Triorganotin and Triorganolead Derivatives of *N*-Acetylamino-acids †

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Triorganotin and triorganolead derivatives of *N*-acetylglycine (AcGly), *N*-acetyl-α-alanine (AcAla), and *N*-acetylmethionine (AcMet), $SnR_3(AcGlyO)$ (R = Me, Bu^n, or Ph), $PbR_3(AcGlyO)$ (R = Me or Ph), $SnR_3(AcAlaO)$ (R = Me, Bu^n, or Ph), $PbPh_3(AcAlaO)$, $SnR_3(AcMetO)$ (R = Me or Ph), and $PbPh_3(AcMetO)$, have been prepared from $MR_3(OH)$ (R = Me or Ph) or $(SnBu^n_3)_2O$ and the appropriate *N*-acetylamino-acid. According to i.r., Raman, and Mossbauer data the compounds are five-co-ordinate and polymeric in the solid state. The MR_3 groups are co-ordinated by unidentate carboxylic groups and the oxygen of CO_{amido}. Co-ordination by NH groups is excluded. The compounds are essentially monomeric in solutions of $CHCl_3$, C_6H_6, acetone, tetrahydrofuran, or pyridine. In dimethyl sulphoxide co-ordination occurs to form five-co-ordinate species.

Knowledge on specific or selective bonding of metal and organometal species to donor sites in biological structures and even in simple biologically relevant oligofunctional molecules is rather scarce. One line of our work in this broad field concentrates on studies of organo-compounds of Group 4 elements and amino-acids, their derivatives, and appropriate model compounds. First results showed great structural variety in such compounds[1,2] and it seemed desirable to extend the investigations to further types of compounds to elucidate the underlying rules for bonding and co-ordinating interactions. We planned to prepare and characterize triorganotin and triorganolead derivatives of *N*-acetylamino-acids, the latter ligands also having biological importance. Only little is known of these compounds: $SnR_3(AcGlyO)$ [R = Bu^n or Ph; AcGlyO = $CH_3C(O)NHCH_2CO(O^-)$] is described in a patent [3] as a biocide. Frankel *et al.*[4] studied the applicability of trialkyltin derivatives of acylamino-acids as intermediates in peptide synthesis. Domazetis *et al.*[5,6] prepared *N*-acetyl-L-cysteinates $(SnR_3)_2(AcCysOS)$ (R = Me or Bu^n) and studied their structures. Structural information on other *N*-acylcysteinates or on *N*-acylamino-acid derivatives of organocompounds of Group 4 elements containing no metal–sulphur bond is not available. An n.m.r. study of co-ordination of $PbMe_3^+$ and $AcGlyO^-$ in water is the only report on organolead derivatives of *N*-acylamino-acids.[7]

Experimental

Infrared spectra (CsBr pellets) were recorded with a Perkin-Elmer 580B grating i.r. spectrophotometer, Raman spectra with a Coderg PHO spectrometer and, n.m.r. spectra with a Perkin-Elmer R 32 90 MHz spectrometer. Mossbauer spectra were determined using the apparatus and techniques previously described,[8] with a $Ca^{119}SnO_3$ source (10 mCi, Radiochemical Centre, Amersham) at room temperature, with constant acceleration and a triangular wave-form. Suitable computer programs have been employed in fitting experimental spectra with Lorentzian line-shapes.

† Throughout this paper, deprotonation at carboxylic OH or thiol SH is indicated by appending the symbols O or S to the amino-acid abbreviations.

Literature procedures were used to prepare $SnPh_3(OH)$,[9] $PbPh_3(OH)$ [9,10] $SnMe_3(OH)$,[11] $PbMe_3(OH)$,[12] and *N*-acetylamino-acids.[13]

Preparations.—The compounds listed in Table 1 were obtained according to the following methods.

Method 1. A solution of *N*-acetylamino-acid (5 mmol) in methanol (20 cm^3) was added to a solution of $SnMe_3(OH)$ (5 mmol) in methanol (10 cm^3). After stirring the solution overnight, or alternatively after refluxing for 2 h, the larger part of the solvent was removed by evaporation. Diethyl ether and light petroleum (b.p. 40—60 °C) were then added until turbidity was observed, and the mixture was kept in a freezer for crystallization. (When, occasionally, no crystallization occurred the methanol was completely removed and repeated treatment of the remaining viscous mass with a low-boiling point solvent, *e.g.* $CHCl_3$, followed by evaporation, yielded a solid crystallizable residue.) The crystals were washed and dried *in vacuo*. The complex $PbMe_3(AcGlyO)$ was formed from $PbMe_3(OH)$ and AcGly in ethanol (analytical grade) under cooling with a NaCl–ice mixture in a similar manner.

Method 2. Addition of $(SnBu^n_3)_2O$ (2.5 mmol) to a suspension of *N*-acetylamino-acid (5 mmol) in methanol gave a clear solution, which was refluxed for 4 h. On evaporation of the solvent, unreacted *N*-acetylamino-acid first precipitated. After filtration and addition of small portions of light petroleum (b.p. 40—60 °C) to the viscous residue the product crystallized on standing for *ca.* 1 d in a freezer. The crystals were washed with cold light petroleum (b.p. 40—60 °C) and dried *in vacuo*.

Method 3. A solution of *N*-acetylamino-acid (2.5 mmol) in ethanol (25 cm^3) was added to a suspension of $MPh_3(OH)$ (M = Sn or Pb) in ethanol (25 cm^3). The reaction mixture was stirred under reflux and became clear or nearly clear after *ca.* 15 (M = Pb) or *ca.* 45 min (M = Sn), respectively. A white product crystallized from the hot filtrate on cooling which was washed with a small amount of ethanol, then diethyl ether, and was dried *in vacuo*. A further portion of product (depending on solubility sometimes the main amount) was obtained after evaporation of solvent from the filtrate, adding diethyl ether and light petroleum (b.p. 40—60 °C), and standing in a refrigerator. [During the reaction of $PbPh_3(OH)$ with AcAla no clear solution was obtained; $PbPh_3(AcAlaO)$ was present not only in the filtrate but also in the undissolved ' residue ' of the reaction mixture.] Methanol,

Table 1. Analytical data for triorganotin and triorganolead derivatives of *N*-acetylamino-acids

Compound	M.p. (°C)	Method	Yield (%)	Analysis [a] (%) C	H	N	*M* [b]	Solvent
$SnMe_3(AcGlyO)$	138	1	80	29.90	5.15	4.90	291	$CHCl_3$
$C_7H_{15}NO_3Sn$	(decomp.)			(30.05)	(5.40)	(5.00)	(279.9)	
$SnBu^n_3(AcGlyO)$	119.5	2	74	47.45	8.15	3.45	401	$CHCl_3$
$C_{16}H_{33}NO_3Sn$				(47.30)	(8.20)	(3.45)	(406.1)	
$SnPh_3(AcGlyO)$	160	3	77	56.55	4.65	2.80	494	$CHCl_3$
$C_{22}H_{21}NO_3Sn$	(decomp.)						(466.1)	
	159	4	49	56.75	4.65	2.80		
	(decomp.) [c]			(56.70)	(4.55)	(3.00)		
$PbMe_3(AcGlyO)$ [d]	115	1	41	23.25	4.05	3.40		
$C_7H_{15}NO_3Pb$	(decomp.)			(22.80)	(4.10)	(3.80)		
$PbPh_3(AcGlyO)$ [e]	184	3	54	47.95	3.85	2.35	553	$CHCl_3$
$C_{22}H_{21}NO_3Pb$	(decomp.)			(47.65)	(3.80)	(2.55)	(554.6)	
$SnMe_3(AcAlaO)$	178	1	86	32.85	5.65	4.85	276	$CHCl_3$
$C_8H_{17}NO_3Sn$	(decomp.)			(32.70)	(5.85)	(4.75)	(293.9)	
$SnBu^n_3(AcAlaO)$	89	2	30	48.20	8.10	3.25	424	C_6H_6
$C_{17}H_{35}NO_3Sn$				(48.60)	(8.40)	(3.35)	427	$CHCl_3$
							(420.2)	
$SnPh_3(AcAlaO)$	169	3	77	56.95	4.85	3.05	492	$CHCl_3$
$C_{23}H_{23}NO_3Sn$	(decomp.)			(57.55)	(4.85)	(2.90)	(480.1)	
$PbPh_3(AcAlaO)$ [f]	202	3	63	48.80	3.95	2.30	616	thf
$C_{23}H_{23}NO_3Pb$	(decomp.)			(48.60)	(4.10)	(2.45)	(568.6)	
$SnMe_3(AcMetO)$	141	1	99	33.65	6.20	4.30	366	$CHCl_3$
$C_{10}H_{21}NO_3SSn$	(decomp.)			(33.90)	(5.95)	(3.95)	360	Me_2CO
							(354.0)	
$SnPh_3(AcMetO)$	177	3	78	55.65	4.85	2.35	558	$CHCl_3$
$C_{25}H_{27}NO_3SSn$	(decomp.)			(55.55)	(5.00)	(2.60)	536	thf
							(540.2)	
$PbPh_3(AcMetO)$ [g]	204	3	62	47.85	4.45	2.00	609	py
$C_{25}H_{27}NO_3PbS$	(decomp.)			(47.80)	(4.35)	(2.25)	(628.7)	

[a] Calculated values in parentheses. [b] Calculated values in parentheses. Molecular weight, determined osmometrically in $CHCl_3$, C_6H_6, and acetone at 37 °C, in thf at 45 °C, and in pyridine (py) at 60 °C. [c] Ref. 3, m.p. = 160.5 °C. [d] Pb 55.8 (56.25)%. [e] Pb 37.0 (37.35)%. [f] Pb 36.9 (36.45)%. [g] Pb 32.9 (33.0).

being a better solvent for the starting compounds, can be used instead of ethanol; the mixture can be reacted at room temperature which is advisable when less stable products like acetylmethioninates or alkyl-lead compounds are involved. Products however crystallize better from ethanol.

Method 4. The compounds $SnPh_3(OH)$ (2 mmol) and AcGly (2 mmol) were reacted [3] in boiling benzene (25 cm^3), distilling water off azeotropically. After 12 h the hot mixture was filtered and the filtrate evaporated till crystals appeared. These were washed with light petroleum (b.p. 40—60 °C) and dried *in vacuo*.

Results and Discussion

The triorganotin and triorganolead derivatives of AcGly (*N*-acetylglycine), AcAla (*N*-acetyl-α-alanine), and AcMet (*N*-acetylmethionine) listed in Table 1 could best be prepared by neutralization of the appropriate organometal hydroxide or oxide and free acid. In all cases the composition showed a 1 : 1 molar ratio. Other preparative methods have been applied but without success: AcGly did not react with MPh_4 (M = Sn or Pb) in $CHCl_3$, benzene, benzene–methanol, or toluene or with $PbMe_4$ in toluene–methanol on refluxing. Addition of silica gel had no effect. Ligand exchange was not feasible because of solubility difficulties. Alcohol proved to be a useful solvent for the neutralization reaction since the acetylamino-acids and also $SnMe_3(OH)$ are highly soluble in it. The triphenylmetal derivatives precipitated in some cases during the reaction, in others on cooling the reaction mixture. The trialkylmetal compounds, having higher solubilities, were obtained after addition of diethyl ether and light petroleum to the reaction mixtures.

Depending on MR_3 and the acetylamino-acid, respectively, most of the compounds prepared were more or less soluble in polar organic solvents, *e.g.* $CHCl_3$, acetone, methanol, ethanol, dimethyl sulphoxide (dmso), or tetrahydrofuran (thf). In less polar solvents, like benzene or toluene, the compounds [except $SnBu^n_3(AcAlaO)$] showed appreciable solubility only on heating. They were insoluble in CCl_4, diethyl ether, light petroleum, and pentane. On standing the solubility of the compounds decreased, apparently by ageing. Molecular weight measurements (see Table 1) showed that all compounds were monomeric in solution; only from data obtained for solutions of $SnPh_3(AcGlyO)$ and $PbPh_3(AcAlaO)$ could a tendency to association be inferred. Weissenberg photographs established that $SnPh_3(AcGlyO)$ and $PbPh_3$-(AcGlyO) are isomorphous and that they crystallize in the space group $P2_12_12_1$ with the lattice parameters a = 2 172.5(8), b = 1 173.0(5), c = 954.7(5) pm for $SnPh_3(AcGlyO)$ and a = 2 121.1(3), b = 1 169.0(2), c = 952.7(2) pm for $PbPh_3$-(AcGlyO) (Z = 4 for both complexes). Insufficient quality of crystals prevented complete *X*-ray structure analyses. Also from the other compounds no suitable single crystals could be obtained.

Structural proposals are based on vibrational data, collected in Table 2; valuable additional information came from Mossbauer measurements of triorganotin derivatives. In the spectra of the compounds vibrations associated with the CO(OH) of the free *N*-acetylamino-acids have disappeared, so that it can be concluded that the MR_3 groups are bound through the carboxylic group to the acetylamino-acid moiety.

Table 2. Infrared data (cm^{-1}) of triorganotin and triorganolead derivatives of *N*-acetylamino-acids

Compound	ν(NH)	$\nu(CO_{amido})$	ν(CN) + δ(NH)	$\nu_{asym}(COO)$	$\nu_{sym}(COO)$	Δν(COO)
$SnMe_3$(AcGlyO)	3 285m	1 627vs	1 565vs	1 654vs	1 381vs	273
$SnBu^n_3$(AcGlyO)	3 275m,br 3 100w	1 637vs,sh	1 575m	1 629vs	1 390vs	239
in $CHCl_3$	3 430m 3 320	1 657vs	1 512m	1 652vs	1 390vs	262
$SnPh_3$(AcGlyO)	3 270m,br	1 626vs (sh)	1 585m	1 613vs,br	1 378s (sh)	235
in $CHCl_3$	3 430m,br	1 653vs	1 515m,br	1 648vs	1 390vs	258
$PbMe_3$(AcGlyO)	3 270m	1 620vs	1 565s	1 645vs, br	1 385vs	260
$PbPh_3$(AcGlyO)	3 293vs	1 639vs	1 556m	1 624vs	1 339vs	285
in $CHCl_3$	3 422m 3 300s,br	1 653s (sh)	1 520m,br	1 630vs,br 1 595vs	1 390vs	240 205
$SnMe_3$(AcAlaO)	3 295s,br	1 630s	1 540s	1 595vs	1 390vs	205
$SnBu^n_3$(AcAlaO)	3 260s,br	1 620vs,br	1 565vs	1 620vs,br	1 390s	230
$SnPh_3$(AcAlaO)	3 270m,br	1 645vs	1 568s	1 602vs	1 388s	214
in $CHCl_3$	3 425m 3 300vw	1 648vs	1 510s	1 648vs 1 592m	1 383s	265 209
$PbPh_3$(AcAlaO)	3 363vs	1 632vs	1 515vs	1 618vs,br	1 392vs	226
$SnMe_3$(AcMetO)	3 300m	1 632s	1 540s,br	1 598vs	1 395s	203
$SnPh_3$(AcMetO)	3 350s	1 641vs	1 516s,br	1 616vs	1 388vs,br	228
$PbPh_3$(AcMetO)	3 360s	1 635vs	1 513vs	1 615vs	1 393vs	222

The type of bonding of the carboxylic group follows, taking MPh_3(AcGlyO) (M = Sn or Pb) as examples, from the frequencies of $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ which appear at 1 613 and 1 378 cm^{-1} (M = Sn) and at 1 624 and 1 339 cm^{-1} (M = Pb) in the solid state. Band positions and also Δν (235 and 285 cm^{-1}) are distinctly different from those of the appropriate alkali-metal compounds M(AcGlyO) [14] (M = Na; 1 600 and 1 400 cm^{-1}, Δν = 200 cm^{-1}; M = K, 1 600 and 1 405 cm^{-1}, Δν = 195 cm^{-1}) and Ag(AcGlyO) [15] (1 595 and 1 397 cm^{-1}, Δν = 198 cm^{-1}). Ionic bonding and also bridging or chelation can therefore be excluded, and carboxylic groups bonding M unidentately must be assumed. The modes of $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ for MMe_3(AcGlyO) (M = Sn or Pb) correspond to values found by Ho and Zuckerman [16] in $SnMe_3$ amino-acid derivatives with unidentate carboxylic groups. An *X*-ray structure determination of $[Cu(AcGlyO)_2]\cdot 4H_2O$ [17] showing $\nu_{asym}(COO)$ at 1 614 and $\nu_{sym}(COO)$ at 1 397 cm^{-1} (Δν = 217 cm^{-1}) [14] revealed unsymmetric carboxylate groups with one oxygen atom strongly and one oxygen atom (at the apex of a Jahn-Teller distorted octahedron) only weakly bonded to Cu; the latter oxygen atom however is involved in hydrogen bonding. A similar situation has been found in $[Cu(AcAlaO)_2L_2]\cdot 2H_2O$ [18] (L = *N*-methylimidazole) one carboxylic oxygen atom forming a hydrogen bond with an adjacent peptidic nitrogen atom; the carboxylate stretching frequencies of this compound [18] (ν_{asym} 1 609, ν_{sym} 1 403 cm^{-1}) correspond with those of MR_3(AcAlaO) (M = Sn or Pb; Table 2) and $[Cu(AcGlyO)_2]\cdot 4H_2O$ and are also comparable to those of the other triorganotin and triorganolead acetylamino-acid derivatives of Table 1. For all these compounds similar bonding situations can be inferred from data of Table 2. We suppose that the fact that $\nu_{asym}(COO)$ appears in the compounds discussed at appreciably lower wavenumbers than in $SiMe_3$(AcGlyO) [19] (1 739 cm^{-1}) and AcGlyOEt [20] (1 724 cm^{-1}), both having unidentate carboxylic groups, is due not least to the influence of hydrogen bonding.

Information on the occurrence of metal co-ordination by the basic atoms of the amide group may be obtained from the infrared frequencies of the modes Amide I [essentially ν(C=O)] and Amide II [ν(C–N) + δ(NH)] [21,22] as well as ν(NH). According to the literature,* the following general pattern is observed upon co-ordination by oxygen (nitrogen) of the amido-group to a metal atom: (*i*) the frequency of the Amide I absorption band decreases (increases), and (*ii*) that of Amide II increases (decreases), with respect to values observed for the free groups; furthermore, (*iii*) eventual ν(NH) bands are nearly unchanged (in the absence of hydrogen bonding). For the solid complexes studied here the frequencies of Amide I decreased and of Amide II [with the exception of Amide II of MPh_3(AcMetO) and $PbPh_3$(AcAlaO)] increased with respect to those found in AcGlyOEt [20] (Amide I at 1 665, Amide II at 1 545 cm^{-1}) and $SiMe_3$(AcGlyO) [19] (Amide I at 1 666, Amide II at 1 549 cm^{-1}). The compounds also show a spectral behaviour according to (*i*) and (*ii*) similar to that found in carbonyl-O-co-ordinated $SnCl_4$–amide adducts.[23] Therefore CO–M co-ordination can be inferred, and N–M co-ordination is clearly ruled out.

A comparison with spectral data of the free acetylamino-acids must take into account that the amide frequencies are affected by interactions such as hydrogen bonding. In particular Amide I is lowered (AcGly: [24] Amide I = 1 590vs, br cm^{-1}; Amide II = 1 560s cm^{-1}; AcAla: [25] 1 614vs, 1 555vs cm^{-1}; AcMet: [26] 1 620s, 1 550s cm^{-1}). For the alkali-metal and silver salts of AcGly and AcAla showing Amide I between 1 625 and 1 650 cm^{-1} and Amide II around 1 550 cm^{-1},[14,15,25] no amide group metal co-ordination is stated. However, compared with the compounds studied here, they show a different absorption pattern in the COO group region (see below).

It is also noteworthy that the frequencies of the Amide I and II modes in the solids (Table 2) are lesser and larger, respectively, than the corresponding frequencies detected in solution (where monomeric species occur, see Table 1), Δν values being of the order of literature reports concerning metal co-ordination by carbonyl oxygen.* As far as ν(NH) vibrations are concerned, frequency positions and broadening in the solid *N*-acetyl-glycinates, -alaninates and -methioninates have been taken to be indicative of intermolecular hydrogen bonding of the type NH · · · O.[22] This corresponds to changes

* See for example refs. cited in 'Spectroscopic Properties of Inorganic and Organometallic Compounds,' a specialist Periodical Report, Chem. Soc., London, vol. 5 (a review of the literature published during 1971) to vol. 12 (a review of the literature published during 1978); see also ref. 23 for an early example concerning tin(IV) adducts.

Table 3. Mossbauer parameters of triorganotin(IV) complexes [a]

Compound	δ [b]/mm s^{-1}	ΔE_{exptl} [c]/ mm s^{-1}
$SnMe_3$(AcGlyO)	1.31	3.49
$SnBu^n_3$(AcGlyO)	1.45	3.55
$SnMe_3$(AcAlaO)	1.33	3.45
$SnBu^n_3$(AcAlaO)	1.46	3.54
$SnMe_3$(AcMetO)	1.35	3.65
$SnPh_3$(AcGlyO)	1.28	3.31
$SnPh_3$(AcAlaO)	1.26	3.19
$SnPh_3$(AcMetO)	1.30	3.12

[a] Determined at 77.3 K. Sample thicknesses were in the range 0.3—0.6 mg ^{119}Sn cm^{-2}. Full widths at half-height of the resonant peaks are around 0.85—0.95 mm s^{-1}. [b] Isomer shift with respect to room temperature $CaSnO_3$; standard error $\pm$0.01 mm s^{-1}, see R. Barbieri, A. Silvestri, G. van Koten, and G. Noltes, *Inorg. Chim. Acta*, 1980, **40**, 267. [c] Experimental nuclear quadrupole splitting. Standard error $\pm$0.01 mm s^{-1} (see ref. for footnote *b*).

of i.r. data on dissolving the compounds in $CHCl_3$ (see Table 2): ν(NH) is shifted to 3 430 and 3 422 cm^{-1}, the range of free NH groups. This can be understood as a result of breaking H bonds and the presence of monomeric species, as shown by molecular weight measurements. Hydrogen bonding is an essential structural parameter also in *N*-acetylamino-acids [25-28] and ν(NH) frequencies are shifted to lower values (AcGly,[26] 3 360; AcAla,[25] 3 313; AcMet,[26] 3 360 cm^{-1}). The ν(NH) frequencies of $PbPh_3$(AcAlaO) and MPh_3(AcMetO) (M = Sn or Pb) are higher than those of the other derivatives investigated here, but lying in the same range of ν(NH) of the acids; there is no reason to assume that hydrogen bonding should have to be excluded.

Neither Raman nor far-i.r. spectra of the *N*-acetylmethioninates showed any indication of sulphur–metal co-ordination, as was found in some complexes.[29] The ν(CS) mode was also unchanged compared to AcMet. In the Raman spectrum of $SnMe_3$(AcGlyO) a very strong band at 523 cm^{-1} can be assigned to ν_{sym}(SnC), and a band at 552 cm^{-1} to ν_{asym}(SnC), having only about 20% intensity compared to that of ν_{sym}(SnC). In the i.r. spectrum these bands are observed at 530 cm^{-1} (as a shoulder) and at 552m cm^{-1} with reversed intensities. A similar situation is found in the spectra of $PbMe_3$(AcGlyO), $SnMe_3$(AcAlaO), and $SnMe_3$(AcMetO) (ν_{asym} in i.r. at 498vs, 552vs, and 542m cm^{-1}, respectively; ν_{sym} in Raman at 470vs, 523vs, and 516vs cm^{-1}). Local C_{3v} symmetry of the MC_3 skeleton is therefore suggested, the deviation from planarity being not very serious. Weak i.r. bands at 612 and 520(sh) cm^{-1} for $SnBu^n_3$(AcGlyO) and at 605 and 520 cm^{-1} for $SnBu^n_3$(AcAlaO) can be assigned to ν_{asym}(SnC) of *trans* and *gauche* isomers,[30] Raman bands at 600 and 512 cm^{-1} and at 596 and 510 cm^{-1} (solid and $CHCl_3$ solution respectively) can be assigned to ν_{sym}(SnC) of the appropriate isomers.[30]

Tin-119 Mossbauer spectroscopy has been employed to obtain further structural information, and the results obtained for $Sn^{IV}R_3$ derivatives are reported in Table 3. Isomer shifts, δ, are in the range typical of $Sn^{IV}R_3$ compounds, while nuclear quadrupole splittings, ΔE, suggest the occurrence of five-co-ordinate species.[31,32] Well formed spectra have been generally obtained, where the two component peaks exhibit comparable values of resonance effect and linewidth, with a consequent low variance of the Lorentzian fits. This implies no vibrational dissymmetries at tin sites at 77.3 K.

The consistency of ΔE_{exptl} values with the structure in Figure 1, the latter as extracted from the i.r. study, has been checked through calculations of ΔE by the point-charge model formalism,[31,32] using a suitable computer program.

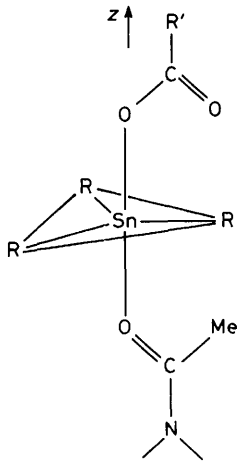


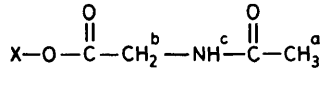
Figure 1. The regular trigonal bipyramidal structure of tin sites in SnR_3 complexes of *N*-acetylamino-acids assumed in point-charge model calculations of nuclear quadrupole splittings, ΔE_{calc}. The direction of the principal component of the electric field gradient tensor, V_{zz}, is shown. The values of ΔE_{calc} are -1.51 (R = alkyl) and -3.06 mm s^{-1} (R = Ph) (see text)

Partial quadrupole splitting values (p.q.s.) of $\{alkyl\}^{tbe} = \{\overset{R'}{\underset{|}{}}\}^{tbe}$ -1.13, $\{Ph\}^{tbe} = -0.98$, and $\{O{-}\overset{}{C}{=}O^t\}^{tba} = -0.10$ mm s^{-1}, employed in the calculations, were taken from the literature (tba, tbe = trigonal-bipyramidal-apical and -equatorial, R' = alkyl).[32,33] The value for $\{O{=}C{-}N\overset{Me}{\underset{|}{}}\}^{tba}$ (Figure 1) has been considered to correspond to that of *NN*-dimethylacetamide (dma),[32] $\{dma\}^{tba} = +0.16$ mm s^{-1}, in view of the fact [34] that *NN*-dialkylamides co-ordinate organotins through carboxylamide oxygens. The results of the calculations are reported in the legend to Figure 1; taking into account the maximum accepted difference [35] $|\Delta E_{exptl} - \Delta E_{calc}| = 0.4$ mm s^{-1}, it follows that the structure in Figure 1 is highly reliable also from the rationalization of ΔE_{exptl} data.

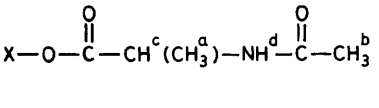
It seems worth mentioning that other structures, in principle possible but ruled out by the i.r. study, are equally excluded in the majority of cases by point-charge model calculations of ΔE. For example, assuming bonding by the sulphur atom in acetylmethioninates (Figure 1, with $\rangle S \longrightarrow$ Sn in place of C=O $\longrightarrow$ Sn), $\Delta E_{calc} = -2.00$ and -1.55 mm s^{-1} for R = alkyl and Ph, respectively, using the p.q.s. values listed above and the value [33] $\{S\}^{tba} = -0.60$ mm s^{-1}. On the other hand, the supposition that the amido-group co-ordinates through nitrogen (see Figure 1) would imply $\Delta E = (-)3.22$ mm s^{-1} for R = alkyl and $\Delta E_{calc} = -2.76$ mm s^{-1} for R = Ph (the first figure being the average value for a series of amino-acid complexes with an analogous structure,[16,33,36] and the second being obtained by using the p.q.s.[32] $\{N\text{-}(COMe)\}^{tba} = \{piperidine\}^{tba} = +0.01$ mm s^{-1}); these structures are then excluded for some terms of the series (see ΔE_{exptl} of Table 3), and finally appear to be less reliable than that in Figure 1. Instead, data for trigonal bipyramidal structures with axially bridging carboxyl groups are $\Delta E = -3.68$ and -3.23 mm s^{-1} for trialkyl- and triphenyl-tin(IV) acetato-complexes, respectively,[32] which are consistent with ΔE_{exptl} data in Table 3; on the other hand, the i.r. and mass spectra (see below) unequivocally rule out this solid-state configuration for the majority of the complexes studied here.

The structural proposals for the solids investigated here (Figure 1, and text) are also consistent with the following observations. Mass spectra showed as peaks of maximum

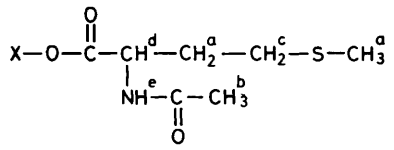
Table 4. Proton n.m.r. data of triorganotin and triorganolead derivatives of *N*-acetylamino-acids, chemical shifts (p.p.m.)[a], and coupling constants $J(^{119}Sn-^{1}H)$ or $J(^{207}Pb-^{1}H)$ (Hz)



(1) AcGly



(2) AcAla



(3) AcMet

Compound	X	δ (MR_3)	δ [a]	δ [b]	δ [c]	δ [d]	δ [e]	*J*	Solvent (concentration/ mol dm^{-3})
(1)	H		1.86	3.71(d)	8.10(br)				$[^2H_6]$dmso
	$SnMe_3$	0.58	2.05	3.89(d)	6.69(br)			60	$CDCl_3$ (0.43)
		0.58	2.05	3.97(d)	6.23(br)			60	$CDCl_3$ (0.07)
		0.45	1.91	3.68	*b*			67	CD_3OD (0.45)
		0.36	1.74	3.48(d)	7.76(br)			70	$[^2H_6]$dmso (0.36)
	$SnPh_3$	7.3—8.2	1.97	4.10(d)	6.03(br)				$CDCl_3$
		7.3—8.4	1.79	3.60(d)	*c*				$[^2H_6]$dmso
	$PbMe_3$	1.48	1.98	3.85(d)	6.40(br)			73	$CDCl_3$
		1.24	1.80	3.47(d)	7.70(br)			84	$[^2H_6]$dmso
	$PbPh_3$	6.9—8.4	1.90	3.93(d)	6.08(br)				$CDCl_3$
		7.2—8.6	1.80	3.54(d)	*c*				$[^2H_6]$dmso
(2)	H		1.39(d)	1.97	4.44(q)	*b*			CD_3OD
			1.24(d)	1.82	4.20(qnt)	8.13(d)			$[^2H_6]$dmso
	$SnMe_3$	0.58	1.40(d)	1.98	4.40(qnt)	6.36(d,br)		62	$CDCl_3$
		0.41	1.17(d)	1.79	4.06(qnt)	7.79(d,br)		70	$[^2H_6]$dmso
	$SnPh_3$	7.3—8.3	1.39(d)	1.95	4.69(qnt)	6.29(d)			$CDCl_3$
	$PbPh_3$	6.8—8.7	1.43(d)	1.91	4.46(qnt)	6.26(d,br)			$CDCl_3$
		7.2—8.6	1.10(d)	1.76	4.10(qnt)	*c*			$[^2H_6]$dmso
(3)	H		1.94	2.08	2.54(t)	4.42(q)	8.06(d)		$CDCl_3$-$[^2H_6]$dmso (1 : 1)
	$SnMe_3$	0.59	2.00	2.12	2.55(br)	4.58(q)	6.47(d)	63	$CDCl_3$
		0.39	1.81	2.01	2.39(br)	4.15(q)	7.79(d)	71	$[^2H_6]$dmso
	$SnPh_3$	7.3—8.2	1.91	1.94	2.30(br)	4.70(br)	6.24(d)		$CDCl_3$
		7.2—8.5	1.78	1.92	2.17(br)	4.20(br)	*c*		$[^2H_6]$dmso
	$PbPh_3$	7.2—8.7	1.84	1.95	2.26(br)	4.25(br)	*c*		$[^2H_6]$dmso

[a] d = Doublet, t = triplet, q = quartet, qnt = quintet, br = broad. [b] Not observable due to deuteriation. [c] Superimposed by phenyl-H signals.

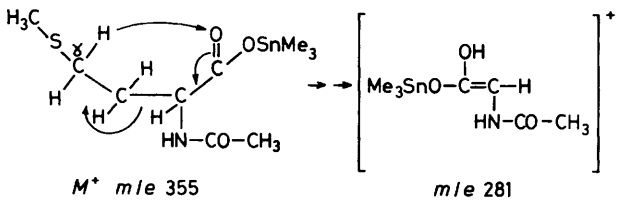


Figure 2. Rearrangement of $SnMe_3$(AcMetO) producing a fragment ion with *m/e* = 281 (schematic proposal according to McLafferty [37])

mass those of the molecule ions: $SnBu^n_3$(AcGlyO), 407; $SnPh_3$(AcGlyO), 467; $SnMe_3$(AcMetO), 355; and $PbPh_3$-(AcGlyO), 555. This is an indication that monomers exist under the conditions in the mass spectrometer [16, 180; 70, 170; and 70 eV, 190 °C (1 eV ≈ 1.60×10^{-19} J)]. In the mass spectrum of $SnMe_3$(AcMetO) a peak at *m/e* =281 can be interpreted as caused by a fragment ion resulting from a McLafferty rearrangement.[37] As the scheme in Figure 2 shows, this rearrangement can only proceed when a unidentate

group is available. (Since AcGly and AcAla derivatives do not contain a C^γ atom an analogous rearrangement cannot occur.)

In the ^1H n.m.r. spectra (Table 4) of all compounds studied the CO(OH) signal of the free acid is missing and the NH signal is shifted to higher field (if not obscured by superposition by phenyl protons in $[^2H_6]$dmso solutions of MPh_3 compounds). The extent of the shift depends on the solvent and the concentration. In $CDCl_3$ solutions of $SnMe_3$(AcGlyO) at lower concentration the NH signal is markedly shifted to higher field, while the N*CH*$_2$ signal is shifted a little to lower field. This effect can be correlated with an increase of breaking of the hydrogen bonds present in the solid state. It also corresponds to the shift of ν(NH) to higher, and of δ(NH) + ν(C–N) to lower wavenumbers on dissolution of the solid AcGly derivatives (see Table 2). Analogous shifting of chemical shift values δ of NH and N*CH* on dilution of $(SnBu^n_3)_2$(Ac-L-CysOS) [5] has been interpreted in the same way. The N*CH*$_2$ signal appears in $CDCl_3$ and $[^2H_6]$dmso solutions as a doublet with coupling constants $^3J(CH_2-NH)$ of *ca.* 4—5 Hz. The NH signal is also split; however the signal is very broad and therefore exact determination of the coupling is not possible. It can be generally concluded that in $CDCl_3$ and $[^2H_6]$dmso solution the NH group does not significantly participate in hydrogen bonding. The same considerations also apply to the other acetylamino-acid derivatives.

The signals of the $SnMe_3$ protons of the different $SnMe_3$ derivatives dissolved in $[^2H_6]$dmso are, compared to values in $CDCl_3$ solutions, shifted to higher field. We assume therefore that stable complexes with dmso are formed. The shift to higher fields increases with increasing donor strength of the

solvents [38] in the series $CDCl_3$, CD_3OD, dmso, as does $J(^{119}Sn-^{1}H)$ (see Table 4). Using the coupling constants $J(^{119}Sn-^{1}H)$ as indicators for the co-ordination state of the central Sn atom [39] the measured values of the $SnMe_3$ derivatives in $CDCl_3$ (60—63 Hz, *s*-character = 28—29% [39]) indicate four-co-ordination; $J(^{119}Sn-^{1}H)$ of four-co-ordinate $SnMe_3Cl$ in $CHCl_3$ was found [38] to be 57.8 Hz (27% *s*-character). The values of 70—71 Hz measured in dmso solutions are in the range for five-co-ordinate compounds,[38] due to adduct formation with the donor solvent.

These results are confirmed by ^{13}C n.m.r. spectra of $SnBu_3$-(AcGlyO); the value of $J(^{13}C-^{119}Sn)$ in $CDCl_3$ solution was 352.5 Hz, in [$^2H_6$]dmso solution the value is between 444 and 466 Hz (due to line overlap no exact value can be given). It can be concluded that this increase is a consequence of an increase of the co-ordination number of Sn from four to five, since in four-co-ordinate $Sn(alkyl)_3$ compounds *J* values of 330—390 Hz and in five-co-ordinate compounds values of 450—480 Hz have been found.[40] Different co-ordination numbers for Sn are also indicated by chemical shift values δ (^{119}Sn) of +129.22 p.p.m. in $CDCl_3$ solution and of −7.65 p.p.m. in dmso solution [standard $SnMe_4$, δ (^{119}Sn) = 0 p.p.m.]. From values of $J(^{207}Pb-^{1}H)$ of $PbMe_3(AcGlyO)$ in $CDCl_3$ (73 Hz) and dmso solution (84 Hz) it can also be concluded that the co-ordination number of Pb is increased [38] on going from $CDCl_3$ to dmso by co-ordination of one dmso molecule.

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