Glu$ is monomeric and contains monodentate carboxylate groups, while for $(Me_3Sn)_2Glu$ and for $(Ph_3Pb)_2Glu$ obtained from methanol a polymeric structure with $M\text{–}NH_2$-coordination and both mono- and bi-dentate carboxylate groups are proposed. An isomeric compound $(Ph_3Pb)_2Glu$ having a different polymeric structure was obtained from benzene.

Introduction

Organotin and organolead derivatives of aminoacids and peptides show an appreciable structural variability and offer striking examples for the response of the bonding and coordination tendencies of the organometallic moiety to the quality and quantity of the different ligand donor centers [1–9]. Zuckerman and his group opened this interesting field of investigations by advancing structural proposals for

---

* In memoriam Prof. Dr. J.J. Zuckerman.

0022-328X/89/$03.50

a series of trialkyltin derivatives of amino acids and dipeptides on the basis of IR and Mössbauer data [10]. We extended our previous studies by synthesizing and characterizing triorganotin and triorganolead derivatives of the aminodicarboxylic acids aspartic acid (H_2Asp) and glutamic acid (H_2Glu) to examine the behavior of an additional carboxylate group in the amino acid ligand (being not adjacent to the amino group) and its structural effects in such amino acid derivatives. Compounds of this type had not been studied before in detail and only a short preliminary note on triorganolead aspartates has been published [5].

Experimental

Me_3SnOH, Ph_3SnOH and Ph_3PbOH were prepared according to common methods. Amino acids, $(n\text{-}Bu_3Sn)_2O$ and solvents were commercial products (Merck, Fluka). The solvents were dried before use.

$Me_3SnHGlu$ (**1**), $n\text{-}Bu_3SnHGlu$ (**2**), $Me_3SnHAsp$ (**3**), $(Ph_3Sn)_2Glu$ (**5**) and $(Ph_3Pb)_2Glu$ (**6**) were synthesized by refluxing a 2/1 molar mixture of R_3MOH and amino acid (1 mmol) or a 1/1 mixture of $(n\text{-}Bu_3Sn)_2O$ and H_2Glu (1 mmol) in boiling methanol (70 ml). 2,2-Dimethoxypropane was added to remove the water of neutralization. After several hours (see Table 1) the volume of the solution was reduced by evaporating about 55 ml solvent. Then diethyl ether was added until the product precipitated.

Compounds **1**, $(Me_3Sn)_2Glu$ (**4**), **5** and $(Ph_3Pb)_2Glu$ (**7**) (an isomer of **6**) were synthesized similar to a general procedure given in refs. 10 and 11 by refluxing a 2/1 molar mixture of R_3MOH and H_2Glu (1 mmol) in benzene (70 ml) and

Table 1

Analytical data for triorganometal derivatives of glutamic and aspartic acid

Compound	Reaction-time (h)	Yield (%)	Mp. (°C)	Analytical data (Found (calcd.)(%))			Molecular weight (Found in MeOH, DMSO [a] (calcd.))
				N	C	H	
$Me_3SnHGlu$ (**1**)	2 [b], 7 [c]	56.5 [b]	180 [d]	4.6	30.8	5.3	(298 [a]) [e]
		78.3 [c]		(4.6)	(31.2)	(5.2)	(310)
$n\text{-}Bu_3SnHGlu$ (**2**)	6 [b]	34.5	93	2.9	46.3	8.2	455
				(3.2)	(47.0)	(7.8)	(434)
$Me_3SnHAsp$ (**3**)	6 [b]	62.7	132	4.6	28.0	4.9	313
				(4.8)	(28.5)	(5.1)	(297)
$(Me_3Sn)_2Glu$ (**4**)	2.5 [c]	72.3	171 [d]	3.0	27.9	5.3	243 [f] (491 [a])
				(3.0)	(28.0)	(5.3)	(471)
$(Ph_3Sn)_2Glu$ (**5**)	16 [b], 36 [c]	83.0	75	1.5	56.8	4.2	423
				(1.7)	(58.4)	(4.4)	(843)
$(Ph_3Pb)_2Glu$ [g] (**6**)	5 [b]	69.8	125	1.3	47.2	3.9	492 [f]
			167 [d]	(1.4)	(48.2)	(3.8)	1021
$(Ph_3Pb)_2Glu$ [h] (**7**)	20 [c]	73.4	132	1.3	47.6	4.0	[e]
			210 [d]	(1.4)	(48.2)	(3.8)	1021

[a] In DMSO. [b] In methanol. [c] In benzene. [d] Decomposition. [e] Not determined due to unsufficient solubility or unsolubility in methanol. [f] Conductivity measurements (T 293 K, c 1×10^{-3} mol l^{-1}) (S cm^2 mol^{-1}): (**4**) 17.3; (**6**) 17.9. [g] Pb-analysis: found 40.2% calcd. 40.6%. [h] Pb-analysis: found 40.4%, calcd. 40.6%.

removing water of neutralization by azeotropic distillation. The residue was filtered off after several hours (see Table 1). In the case of **5** the solvent was evaporated in vacuo giving an oil which solidified on addition of diethyl ether.

Analytical data are summarized in Table 1. C, H, N analyses were performed on a Carlo Erba Strumentazione Elemental Analyzer 1106. The melting points are uncorrected and were determined in the usual way. Molecular weights were determined osmometrically.

$(Me_3Sn)_2Asp$ (**8**) and $(Ph_3Pb)_2Asp$ (**9**) were prepared from R_3MOH and H_2Asp in benzene according to [5]. Compound **8** has been obtained analogously using methanol as solvent when the reaction time was limited to < 3 h.

IR spectra (KBr disks) were recorded on a Perkin–Elmer grating spectrometer PE 580B, Raman spectra on a Coderg PHO spectrometer, ^1H NMR spectra on a Perkin–Elmer 90 MHz spectrometer R32, and ^{119}Sn and ^{13}C NMR spectra on a Bruker Multispin AM 300.

Single crystals of **1** crystallized from a solution of **4** in methanol after addition of diethyl ether. Crystal data: $C_8H_{17}O_4NSn$, $M = 309.9$, trigonal, space group $P3_1$, a 9.317(5), c 12.895(5) Å, V 964(8) Å^3, $Z = 3$, $D_c = 1.587$ Mg m^{-3}, $F(000) = 459$, μ(Mo-K_α) 1.97 mm^{-1}, graphite-monochromated Mo-K_α radiation, λ 0.71073 Å, crystal size $0.32 \times 0.32 \times 0.48$ mm, temperature 291(1) K, lattice parameters from least-squares fit with 25 reflexions up to 2θ 28.2°, CAD 4 diffractometer, $2\theta/\omega$ scans, scan speed 3.3° min^{-1}, four standard reflexions recorded every 2.5 h, only random deviations; 5954 reflexions measured in the range $1 \leqslant \theta \leqslant 30°$, $-13 \leqslant h \leqslant 13$, $-13 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 18$; after averaging 1962 unique reflexions ($R_{int} = 0.017$). The following corrections were applied: Lorentz polarization correction and absorption correction via ψ-scans; max./min. transmission, 1.00/0.96; systematic absences: (001) $l = 3n + 1$, $l = 3n + 2$ and diffraction symmetry conform to space groups $P3_1$ and $P3_2$; structure solution in space group $P3_1$ (No. 144) via Patterson synthesis, ΔF synthesis, and full matrix least squares on F with 1730 observed $F^2 \geqslant 3.0\sigma(F^2)$ values and 127 refined parameters; all non-H atoms were refined anisotropically and a common isotropic temperature factor was refined for all H-atoms, which were placed in geometrically calculated positions (C–H 0.95, N–H 0.96 Å); H(11) was placed on the line connecting N(1) and O(3) $(1 - x + y, 1 - x, z - 1/3)$ and H(12) on the line connecting N(1) and O(4) $(2 - x + y, 1 - x, z - 1/3)$. The position of the third H atom H(13) at N(1) was calculated such that a nearly tetrahedral environment around N(1) is formed. Weighting scheme $w^{-1} = [\sigma^2(F^2) + (0.07F^2)^2]^{1/2}$, $S = 0.74$, R (unweighted) $= 0.022$, R (weighted) 0.030, max. $\Delta/\sigma = 0.01$, no extinction correction; largest peak in final ΔF map $= \pm 0.5(2)$ e Å^{-3}; complex neutral-atom scattering factors from ref. 12; Programs; Enraf–Nonius Structure Determination Package [13], ORTEP [14], PARST [15], SHELXTL PLUS [16].

Results and discussion

The compounds listed in Table 1 were prepared by reaction of R_3MOH with H_2Glu or H_2Asp in the molar ratio 2/1 or by reaction of $(n\text{-}Bu_3Sn)_2O$ with H_2Glu in equimolar ratio. Methanol or benzene were used as solvents.

From the reactions of Ph_3MOH with H_2Glu products of the type $(Ph_3M)_2Glu$ (**5**, **6**, **7**) were obtained in all cases. The reaction rates were higher in methanol than in benzene (see Table 1). Compounds **6** and **7** obtained from methanol and benzene, respectively, had the same analytical composition $(Ph_3Pb)_2Glu$ but showed physical properties, which like the melting points (see Table 1) or solubilities were in part appreciably different. Compound **4** could be obtained only from benzene solution; with methanol as solvent as well as in the presence of water only **1** was produced. Attempts to recrystallize **4** at room temperature ended in the formation of **1** apparently as a consequence of solvolysis. Similarly, only **2** instead of $(n\text{-}Bu_3Sn)_2Glu$ was isolated from boiling methanolic solution even after an extended reaction time (see Table 1). Me_3PbOH did not react with H_2Glu, presumably due to the low reaction temperature which had to be observed to prevent thermal decomposition. The reaction of equimolar amounts of Me_3SnOH and H_2Glu in benzene gave a mixture of **1**, **4** and Me_3SnOH.

Experiments to employ the "NaCl method" for preparing R_3MHGlu were only successful with Me_3SnCl and NaHGlu in methanol and lead to pure **1**. Compound **4** hydrolyzed readily in water to produce a mixture of **1** and Me_3SnOH. The tendency of the glutamates to solvolyze increases in the order $Ph_3Sn < Ph_3Pb < Me_3Sn < n\text{-}Bu_3Sn < Me_3Pb$ obviously being determined by the polarisability and the ionic character of the R_3M group and depends from the polar and protic character of the solvent used.

The aspartates are less inclined to solvolyse than the glutamates. So **3** can be obtained by methanolysis of **8** but as a pure compound only after heating the methanol solution for more than 20 h, and for preparing **9** it is not necessary to remove the water formed during neutralization.

The glutamates and aspartates are colorless except **2** and **5** which are slightly yellow. They are soluble in methanol (except **1** which is only slightly soluble and **7** which is insoluble) but only slightly soluble in chloroform (except **1** and **7** which are insoluble). All are very soluble in DMSO.

Molecular weights corresponding to monomeric species have been observed for **2** and **3** in methanol and for **1** and **4** in DMSO solution, while **4**, **5** and **6** gave only

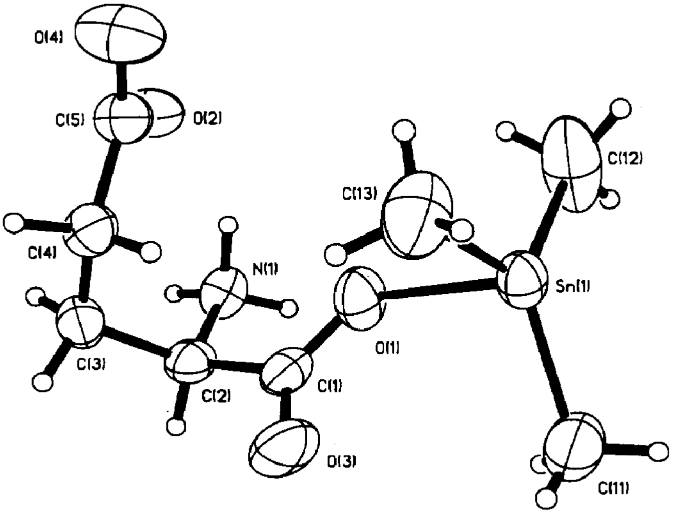

Fig. 1. General view of a molecule of $Me_3SnHGlu$ (**1**), showing atom numbering.

about one half of the values calculated for monomers (see Table 1). The low values of the conductivity of solutions of **4** and **6** in methanol excluded that these compounds dissociate into ions [17]. The molecular weight data obtained from solutions of compounds of the type $(R_3M)_2$Glu in methanol would then be consistent with the assumption of methanolysis and formation of two molecular species, presumably R_3MHGlu and R_3MOR. In the case of the phenyltin compounds the solvolysis is reversible, since $(Ph_3M)_2$Glu is recovered after evaporation of the solvent. In contrast only **1** was isolated from a solution of **4**.

The solid state structure of **1** could be determined by X-ray diffraction. A molecular unit of this compound is shown in Fig. 1 and the unit cell in Fig. 2. Atomic parameters and equivalent values of the anisotropic temperature factors for the non-H atoms are given in Table 2, and bond lengths and bond angles in Table 3. Tin has a slightly distorted trigonal bipyramidal surrounding, the C-atoms of the three methyl groups forming the equatorial plane and the two O-atoms O(1) and O(2) being in the apical positions. The tin atom is displaced 0.015 Å from the plane through C(11), C(12), C(13) in the direction of O(1). The angle O(1)–Sn(1)–O(2) was found to be 174.8°. Each tin atom links two glutamate ligands, one via O(1) of the α-carboxylate group and the other ligand via O(2) of the γ-carboxylate group, thereby forming a chain-like polymeric skeleton, α- and γ-carboxylate groups are monodentate.

Both Sn–O distances (Sn(1)–O(1) 2.222(3) Å; Sn(1)–O(2) 2.301(3) Å) are longer than the sum of the covalent radii of 2.09 Å [18]. While the distance Sn(1)–O(1) corresponds to bond lengths found in analogous pentacoordinated compounds like Me_3SnGly [19] (Sn–O 2.21(1) Å), the bond length Sn(1)–O(2) is similar to that in α-trimethyltin phenylphosphonate (2.319(5) Å) [20], in which the Sn–O bond has

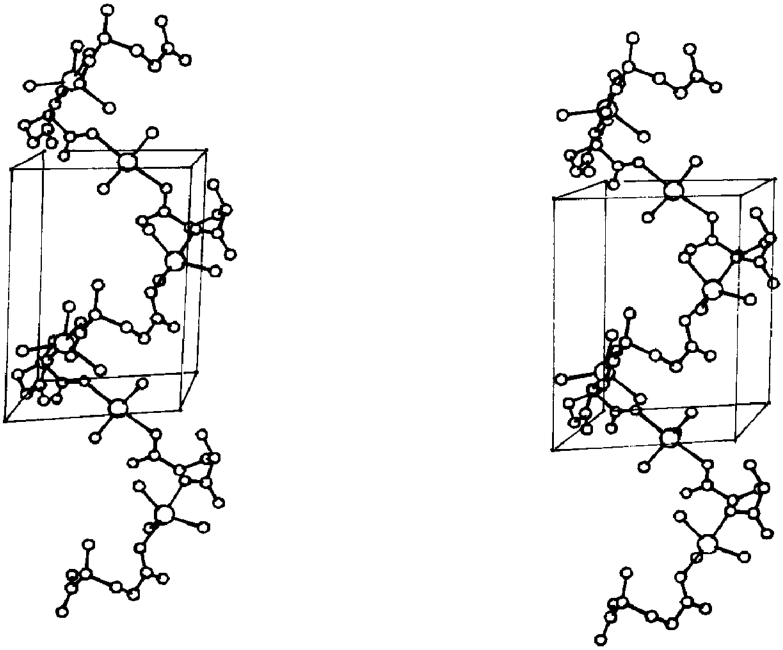

Fig. 2. Stereoscopic view of a fragment of the polymeric chain of Me_3SnHGlu (**1**), showing also the unit cell (a horizontal, c vertical).

Table 2

Atomic coordinates and equivalent isotropic thermal parameters (Å × 10^3); $U_{eq} = (1/3)(U_{11} + U_{22} + U_{33})$

	x	y	z	U_{eq}
Sn(1)	0.36417(3)	−0.00748(3)	0.97480(0)	43
O(1)	0.5789(3)	0.0880(4)	0.8672(2)	53
O(2)	0.7556(4)	−0.1268(3)	0.7401(2)	48
O(3)	0.7642(4)	0.2908(4)	0.9674(3)	66
O(4)	0.7412(5)	−0.2713(4)	0.8791(3)	67
N(1)	0.7689(4)	0.1659(4)	0.7047(2)	44
C(1)	0.7206(4)	0.2082(4)	0.8870(3)	45
C(2)	0.8511(4)	0.2459(4)	0.8039(3)	40
C(3)	0.9699(4)	0.1857(5)	0.8400(3)	43
C(4)	0.8918(4)	0.0200(4)	0.8956(3)	44
C(5)	0.7892(4)	−0.1373(4)	0.8357(3)	44
C(11)	0.3887(7)	0.2296(6)	0.9935(5)	77
C(12)	0.2138(7)	−0.1559(9)	0.8528(5)	94
C(13)	0.4742(7)	−0.1140(7)	1.0711(5)	83

Table 3

Bond lengths (Å) and bond angles (°) in $Me_3SnHGlu$ (**1**) with e.s.d.'s in parentheses [a]

Sn(1)–C(11)	2.118(7)	C(12)–Sn(1)–C(11)	117.4(3)
Sn(1)–C(12)	2.101(6)	C(12)–Sn(1)–C(13)	116.4(3)
Sn(1)–C(13)	2.143(7)	C(11)–Sn(1)–C(13)	126.2(3)
Sn(1)–O(1)	2.222(3)	C(12)–Sn(1)–O(1)	88.1(2)
Sn(1)–O(2)	2.301(3)	C(12)–Sn(1)–O(2)	86.8(2)
O(1)–C(1)	1.259(4)	C(11)–Sn(1)–O(1)	92.7(2)
O(3)–C(1)	1.233(5)	C(11)–Sn(1)–O(2)	88.9(2)
O(2)–C(5)	1.289(5)	C(13)–Sn(1)–O(1)	90.2(2)
O(4)–C(5)	1.230(5)	C(13)–Sn(1)–O(2)	92.8(2)
C(1)–C(2)	1.523(5)	O(1)–Sn(1)–O(2)	174.8(2)
C(2)–N(1)	1.486(4)	C(1)–O(1)–Sn(1)	124.3(3)
C(2)–C(3)	1.543(7)	C(5)–O(2)–Sn(1)	118.9(3)
C(3)–C(4)	1.518(5)	O(1)–C(1)–O(3)	126.7(4)
C(4)–C(5)	1.502(5)	O(3)–C(1)–C(2)	118.2(3)
		O(1)–C(1)–C(2)	115.1(3)
		N(1)–C(2)–C(1)	109.8(3)
		N(1)–C(2)–C(3)	111.2(3)
		C(1)–C(2)–C(3)	109.8(3)
		C(2)–C(3)–C(4)	116.5(4)
		C(3)–C(4)–C(5)	119.8(3)
		O(4)–C(5)–C(4)	119.2(4)
		O(2)–C(5)–C(4)	118.6(3)
		O(2)–C(5)–O(4)	122.3(4)

Intra- and inter-molecular hydrogen bond distances [b]

N(1)...O(1)(x, y, z)	2.601(4)
N(1)...O(2)(x, y, z)	2.706(5)
N(1)...O(3)($1-x+y, 1-x, z-1/3$)	2.797(6)
N(1)...O(4)($2-x+y, 1-x, z-1/3$)	2.709(5)
H(13)...O(1)	2.502(8)
H(13)...O(2)	1.860(8)
H(11)...O(3)	1.837(4)
H(12)...O(4)	1.749(4)

Plane through C(11), C(12), C(13)
$0.6992x + 0.3877y - 0.6007z = 5.1923$

---

[a] Numbering of atoms according to Fig. 1. [b] Hydrogen positions have been calculated (see text).

been assumed to have a partial charge. We presume that the Sn(1)–O(2) bond in **1** is also rather ionic.

Because the overall stoichiometry of the unit cell includes one $Me_3Sn(+1)$ group and one glutamate ligand coordinating to tin through two carboxylate groups, neutrality of the unit cell requires that the glutamate be monoanionic and thus one of the carboxylic acid "ends" of H_2Glu being deprotonated and in anionic form while the other exists in zwitter ion form. The presence of NH_3^+ is actually inferred from IR data (vide infra), and also the distance C(2)–N(1) of 1.486(4) Å corresponds to bond lengths $C-NH_3^+$ in H_2Glu (1.45 Å) and in other amino acids [21]. The NH_3^+ group may be expected to form easily hydrogen bonds. In fact, the distances between N(1) and the four oxygen atoms O(*n*) (*n* = 1, 2, 3, 4) are in the range of 2.6 to 2.7 Å, which is markedly shorter than the sum of the van der Waals-radii (3.11 Å) [22], indicating strong hydrogen bonds.

Taking the calculated positions of the three H-atoms H(*m*) (*m* = 11, 12, 13) at N(1) distances to the O-atoms O(*n*) (*n* = 1 to 4) in the range of about 2.50 to 1.75 Å result, and two types of hydrogen bonds can be distinguished: (i) intramolecular bonds which are bifurcated (three-center bonds) (N(1)H(13)...O(1)/O(2)) and which appear to stabilize the helical arrangement of the chain, and (ii) intermolecular two center-bonds (N(1)H(12)...O(4) and N(1)H(11)...O(3)) which link the helices. The NH_3^+ group has been found in a great number of the crystal structures of amino acids to form two two-center and one three-center bonds, and also the appropriate calculated distances (H(13)...O(1) 2.502(8); H(13)...O(2) 1.860(8) Å are comparable with established values [23].

The carbon–oxygen bond lengths in the α- and γ-carboxylate groups (C(1)–O(1/3) 1.259(4)/1.233(5) Å; C(5)–O(2/4) 1.289(4)/1.230(5) Å) show less differences than would be expected for a monodentate mode of bonding and as found in trimethyltin glycinate [19] (C–O 1.34(3)/1.23(3) Å) or in tricyclohexylstannyl 3-indolylacetate [24] (C–O 1.302(7)/1.213(7) Å) which also contain unidentate carboxylate groups. These bond lengths, especially considering the α-carboxylate group, correspond more to those in compounds containing bridging carboxylate groups, e.g. in trimethyltin acetate (C–O 1.27(5)/1.24(6) Å) [25]. The diminuition of the differences of C–O and C=O bond lengths of α- and of γ-carboxylate group may be caused by the formation of the hydrogen bonds via the "carbonyl"-oxygen atom, but also delocalization of the negative charge residing on the carboxylate groups has to be considered.

The IR spectrum of **1** shows a broad and strong absorption at 3050 cm^{-1} corresponding to NH_3^+ in H_2Glu [26] as well as an additional broad structured band between 3000 and 2500 cm^{-1} which also had been ascribed to $\nu(NH_3^+)$ in H_2Glu and other amino acids [26]. An absorption at 1610 cm^{-1} is assigned to $\delta(NH_3^+)$; it corresponds to $\delta(NH_3^+)$ at 1595 cm^{-1} in H_2Glu [26]. The two absorptions at 1650 and 1635 cm^{-1} both are ascribed to $\nu_{as}(COO)$. The corresponding absorptions due to $\nu_s(COO)$ appear at 1400 and 1390 cm^{-1}. The fact that both $\nu_{as}(COO)$ and $\nu_s(COO)$ appear twice is interpreted as a consequence of the bond differences of α- and γ-carboxylate groups revealed by the different bond lengths which have been found by X-ray diffraction (v.s.). Evidence for the structure of the SnC_3 skeleton could not be taken from IR data since an absorption due to the glutamate ligand in the range of Sn–C absorptions prevented a reliable assignment of $\nu(SnC)$. However, since the Raman absorption at 520 cm^{-1} due to $\nu_s(SnC)$ is very

Table 4

Characteristic IR data (cm^{-1}) for triorganotin and triphenyllead derivatives of glutamic and aspartic acid ((v)s, (very) strong; m, middle; w, weak; (v)b, (very) broad)

Compound	$\nu(NH_3^+$ or $NH_2)$ [a]	$\nu_{as}(COO)$	$\nu_s(COO)$
$Me_3SnHGlu$ (**1**) [b]	3050s,b	1650s	1400s
		1635vs	1390s
n-$Bu_3SnHGlu$ (**2**) [b]	3100s,b	1640vs	1405vs
		1625vs	1395vs
$Me_3SnHAsp$ (**3**) [b]	3170m,vb	1640vs,b	1390s,b
$(Me_3Sn)_2Glu$ (**4**)	3315s	1630vs	1410s
	3290s	1605vs	1375s
$(Ph_3Sn)_2Glu$ (**5**)	3400m,b	1660vs,b	1395m
$(Ph_3Pb)_2Glu$ (**6**)	3390m,b	1620m,sh	1390s,b
	3290m,b	1550vs	
$(Ph_3Pb)_2Glu$ (**7**)	3400w,b	1670s	1380m,b
		1620s	
		1585vs	

[a] $\nu(NH_3^+)$: **1** to **3**; $\nu(NH_2)$: **4** to **7**. [b] $\delta(NH_3^+)$: (**1**) 1610vs, (**2**) 1595vs, (**3**) 1600vs,b.

intense it is inferred considering the exclusion principle that the SnC_3 skeleton is nearly trigonal planar. This is confirmed by X-ray diffraction (v.s.). The IR-spectrum of **2** is very similar to that of **1** (see Table 4), suggesting an analogous structure.

In the IR-spectrum of **3** only one broad band can be detected in the range of $\nu_{as}(COO)$ as well as of $\nu_s(COO)$ (see Table 4). From the unusual broadness of both bands we infer that they are composed of two overlapping absorptions arising from the two carboxylate groups, which then show only slight differences. $\nu_{as}(SnC)$ and $\nu_s(SnC)$ comply rather well with the exclusion principle (IR/Ra: 550s/–; 555w/525vs) indicating a trigonal planar SnC_3 skeleton, which might be slightly distorted. We therefore propose that **3** has in principle a structure analogous to that of **1**.

The IR spectrum of **5** shows a broad adsorption at 3400 cm^{-1} characteristic for a non-coordinating NH_2-group. The broad absorptions at 1600 and 1395 cm^{-1} are assigned to $\nu_{as}(COO)$ and $\nu_s(COO)$, respectively, their broadness being caused by overlapping of the absorptions of the two carboxylate groups. From the characteristic positions of $\nu_{as}(COO)$ and $\nu_s(COO)$ and considering the difference of $\nu_{as}(COO) - \nu_s(COO) = \Delta\nu$ [27] it then can be concluded that both α- and γ-carboxylate group are essentially monodentately bonding to tin. As a consequence of this type of bonding and of the presence of non-coordinating NH_2 groups tetracoordination of Sn and a monomeric character of **5** is postulated. However, we assume that the molecular units are associated by hydrogen bonds between NH_2 and "carbonyl" oxygen atoms of the carboxylate groups.

In contrast, the spectrum of **4** shows $\nu(NH_2)$ at 3315 and 3290 cm^{-1}, the shift to lower frequencies indicating coordination of the NH_2 group. Another difference to the spectrum of **5** is the appearance of two absorptions at 1630 and 1605 cm^{-1} which are assigned to $\nu_{as}(COO)$ and of two absorptions at 1410 and 1375 cm^{-1} which are assigned to $\nu_s(COO)$. The positions of these absorptions and a consideration of $\Delta\nu$ [27] indicates that one carboxylate group has to be assumed to be

Table 5

^1H, ^{13}C and ^{119}Sn NMR data (ppm) of $Me_3SnHGlu$ (**1**) and $(Me_3Sn)_2Glu$ (**4**) in CD_3OD and DMSO

Compound	Solvent	^1H NMR		$^2J(^{119}Sn-^1H)$ (Hz)	^{13}C NMR		$^1J(^{117/119}Sn-^{13}C)$ (Hz)	^{119}Sn NMR
		Me(–Sn)	Glutamate		Me(–Sn)	Glutamate		
1	CD_3OD	0.40	3.56; 2.26; 1.96	69				
1	DMSO	0.36	3.16; 2.00; 1.69	71	0.71	176.27; 171.53; 53.80; 33.37; 27.57	536.6	−55.80
4	CD_3OD	0.44	3.53; 2.35; 2.05	66	−3.14	180.25; 175.34 55.75; 34.15; 29.10	497.2	44.65
4	DMSO	0.37	3.11; 2.04; 1.67	70	0.3	178.08; 177.00; 54.75; 32.66; 31.69	530.3	−17.3

monodentate, the other to be asymmetrically bridging. Two absorptions are observed for ν_{as}(SnC) and also for ν_s(SnC) of the two Me_3Sn groups and comply rather well with the exclusion principle (IR/Ra: 565vs, 550vs/560w, 550w; 520w, 510w/525vs, 520vs).

In the IR spectrum of **6** the weak absorptions at 3390 and 3290 cm^{-1} are assigned to $\nu(NH_2)$, the absorptions at 1620 and 1550 cm^{-1} to ν_{as}(COO), and the broad absorption at 1390 cm^{-1} to ν_s(COO). From these data for **6** a structure analogous to that of **4** is proposed, however, the one lower value of ν_{as}(COO) at 1550 cm^{-1} and the lower $\Delta\nu$ value of 160 cm^{-1} [27] indicates that the mode of bridging of the bidentate carboxylate group in **6** is more symmetric than in **4**. These structural proposals for **4** and **6** are in accordance with the previous suggestions for the structures of **8** and **9** [5]. Considering that in triorganotin carboxylates $R_3SnOOCR'$ with alkyl groups R′ being unbranched at the α-C atom [25,28] as well as in triorganotin and triorganolead biscarboxylates $R_3MOOCXOOCMR_3$ (M = Sn, Pb; R = Me, Ph; X = C_6H_4, C≡C) [29] the carboxylate group is bridging and that in appropriate triorganometal derivatives of amino acids monodentate carboxylate groups and $M \leftarrow NH_2$ coordination is found [5,10,19] we assume the α-COO group in $(R_3M)_2$Glu and $(R_3M)_2$Asp to be the monodentate and the γ-COO and β-COO group, respectively, to be the bidentate bridging carboxylate group. An exception to this general pattern apparently is **7**. NH_2 appears at 3400 cm^{-1} indicating a non-coordinating NH_2 group and in the ν_{as}(COO) range an additional strong absorption is found at 1670 cm^{-1}. Further data are necessary to make a detailed structural proposal for this isomer of **6**.

Preliminary Mössbauer data of **1** (δ 1.29 mm s^{-1}; ΔE 3.38 mm s^{-1}) and **4** (δ 1.31 mm s^{-1}; ΔE 3.36 mm s^{-1}) [30] correspond to data of other comparable Me_3Sn derivatives with a trigonal bipyramidal environment of Sn with planar arrangement of the three methyl groups like Me_3Sn glycylglycinate [10] and Me_3Sn derivatives of amino acids [10,31,32]. The Γ values of **4** are remarkably small (0.87; 0.84) indicating that the environment of each tin atom is not substantially different. A point charge model calculation, based on a regular trigonal bipyramidal environment at tin gave a value ΔE_{calc} for **1** of −2.99 mm s^{-1} [30], the deviation $|\Delta E_{calc}| - |\Delta E_{exp}| = 0.4$ mm s^{-1} being within the limit of error [33].

In the ^1H-, ^{13}C- and ^{119}Sn-NMR spectra (Table 5) of solutions of **1** and **4** in DMSO-d_6 in which both compounds are monomeric (Table 1), as well as in methanol in which **4** is subject to methanolysis, there is only one signal for the Me_3Sn group. Since also after addition of a solution of Me_3SnOH to the solution of **1** in CD_3OD only one signal at 0.44 ppm is observed we conclude that this effect is caused by a fast exchange in the solutions.

The coupling constants of **1** and **4** obtained from solutions in CD_3OD (Table 5) are generally in the range of pentacoordinated triorganotin compounds [34,35,36]. ^2J(Sn–H) for **1** and ^1J(Sn–C) for **1** and **4** increase as well as the δ values slightly when CD_3OD is substituted by DMSO-d_6 indicating an increase in the mean coordination number with increasing donor strength of the solvent.

Acknowledgement

Financial assistance by Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

1 L. Pellerito, M.T. Lo Giudice, G. Ruisi, N. Bertazzi, R. Barbieri and F. Huber, Inorg. Chim. Acta, 17 (1976) L21.

2 F. Huber, H.-J. Haupt, H. Preut, R. Barbieri and M.T. Lo Giudice, Z. Anorg. Allg. Chem., 432 (1977) 51.

3 R. Barbieri, L. Pellerito and F. Huber, Inorg. Chim. Acta, 30 (1978) L321.

4 C.-D. Hager, F. Huber, R. Barbieri and A. Silvestri, Z. Anorg. Allg. Chem., 471 (1980) 194.

5 G. Roge and F. Huber, Z. Naturforsch. B, 36 (1981) 945.

6 R. Barbieri, L. Pellerito, G. Ruisi, M.T. Lo Giudice, F. Huber and G. Atassi, Inorg. Chim. Acta, 66 (1982) L39.

7 F. Huber, G. Roge, L. Carl, G. Atassi, F. Spreafico, S. Filippeschi, R. Barbieri, A. Silvestri, E. Rivarola, G. Ruisi, F. Di Bianca and G. Alonzo, J. Chem. Soc. Dalton Trans., (1985) 523.

8 G. Ruisi, A. Silvestri, M.T. Lo Giudice, R. Barbieri, G. Atassi, F. Huber, K. Grätz and L. Lamartina, J. Inorg. Biochem., 25 (1985) 229.

9 H. Preut, B. Mundus, F. Huber and R. Barbieri, Acta Cryst. C, 42 (1986) 536.

10 B.Y.K. Ho and J.J. Zuckerman, Inorg. Chem., 12 (1973) 1552.

11 M. Frankel, D. Gertner, D. Wagner and A. Zilkha, J. Org. Chem., 30 (1965) 1596.

12 International Tables for X-ray Crystallography. Vol. IV, Tables 2.2B and 2.3.1. Birmingham, Kynoch Press, 1974.

13 B.A. Frenz, Enraf–Nonius Structure Determination Package (SDP-PLUS, V3.0), Enraf–Nonius, Delft, The Netherlands, 1985.

14 C.K. Johnson, ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, 1976.

15 M. Nardelli, PARST. A System of Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analysis. Univ. of Parma, Italy, 1982.

16 G.M. Sheldrick, SHELXTL PLUS (Release 2) for Nicolet R3m/V Crystallographic Systems for Solving, Refining, and Displaying Crystal Structures from Diffraction Data, Univ. of Göttingen, FRG, 1987.

17 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.

18 L. Pauling, Die Natur der chemischen Bindung, Verlag Chemie GmbH, Weinheim, 1968.

19 B.Y.K. Ho, K.C. Molloy, J.J. Zuckerman, F. Reidinger and J.A. Zubieta, J. Organomet. Chem., 187 (1980) 213.

20 K.C. Molloy, M.B. Hossain, D. van der Helm, D. Cunningham and J.J. Zuckerman, Inorg. Chem., 20 (1981) 2402.

21 S. Hirokawa, Acta Cryst., 8 (1955) 637.

22 A.J. Kitaigorodski, Molekülkristalle, Akademie-Verlag, Berlin 1976.

23 G.A. Jeffrey and J. Mitra, J. Am. Chem. Soc., 106 (1984) 5546.

24 K.C. Molloy, T.G. Purcell, E. Hahn, H. Schumann and J.J. Zuckerman, Organometallics, 5 (1986) 85.

25 H. Chih and B.R. Penfold, J. Cryst. Mol. Struct., 3 (1973) 285.

26 R.S. Krishnan, V.N. Sankaranarayanan and K. Krishnan, J. Indian Inst. Sci., 55 (1973) 66.

27 G.B. Deacon and R.J. Phillips, Coord. Chem. Rev., 33 (1980) 227.

28 N.W. Alcock and R. Timms, J. Chem. Soc. A, (1968) 1873; B.F.E. Ford, B.V. Liengme and J.R. Sams, J. Organomet. Chem., 19 (1969) 53; B.F.E. Ford and J.R. Sams, J. Organomet. Chem., 21 (1970) 345.

29 A. Glowacki, F. Huber and H. Preut, Recl. Trav. Chem. Pays Bas, 107 (1988) 278.

30 R. Barbieri, private communication.

31 S.W. Ng and J.J. Zuckerman, J. Organomet. Chem., 249 (1983) 81.

32 G. Roge, F. Huber, H. Preut, A. Silvestri, R. Barbieri, J. Chem. Soc. Dalton Trans., (1983) 595.

33 M.G. Clarc, A.G. Maddock and R.H. Platt, J. Chem. Soc. Dalton Trans., (1972) 281.

34 J.R. Holmes and H.D. Kaesz, J. Am. Chem. Soc., 83 (1961) 3903.

35 T.N. Mitchell, J. Organomet. Chem., 59 (1973) 189.

36 P.J. Smith and A.P. Tupciauskas, Ann. Reps. NMR-Spectrosc., 9 (1978) 291.