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Trialkyltin Derivatives of Amino Acids and Dipeptides¹

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Seventeen compounds of the type R_3SnAA , where R = methyl (Me) or cyclohexyl (Cyh), and AA is the anion of glycine (gly), DL- α -alanine (ala), DL- α -amino-*n*-butyric acid (but), DL- α -valine (val), DL- α -leucine (leu), L- α -isoleucine (isoleu), β -alanine (β -ala), and glycyglycine (glygly), including tri-*n*-butyltin glycinate (*n*-Bu₃Sn(gly)), have been prepared by azeotropic distillation of water from benzene solutions of the corresponding stannol or bis(trialkyltin) oxide and the acids; DMF is added as a catalyst for R = Me and AA = gly and ala and for *n*-Bu₃Sn(gly). From lowered infrared amino group stretching frequencies and enhanced intensities, twelve of the compounds are identified as amino coordinated to tin, including all the Me₃Sn derivatives, *n*-Bu₃Sn(gly), Cyh₃Sn(gly), β -ala, glygly. These compounds, except the last, exhibit Mossbauer QS values in the range 3.2 ± 0.1 mm/sec and ratios of QS to IS generally greater than 2.1, consistent with higher than four-coordination and pronounced line intensity asymmetry (Goldanskii-Karyagin effect) suggesting associated lattices. Me₃Sn(gly), ala, glygly, and *n*-Bu₃Sn(gly) give ambient-temperature Mossbauer spectra confirming polymeric structures. High $\nu(O-C=O)$ stretching frequencies, assigned with the aid of deuterated amino group isotopomers, rule out carboxylate carbonyl oxygen coordination to tin in these cases, and infrared and Raman data in the tin-carbon stretching region [$\nu(Sn-C)$ is assigned at 490 and 420 cm^{-1} for the cyclohexyltin group] rule out precisely planar SnC₃ skeletons. The amino-bridged compounds are depicted as one-dimensional associated lattices of trigonal-bipyramidal units of the axially most electronegative kind. Cyh₃Sn(glygly), whose larger QS value and lack of line asymmetry suggest a different structural type, is from lowered infrared stretching frequency evidence coordinated by the amide carbonyl to give six-coordination at tin which from the large QS value must be in the meridian configuration of which no examples are known. Of the five Cyh₃Sn derivatives lacking amino-coordination, two (but and val) are, from high $\nu(O-C=O)$ and reduced QS values, simple, four-coordinated monomers. The remaining three are higher than four-coordinated from lowered carboxylate stretching frequencies, but QS data rule out axially most electronegative structures. These results are rationalized on the steric effect of the groups at tin and the α -carbon substituent in the ligand; when both are small, the one-dimensional polymer formed by bridging amino groups is the preferred structure; in intermediate cases carboxylate group coordination, utilizing equatorial or equatorial-axial positions presumably through chelation in monomeric units, becomes preferred; when both are large, only simple, four-coordinated monomers are found. Cyh₃SnOH, used for comparison, is shown to be polymeric on the basis of the ambient-temperature Mossbauer spectrum, pronounced line intensity asymmetry, large QS value, and the observation of fragments higher than the molecular ion in the mass spectrum. Preliminary X-ray data for tetragonal Me₃Sn(gly) crystals show four molecules per unit cell of space group $P4_1$ or $P4_3$.

Organotin derivatives of amino acids have been of interest as possible biocides;³ for example, tricyclohexyltin alaninate has been found active as a fungicide and bactericide for seeds and plants⁴ and as intermediates in peptide syntheses.⁵ Being potentially polydentate ligands, amino acids and dipeptides also present interesting structural possibilities when substituted with triorganotin groups at oxygen, since triorganotin compounds adopt higher coordination whenever favorable conditions exist.⁶ Five-coordinated triorganotin carboxylates are well known, and the one-dimensional polymeric structure with the most electronegative groups in the axial positions of a trigonal-bipyramidal arrangement has been confirmed by X-ray study.^{6,7} The choice of coordination number and geometry is known to be governed by the size of the substituent groups at tin⁶ and by the degree of branching in the ligand.⁸

We report here the synthesis of seventeen trialkyltin derivatives of α - and β -amino acids and dipeptides and their study by vibrational, mass, and nuclear γ -ray resonance (Mossbauer) spectroscopies. Methyl and cyclohexyl substituents were chosen for tin in order to provide a range of structural types, and the analogous hydroxides and carbonates have been studied for comparison.

Results

The seventeen compounds synthesized for this study are identified in Table I, along with per cent yields, melting points, and microanalytical data for C, H, N, and Sn. The abbreviations introduced there will be used throughout. The compounds are synthesized by azeotropic distillation of water from benzene solutions of trialkyltin hydroxide or bis(trialkyltin) oxide [DMF is added as a catalyst for R = Me and AA = gly and ala and for *n*-Bu₃Sn(gly)] and the amino acid. The products are white solids, only very slightly soluble in common organic solvents. The cyclohexyl derivatives are, as expected, more soluble. The claimed synthesis of triethyltin β -alaninate (lit. mp 115–116°) from aqueous solution^{3c} has been criticized, and the product from toluene melts at 151–152°.⁵ Likewise, the material produced from α -alanine and trimethyltin hydroxide in aqueous solution (mp 215°)^{3a,c} differs from (CH₃)₃Sn(ala) (mp 141–142°) as prepared in this study. No structural information is reported in any of the published studies, except for a general statement on infrared absorptions, of which at least the assignment of $\nu(Sn-C)$ at 1070–1050 cm^{-1} ^{5a} is certainly incorrect.

Discussion

The structure of the organotin amino acids and dipeptides raises several questions—whether there is coordination to tin

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Table I. Trialkyltin (R_3Sn) Derivatives of Amino Acids and Dipeptide

Compd (abbrev)	Mp, °C	Yield, %	% calcd (found)			
			C	H	N	Sn
R = Me						
Glycinate ($Me_3Sn(gly)$)	163-164 dec	80	25.23 (25.37)	5.51 (5.87)	5.89 (6.13)	49.91 (49.57)
DL- α -Alaninate ($Me_3Sn(ala)$)	141-142 dec 215 ^a	74	28.61 (28.96)	6.00 (6.09)	5.56 (5.74)	47.12 (46.81)
DL- α -Amino- <i>n</i> -butyrate ($Me_3Sn(but)$)	105-108 dec	60	31.62 (32.41)	6.44 (6.62)	5.27 (4.78)	44.64 (43.82)
DL- α -Valinate ($Me_3Sn(val)$)	152-153 dec	70	34.32 (34.46)	6.85 (6.81)	5.00 (5.00)	42.40 (42.30)
DL- α -Leucinate ($Me_3Sn(leu)$)	147-148 dec	76	36.77 (37.17)	7.20 (7.30)	4.77 (4.77)	40.34 (40.39)
L- α -Isoleucinate ($Me_3Sn(isoleu)$)	161-162 dec	54	36.77 (37.11)	7.20 (7.33)	4.77 (4.77)	40.34 (40.38)
β -Alaninate ($Me_3Sn-\beta-ala$)	126-127 dec	44	28.61 (29.24)	6.00 (6.18)	5.56 (5.50)	47.12 (45.50)
Glycylglycinate ($Me_3Sn(glygly)$)	171-172 dec	77	28.50 (29.19)	5.47 (5.69)	9.50 (9.74)	40.25 (40.21)
R = <i>n</i> -Bu						
Glycinate (<i>n</i> - $Bu_3Sn(gly)$)	127-128	35	46.18 (45.76)	8.58 (8.69)	3.85 (4.33)	32.60 (31.96)
R = Cyh						
Glycinate ($Cyh_3Sn(gly)$)	122-123 dec	48	54.32 (54.21)	8.44 (8.52)	3.17 (3.20)	26.84 (26.64)
DL- α -Alaninate ($Cyh_3Sn(ala)$)	142-143 dec	88	53.11 (54.95)	8.62 (8.73)	3.07 (2.15)	26.01 (25.55)
DL- α -Amino- <i>n</i> -butyrate ($Cyh_3Sn(but)$)	131-133 dec	41	56.19 (55.89)	8.79 (8.90)	2.98 (2.34)	25.24 (25.41)
DL- α -Valinate ($Cyh_3Sn(val)$)	131-133 dec	69	57.04 (56.92)	8.95 (9.12)	2.89 (3.00)	24.51 (24.05)
DL- α -Leucinate ($Cyh_3Sn(leu)$)	118-121 dec	88	57.84 (57.27)	9.10 (9.36)	2.81 (3.05)	23.82 (22.96)
L- α -Isoleucinate ($Cyh_3Sn(isoleu)$)	54-57 dec	80	57.84 (56.67)	9.10 (9.31)	2.81 (2.69)	23.82 (23.55)
β -Alaninate ($Cyh_3Sn-\beta-ala$)	140-141	70	53.11 (55.31)	8.62 (8.66)	3.07 (3.23)	26.01 (25.79)
Glycylglycinate ($Cyh_3Sn(glygly)$)	126-127 dec	61	52.92 (53.00)	8.08 (8.23)	5.61 (5.84)	23.77 (23.42)

^a References 3a and 3c.

by the amino group nitrogen or carbonyl group oxygen atoms, which coordination numbers result from these interactions, and the detailed coordination geometry about the tin atom in cases in which the possibility for isomerism exists. In addition, owing to the potentially polydentate nature of the amino acid and dipeptide ligand, it is necessary to distinguish chelated (intramolecular) monomeric structures from bridged (intermolecular) polymeric structures where the latter can adopt either one- or two-dimensional or cyclic oligomeric forms. The commonly encountered flattening of the tetrahedral trimethyltin group to planarity must be considered as well. The combination of vibrational and Mossbauer techniques gives information which can, taken together with other physical evidence, eliminate sufficient of the plausible structures to specify the correct one. The major structural features are taken up in the following sections in turn.

Coordination by the Amino Group. Infrared NH_2 stretching frequencies can help to distinguish coordinated from free amino groups. The amino acids themselves exist in a zwitterionic form in the solid state in which there are NH_3^+ groups. Free NH_2 groups are found in the amino acid salts, but here the species are anionic. The proper comparison is with the matrix-isolated species, but, unfortunately, only the vibrational data for glycine are known to us. For this species, $\nu(NH_2)$ is 3414 and 3411 cm^{-1} , for the asymmetric and symmetric modes, respectively.⁹ Taking the highest energy absorption which is generally the most intense, 3414

cm^{-1} for the matrix-isolated species can be compared with 3380 cm^{-1} for the sodium salt and 3170 cm^{-1} for the zwitterion in which the amino group is protonated. There is thus substantial lowering on protonation. Coordination to metal centers also gives rise to substantial shifts, and X-ray structures are available which show NH_2 groups coordinated to Co, Ni, Cu, and Pt atoms in several chelated complexes of α -¹⁰ and β -amino¹¹ acids and glycylglycine.¹²

Table II lists the infrared frequencies in the NH_2 stretching region for the zwitterionic amino acids and glycylglycine, in their trimethyl- and tricyclohexyltin derivatives and in certain transition metal chelated complexes for which supporting structural data are available. The infrared NH_2 features are

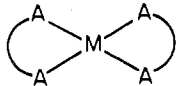
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Table II. Infrared Stretching Frequencies (cm^{-1}) of the Amino Group

Amino acid, H-AA (freq)	Me_3Sn - (AA)			Cy_3Sn - (AA)
Glycine (3170)	3311	M = Pt ^a	M = Ni ^a	3318
	3244	3230	3340	3295
	3224	3090	3280	3185
	3199			
	3154			
α -Alanine (3100)	3322	M = Pt ^b	M = Ni ^b	~3400
	3270	3230	3379	
	3260	3204	3366	
		3093	3275	
α -Amino- <i>n</i> -butyric acid (3090)	3290	M = Pt ^c	M = Ni ^c	3396
	3240	3207	3340	3320
	3160	3131	3280	
		3110	3172	
Valine (3140)	3300	M = Pt ^d	M = Ni ^d	3400
	3268	3217	3326	3340
	3195	3137	3270	
Leucine (3110)	3300	M = Pt ^e	M = Ni ^e	~3400
	3240	3217	3368	
	3130	3120	3276	
Isoleucine (3080)	3290	M = Pt ^f	M = Cu ^f	3400
	3250	3215	3291	3340
	3210	3115	3244	
			3160	
β -Alanine (3310, 3100)	3310			3328
	3240			3280
	3150			
Glycylglycine (3300, 3090)	3280		M = Cu ^g	3320 ^h
	3180		3331	
	3090		3282	

^a R. A. Condrate and K. Nakamoto, *J. Chem. Phys.*, **42**, 2590 (1965). ^b J. F. Jackovitz, J. A. Durkin, and J. L. Walter, *Spectrochim. Acta, Sect. A*, **23**, 67 (1967). ^c B. Y. K. Ho, B.A. Thesis, Marist College, Poughkeepsie, N. Y., 1967. ^d I. Nakagawa, R. J. Hooper, J. L. Walter, and T. J. Lane, *Spectrochim. Acta*, **21**, 1 (1965). ^e J. F. Jackovitz and J. L. Walter, *ibid.*, **22**, 1393 (1966). ^f R. J. Hooper, T. J. Lane, and J. L. Walter, *Inorg. Chem.*, **3**, 1568 (1964). The isoleucine used is a racemic mixture. ^g For (GG)Cu·3H₂O where GG = glycylglycine: A. Rosenberg, *Acta Chem. Scand.*, **11**, 1390 (1957). ^h An additional band is observed at 3370 cm^{-1} (weak, partially overlapping with the 3320- cm^{-1} band).

complex in the solid state where crystal effects give rise to more bands than the expected symmetric and asymmetric stretching absorptions. The values for the tin-bearing derivatives fall into two classes, the first comprising all of the trimethyl- and three of the tricyclohexyltin derivatives in which the highest frequency and most intense band in the spectrum has undergone a substantial lowering from the 3414- and 3380- cm^{-1} values for the matrix-isolated and sodium salt forms of glycine (other amino acid salts have similarly high values: sodium leucinate is at 3378 cm^{-1} , for example) and the second comprising five cyclohexyltin derivatives in which the highest frequency band is at ca. 3400 cm^{-1} .

Examples for direct comparison are lacking for β -alanine, and the frequencies of the glycylglycine derivatives are compared to a copper complex whose structure is also chelated through the amino group^{12a} as is that of the cobalt glycylglycine.^{12b} Tributyltin glycinate exhibits NH₂ stretching frequencies at 3319, 3245, and 3172 cm^{-1} and can thus be placed in the first category.

The absorption intensities for compounds drawn from each class constitute a striking comparison. All the compounds which show substantial lowering of the NH₂ frequencies also show intense absorptions, while the bands at ca. 3400 cm^{-1} in the other compounds are all relatively weak.

We interpret the observed shifts to lower energy and accompanying intensity enhancement as arising from amino group coordination to tin. Coordination increases electron demand at nitrogen and the polarity of the N-H bond. Apparently the change in this dipole during a stretching vibration is also increased, since an increase in total absorption intensity generally accompanies coordination of the amino group.¹³ The intense NH₂ absorptions observed here are relatively narrow, suggesting that hydrogen bonding, usually prominent in amino acids and their derivatives, is not pronounced in the tin compounds.

We thus conclude on this basis that the twelve compounds in the first class enjoy amino coordination to tin in the solid state and that this structural feature is absent in the five cyclohexyltin compounds which constitute the second category.

Compounds with Coordinated Amino Groups. Carbonyl Group Interactions. Infrared O=C=O stretching frequencies can help to distinguish coordinated from free carbonyl groups, but care must be taken to identify the bending absorption of the amino group which is assigned by deuteration and to resolve the symmetric carbonyl stretching band from the methyl group degenerate deformation which occurs in the same region. Carboxylate groups in organotin 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.⁸ Trimethylsilyl acetate, on the other hand, possesses a normal ester structure in which the carbonyl stretching frequently occurs at 1725 cm^{-1} . The corresponding absorption at 1576 cm^{-1} in trimethyltin acetate¹⁴ is typical of the associated tin carboxylates.¹⁵ The X-ray structural determination of tribenzyltin acetate,⁷ where the absorption¹⁶ is at 1565 cm^{-1} , confirms the bridged arrangement of the carboxylate group. The corresponding infrared absorption in tricyclohexyltin acetate is at 1645 cm^{-1} , but the structure as revealed by X-ray diffraction is more ambiguous.¹⁶ While tribenzyltin acetate (mp 112–113°) is unequivocally polymeric and crystallizes as elongated plates with a distinct needle axis, tricyclohexyltin acetate (mp 61–63°) crystallizes in a rodlike form with an almost square cross section which contains discrete, monomeric molecules. However, the second oxygen atom of the carboxylate group lies only 2.95 Å from the tin atom in the same molecule,¹⁶ which raises the question of possible intramolecular association to form a chelated structure. Although such association would have to be weak since the bridging Sn-O distance in the tribenzyltin analog is 2.65 Å,⁷ the carbonyl infrared absorption may be sensitive to an interaction at this distance.

In the trimethylsilyl and germyl derivatives of *N,N*-diethyl- β -alaninate the carbonyl stretching frequencies are 1720 and 1682 cm^{-1} , respectively,¹⁷ again indicative of a normal ester structure. The zwitterionic forms of the amino acids in the solid state have symmetric anionic carboxylate groups as do their salts. The anionic sodium glycinate, the zwitterionic solid glycine itself, and the matrix-isolated molecular glycine have carbonyl absorptions at 1588, 1605, and 1781⁹ cm^{-1} ,

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Table III. Infrared Stretching Absorptions of the Carboxylate Group^a (cm⁻¹)

Compd	ν_{asym}	ν_{sym}	$\nu_{\text{asym}} - \nu_{\text{sym}}$	Compd ^b	ν_{asym}	ν_{sym}	$\nu_{\text{asym}} - \nu_{\text{sym}}$
Me ₃ Sn(gly)	1630	1398	232	Glycine	1605 ^{c,d}	1415 ^c	190
Me ₃ Sn(ala)	1635	1380	255	DL- α -Alanine	1600 ^{d,e}	1412 ^e	188
Me ₃ Sn(but)	1631	1420	211	DL- α -Amino- <i>n</i> -butyric acid	1602 ^f	1422 ^f	180
Me ₃ Sn(val)	1647	1408	239	DL- α -Valine	1600 ^g	1420 ^g	180
Me ₃ Sn(leu)	1638	1390	248	DL- α -Leucine	1590 ^{d,h}	1413 ^h	177
Me ₃ Sn(isoleu)	1635	1395	240	L- α -Isoleucine	1588 ⁱ	1400 ⁱ	188
Me ₃ Sn(β -ala)*	1636	1390	246	β -Alanine	1575 ^j	1390 ^j	185
Me ₃ Sn(glygly)*	1635	1371	264	Glycylglycine	1605 ^k	1410 ^k	195
(Amide CO 1683)				(Amide CO 1678, 1660)			
Bu ₃ Sn(gly)*	1625	1390	235				
Cy ₃ Sn(gly)	1620	1415	205				
Cy ₃ Sn(ala)	1600	1418	182				
Cy ₃ Sn(but)	1657	1420	237				
Cy ₃ Sn(val)	1652	1415	237				
Cy ₃ Sn(leu)	1590	1417	173				
Cy ₃ Sn(isoleu)	1585	1400	185				
Cy ₃ Sn(β -ala)*	1640	1390	250				
Cy ₃ Sn(glygly)*	1639	1390	249				
(Amide CO 1658)							

^a Deuteration of the NH₂ group allows identification of bands arising from the carboxylate group, and those marked with asterisks are assigned by analogy. ^b Assignments for the α -amino acids and dipeptide follow the literature as noted. ^c M. Tsuboi, T. Onishi, I. Nakagawa, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **12**, 253 (1958). The values of ν_{asym} and ν_{sym} are 1610 and 1415 cm⁻¹, respectively. ^d A. Rosenberg, *Acta Chem. Scand.*, **10**, 840 (1956). The values of ν_{asym} of the sodium salts of glycine, alanine, and leucine are given as 1588, 1590, and 1590 cm⁻¹. ^e K. Fukushima, T. Onishi, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **15**, 236 (1959). The values of ν_{asym} and ν_{sym} are 1597 and 1411 cm⁻¹, respectively. ^f B. Y. K. Ho, B.A. Thesis, Marist College, Poughkeepsie, N. Y., 1967. The values of ν_{asym} and ν_{sym} are 1589 and 1410 cm⁻¹, respectively. ^g I. Nakasawa, R. J. Hooper, J. L. Walter, and T. J. Lane, *Spectrochim. Acta*, **21**, 1 (1965). The values of ν_{asym} and ν_{sym} are 1596 and 1411 cm⁻¹, respectively. ^h J. F. Jackovitz and J. L. Walter, *Spectrochim. Acta*, **22**, 1393 (1966). The values of ν_{asym} and ν_{sym} are 1584 and 1413 cm⁻¹, respectively. ⁱ R. J. Hooper, T. J. Lane, and J. L. Walter, *Inorg. Chem.*, **3**, 1568 (1964). The values of ν_{asym} and ν_{sym} for DL- α -isoleucine are 1596 and 1417 cm⁻¹, respectively. ^j K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 4528 (1961). The values of ν_{asym} and ν_{sym} are 1570 and 1390 cm⁻¹, respectively. ^k A. Rosenberg, *Acta Chem. Scand.*, **11**, 1390 (1957). The value of ν_{asym} is 1605 cm⁻¹ and the values for the amide carbonyl are 1678 and 1657 cm⁻¹.

respectively, taking $\nu_{\text{asym}}(\text{O}-\text{C}=\text{O})$ the feature which is most sensitive to structural changes. The carboxylate groups in the first two forms of glycine are in a situation similar to that of a coordinated (bridged) carbonyl, while the matrix-isolated species is like a normal ester. Likewise, $\nu_{\text{asym}}(\text{O}-\text{C}=\text{O})$ values in the anionic sodium acetate (1578 cm⁻¹),¹⁸ the bridged trimethyltin acetate (1576 cm⁻¹),¹⁴ the normal ester-like trimethylsilyl acetate (1725 cm⁻¹),¹⁴ and the acetic acid monomer in the gas phase (1770 cm⁻¹)¹⁹ reflect the structural differences in these acetate forms. The similarity of the anionic and bridging acetate frequencies is also to be expected in the amino acid series.

Table III lists infrared carboxylate stretching absorptions for all seventeen tin compounds studied and the parent amino acids and glycylglycine and the magnitude of the $\nu_{\text{asym}} - \nu_{\text{sym}}$ ($\Delta\nu$) separation in each case. This latter parameter, which has been shown to be useful in drawing structural inferences,²⁰ is larger in those twelve compounds which we have assigned as amino coordinated ($\Delta\nu = 205\text{--}264$ cm⁻¹) than in the amino acids and dipeptide themselves ($\Delta\nu = 177\text{--}195$ cm⁻¹). It is also clear from Table III that the range of $\nu_{\text{asym}}(\text{O}-\text{C}=\text{O})$ values shown by these twelve amino-coordinated compounds (1620-1647 cm⁻¹) is substantially higher than for the zwitterionic compounds (1575-1605 cm⁻¹), anionic salts or bridged carboxylate structures as discussed above. The corresponding $\nu_{\text{sym}}(\text{O}-\text{C}=\text{O})$ absorptions either remain at the same value or move to lower frequencies than in the amino acids themselves. Strong interactions between

the carboxylate carbonyl and the tin atom can thus be ruled out on this basis.

However, the $\nu_{\text{asym}}(\text{O}-\text{C}=\text{O})$ absorptions of the amino-coordinated compounds lie intermediate between those of the ionic and bridged structures and those of the purely normal esters. The lowering of the carboxyl absorption from its normal ester value, for example, from 1781 cm⁻¹ in the matrix-isolated glycine, may find its origin in mass or solid-state effects or in weak interactions which cannot be ruled out.

Geometry of the Trimethyltin Group. The arrangement of the heavy atoms in the Sn(CH₃)₃ skeleton can be deduced from the tin-carbon stretching modes which occur in the 550-500-cm⁻¹ region of the infrared and Raman spectra. A trigonal-planar SnC₃ structure (local D_{3h} symmetry) will give rise to infrared-active $\nu_{\text{asym}}(\text{Sn}-\text{C})$ and Raman-active $\nu_{\text{sym}}(\text{Sn}-\text{C})$ modes, but both bands will appear in both spectra if there is significant deviation from planarity. In this case (local C_{3v} symmetry) the ν_{sym} absorption is generally much less intense in the infrared spectrum since the dipole change is less in symmetric stretching and much more intense in the Raman spectrum because of the greater polarizability change in this mode. As the angles in the SnC₃ group become more acute, the intensities should become more equivalent. A third possible arrangement is T shaped (local C_{2v} symmetry). In this case the double degeneracy of the asymmetric stretching mode is removed, and two absorptions should be observed in the ν_{asym} region. The symmetric stretch is not a degenerate mode. Of course, in the application of simplified local symmetry, accidental degeneracies are not precluded, nor is it certain that symmetry-allowed bands will have appreciable intensities.

The assignments of $\nu_{\text{asym}}(\text{Sn}-\text{C})$ and $\nu_{\text{sym}}(\text{Sn}-\text{C})$ in the

(18) K. Itoch and H. J. Bernstein, *Can. J. Chem.*, **34**, 170 (1956).

(19) W. Weltner, Jr., *J. Amer. Chem. Soc.*, **77**, 3941 (1955).

(20) N. N. Greenwood, "Spectroscopic Properties of Inorganic and Organometallic Compounds," The Chemical Society, London: Vol. 1, 1968, pp 201-202; Vol. 2, 1969, pp 333-334; Vol. 3, 1970, pp 325-327; Vol. 4, 1971, pp 415-419, and references therein.

infrared and Raman spectra are listed in Table IV. The Raman spectrum of the simplest compound, $\text{Me}_3\text{Sn}(\text{gly})$, shows two absorptions in the $650\text{--}450\text{-cm}^{-1}$ region studied, one strong and one weak, which can be assigned to ν_{sym} and ν_{asym} , respectively. The infrared spectrum in the same region shows four bands with the two at lower frequencies corresponding to those in the Raman spectrum with reversed intensities. A strong band at 560 cm^{-1} does not appear in the Raman spectrum and is most likely a rocking mode of the carboxylate group. The remaining strong band at 617 cm^{-1} is probably associated with a carboxylate group wagging mode. These two carboxylate deformation modes, owing to their weak scattering ability, would not be expected to be observed in the Raman spectrum. From these arguments it can be concluded that the arrangement of the SnC_3 group is neither precisely planar nor T shaped and, on the basis of the weak ν_{sym} in the infrared spectrum, that the Sn-C angles of the pyramidal (C_{3v}) SnC_3 group are not very acute.

The intensities of the ν_{sym} absorptions for all the other trimethyltin derivatives in the infrared spectra are weak and the ν_{asym} absorptions strong, with the reverse observed in the Raman spectra. Similar arguments as made above for the glycinate lead to the assignment of local C_{3v} symmetry for the trimethyltin moieties in these derivatives.

The positions of the tin-carbon stretching frequencies are well known for methyltin systems, but the analogous $\nu(\text{Sn-C})$ absorptions are not expected to lie in the same region for the tricyclohexyltin group because of mass effects and the difference in force constant between the primary and secondary carbon bond to tin. The $\nu(\text{Sn-C})$ for the triphenyltin group, for example, occurs below 300 cm^{-1} .²¹ In Table V are relevant far-infrared data for the cyclohexyltin derivatives, where ν_1 and ν_2 can be assigned to the $\nu_{\text{asym}}(\text{Sn-C})$ and $\nu_{\text{sym}}(\text{Sn-C})$ modes, respectively. We assume in this discussion that the cyclohexyl group attachment to tin is as expected on steric grounds predominantly equatorial, like that found in tricyclohexyltin acetate by X-ray study.¹⁶ Bands at 490 and 420 cm^{-1} in trimethylcyclohexyltin were examined in a variable-temperature infrared study in solution where it was shown that the logarithm of the intensity of the band at 420 cm^{-1} varies linearly with the inverse of the temperature, in a process presumably associated with conversion to the axial form in this compound.²² A weak symmetric stretching frequency rules out a precisely planar-trigonal SnC_3 skeleton in tricyclohexyltin hydroxide. All the other tricyclohexyltin derivatives have roughly comparable $\nu_{\text{asym}}(\text{Sn-C})$ and $\nu_{\text{sym}}(\text{Sn-C})$ intensities, suggesting a pyramidal SnC_3 skeleton. Since the ν_1 bands are not split, a precisely T-shaped geometry can be ruled out as well.

The Question of Intra- or Intermolecular Coordination.

Whether the coordination of the amino group nitrogen atom leads to chelation or polymerization can be discussed with reference to the $^{119\text{m}}\text{Sn}$ Mossbauer data listed in Table VI. All of the compounds studied exhibit doublet spectra centered in the $1.2\text{--}1.6\text{-mm/sec}$ region. Our structural inferences will be based mainly upon the magnitude of the quadrupole splitting (QS) and upon the temperature dependence of the Mossbauer effect.

The twelve compounds which we have assigned as amino-coordinated exhibit ratios of QS to isomer shift (IS) generally greater than 2.1 as expected, with the range of ρ ($= \text{QS}/\text{IS}$) values for the trimethyltin derivatives larger (2.37–2.52) than in the *n*-butyl (2.26) or cyclohexyl (2.01–2.18) analogs.

(21) R. C. Poller, *Spectrochim. Acta*, **22**, 935 (1966).

(22) S. Bank and B. A. Puls, private communication, 1972.

Table IV. Infrared and Raman Stretching Absorptions (cm^{-1}) in the $\text{Sn}(\text{CH}_2)_6$ Group

Compd	Infrared		Raman	
	$\nu_{\text{asym}}(\text{Sn-C})$	$\nu_{\text{sym}}(\text{Sn-C})$	$\nu_{\text{asym}}(\text{Sn-C})$	$\nu_{\text{sym}}(\text{Sn-C})$
$\text{Me}_3\text{Sn}(\text{gly})$	545	507	542	507
$\text{Me}_3\text{Sn}(\text{ala})$	541	510	<i>a</i>	514
$\text{Me}_3\text{Sn}(\text{but})$	549	<i>b</i>	<i>a</i>	517
$\text{Me}_3\text{Sn}(\text{val})$	545	512	546	508
$\text{Me}_3\text{Sn}(\text{leu})$	550	515	<i>a</i>	510
$\text{Me}_3\text{Sn}(\text{isoleu})$	547	515	542	510
$\text{Me}_3\text{Sn}(\beta\text{-ala})$	550	520	<i>c</i>	<i>c</i>
$\text{Me}_3\text{Sn}(\text{glygly})$	542	510	<i>c</i>	<i>c</i>

^a Intensity too weak to assign accurately. ^b Overlap with the 530-cm^{-1} band. ^c Not available.

Values of ρ larger than *ca.* 2.1 are generally associated with coordination numbers greater than 4 at tin.²³ It is interesting to note that of the five cyclohexyl derivatives not assigned as amino coordinated, four exhibit ρ values below 1.8, indicative of four-coordination. The case of tricyclohexyltin isoleucinate for which ρ is *ca.* 2.1 will be considered separately.

Tin Mossbauer spectra are generally obtained at liquid nitrogen temperatures where the recoil-free fraction of organotin absorbers is markedly increased. Certain organotin compounds give spectra at ambient temperatures, however, but such behavior has been shown always to be associated with polymeric association in the solid. While several compounds known to be intermolecularly associated fail to exhibit ambient-temperature spectra, no examples of monomeric systems giving rise to room-temperature spectra are known.^{23–25}

Among the trimethyltin derivatives studied, $\text{Me}_3\text{Sn}(\text{gly})$, $\text{Me}_3\text{Sn}(\text{ala})$, and $\text{Me}_3\text{Sn}(\text{glygly})$, exhibit easily observable ambient temperature Mossbauer spectra, establishing intermolecular association in these amino-coordinated compounds. *n*- $\text{Bu}_3\text{Sn}(\text{gly})$ also gives an observable room temperature spectrum, indicative again of a polymeric structure through intermolecular coordination of the amino group.

It is interesting to note that $\text{C}_6\text{H}_5\text{SnOH}$ exhibits an observable room-temperature Mossbauer spectrum as well. Trimethyltin hydroxide has been shown by X-ray study to possess a bridged, one-dimensional structure consisting of chains of oxygen atoms almost equidistant between planar trimethyltin groups which are inclined by 15° with respect to a plane perpendicular to the chain axis. This inclination gives rise to an 8_3 helical arrangement of five-coordinated tin atoms along the chain.^{6,15,26} Apparently, substitution of three bulky cyclohexyl groups does not disrupt the polymerization, further evidence for which is inferred from mass spectrometric data discussed below.

Tricyclohexyltin hydroxide has a QS which is the same within experimental error as that of trimethyltin hydroxide, which interestingly enough is a compound of known polymeric structure which does not exhibit an ambient temperature Mossbauer spectrum. We infer that these two hydroxides share the five-coordinated bridged polymeric structure on the basis of the similarity in Mossbauer spectral behavior.

Likewise, we infer that except for $\text{C}_6\text{H}_5\text{Sn}(\text{glygly})$, the

(23) J. J. Zuckerman, *Advan. Organometal. Chem.*, **9**, 21 (1970).

(24) R. C. Poller, J. N. R. Ruddick, B. Taylor, and D. L. B. Toley, *J. Organometal. Chem.*, **24**, 341 (1970).

(25) G. M. Bancroft and R. H. Platt, *Advan. Inorg. Chem. Radiochem.*, in press.

(26) N. Kasai, K. Yasuda, and R. Okawara, *J. Organometal. Chem.*, **3**, 172 (1965).

Table V. Far-Infrared (~600 to ~140 cm⁻¹) Data for the Tricyclohexyltin Derivatives^a

Compd	ν_1^b	ν_2^b	
Glycine ^c	608 m, 516 sh, 503 s,	358 m, 204 m, vb, 140 w	
Me ₃ Sn(gly)	617 s, 560 s, 545 s, 507 m,	373 m, 242 s, 172 m, sh, 146 s, 122 s	
Cy ₃ SnOH	664 m, 566 vw,	420 w, 352 m, 294 s, 235 m, 185 m	
Cy ₃ Sn(gly)	610 w, 575 m, b, 522 w,	421 m, 360 m, 324 m, 242 s	
DL- α -Alanine ^d	645 m, 542 s,	496 m, 408 s, b, 325 m, b, 295 s, 258 w, 220 w, 180 w, 100 w	
Cy ₃ Sn(ala)	605 w, 548 s,	494 m, 460 w, sh, 420 m, 325 m, 241 s	
DL- α -Amino- <i>n</i> -butyric acid ^e	650 w, 546 m,	494 m, 434 m, 420 m, 330 m, vb	
Cy ₃ Sn(but)	613 w, sh, 500 m,	494 m, 434 m, 420 m, 323 s, 246 s	
DL- α -Valine ^f	684 s, 534 s	473 m, 425 m, 363 s, b	
Cy ₃ Sn(val)	608 w, 552 m,	495 m, 435 w, 420 m, 358 w, 322 s, 248 s	
DL- α -Leucine ^g	681 s, 539 s,	496 m, 456 sh, 440 s,	401 s, 364 s, 348 s, 220 w, 185 w, 125 w
Cy ₃ Sn(leu)	608 w, 540 s,	490 m, 456 w, 440 s,	418 m, 400 s, 362 s, 323 m, 242 s
DL- α -Isoleucine ^h	681 s, 540 s,	492 m, 486 w, 450 s,	366 vs, b
Cy ₃ Sn(isoleu)	609 vw, 580 w, sh, 560 w, 541 m,	492 m, 442 m,	419 m, 394 m, 323 m, 245 s
Cy ₃ Sn(β -ala)	624 w, 598 w, 570 w, 545 m,	491 m, 437 vw, sh,	415 m, 404 s, 324 s, 243 s
Cy ₃ Sn(glygly)	598 m, 544 s,	492 m,	420 m, 389 m, 334 s, 244 s
(Cy ₃ Sn) ₂ CO ₃	668 m, 570 s,	492 m,	420 m, 371 w, 322 m, 258 s

^a Intensity notations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. ^b Tentative assignments for ν_1 and ν_2 are ν_{asym} (Sn-Cy₃) and ν_{sym} (Sn-Cy₃), respectively. ^c Above 500 cm⁻¹ from T. J. Lane, J. A. Durkin, and R. J. Hooper, *Spectrochim. Acta*, **20**, 1013 (1964); below 500 cm⁻¹ from J. L. Walter and R. J. Hooper, *Spectrochim. Acta, Sect. A*, **25**, 647 (1969). ^d J. F. Jackovitz, J. A. Durkin, and J. L. Walter, *ibid.*, **23**, 67 (1967). The 496-cm⁻¹ band is assigned by the authors as NH₃⁺ torsion. ^e B. Y. K. Ho, B.A. Thesis, Marist College, Poughkeepsie, N. Y., 1967. The 418-cm⁻¹ band is assigned as C-C-C skeletal deformation. ^f I. Nakagawa, R. J. Hooper, J. L. Walter, and T. J. Lane, *Spectrochim. Acta*, **21**, 1 (1965). ^g J. F. Jackovitz and J. L. Walter, *ibid.*, **22**, 1393 (1966). ^h R. J. Hooper, T. J. Lane, and J. L. Walter, *Inorg. Chem.*, **3**, 1568 (1964).

Table VI. Mossbauer Data (at 77°K) of Triorganotin Compounds

Compd	δ		Γ_1	Γ_2	$\rho = \Delta/\delta$
	(± 0.06), mm/sec	(± 0.12), mm/sec			
Me ₃ SnOH ^a	1.23	2.82	1.14	1.10	2.29
(Me ₃ Sn) ₂ CO ₃	1.34	3.05	1.28	1.24	2.28
Me ₃ Sn(gly) ^b	1.26	3.14	1.16	1.07	2.49
Me ₃ Sn(ala) ^b	1.30	3.21	1.50	1.03	2.47
Me ₃ Sn(but)	1.28	3.17	1.41	1.02	2.48
Me ₃ Sn(val)	1.27	3.24	1.44	1.06	2.55
Me ₃ Sn(leu)	1.30	3.28	1.50	1.03	2.52
Me ₃ Sn(isoleu)	1.29	3.23	1.85	1.08	2.50
Me ₃ Sn(β -ala)	1.30	3.08	1.20	1.14	2.37
Me ₃ Sn(glygly) ^b	1.31	3.26	1.13	1.12	2.48
Bu ₃ Sn(gly) ^b	1.42	3.21	1.02	1.19	2.26
Cy ₃ SnOH ^{b,c}	1.46	2.98	1.45	1.18	2.04
(Cy ₃ Sn) ₂ CO ₃	1.62	3.39	0.98	1.33	2.09
Cy ₃ Sn(gly)	1.56	3.14	1.48	1.13	2.01
Cy ₃ Sn(ala)	1.45	2.09	1.59	1.78	1.44
Cy ₃ Sn(but)	1.53	2.41	1.61	1.60	1.58
Cy ₃ Sn(val)	1.54	2.78	1.31	1.21	1.80
Cy ₃ Sn(leu)	1.54	2.75	1.34	1.85	1.78
Cy ₃ Sn(isoleu)	1.54	3.20	1.18	1.13	2.08
Cy ₃ Sn(β -ala)	1.52	3.21	1.06	1.12	2.11
Cy ₃ Sn(glygly)	1.58	3.45	1.21	1.15	2.18

^a Reported as IS = 1.19 \pm 0.05, QS = 2.91 \pm 0.05 [M. Cordey-Hayes, R. D. Peacock, and M. Vucelic, *J. Inorg. Nucl. Chem.*, **29**, 1177 (1967)]; IS = 1.14 \pm 0.09, QS = 2.97 \pm 0.09 [H. A. Stockler and H. Sano, *Phys. Rev.*, **165**, 406 (1968)]; IS = 1.07 \pm 0.03, QS = 2.71 \pm 0.03 mm/sec [R. H. Herber, H. A. Stockler, and W. T. Reichle, *J. Chem. Phys.*, **42**, 2447 (1965)]. ^b These compounds exhibit room-temperature spectra; the IS and QS data are within experimental error of those recorded here. ^c Reported as IS = 1.40 \pm 0.05, QS = 2.99 \pm 0.05 mm/sec [A. G. Maddock and R. H. Platt, *J. Chem. Soc. A*, 1191 (1971)].

amino-coordinated compounds all share the five-coordinated bridged polymeric structure on the basis of the ambient-temperature Mossbauer spectra exhibited by four of the twelve compounds in this class, and the close similarity in the QS values they show. Tricyclohexyltin glycyglycinate,

which exhibits a QS somewhat larger, will be discussed separately below.

Line asymmetries in doublet spectra (Goldanskii-Karyagin effect) are also of interest in discussing associated materials,^{23,25} but small apparent line asymmetries can arise from partial orientation of microcrystalline powders, the presence of a tin-containing impurity giving a single resonance which fortuitously overlaps with one of the wings of the doublet, or from artifacts of computer curve-fitting procedures. There are, as yet, no sure means of sample preparation to remove line asymmetries arising from orientation effects. The absence of line asymmetry is thus more significant than its presence, and interpretation must be cautiously considered. The Mossbauer spectrum of Me₃Sn(gly) at 77°K is shown in Figure 1. The ρ value larger than 2.1 is interpreted in terms of higher coordination at tin; the striking line asymmetry observed is generally taken to reflect a lattice dynamic anisotropy in the recoil-free fraction arising in organotin compounds possessing intermolecular association along particular axes in the solid state.^{23,25} Various means of sample preparation of Me₃Sn(gly) were used in an attempt to remove line asymmetry arising from orientation effects without avail. The Goldanskii-Karyagin effect seen in the Mossbauer spectra of the compounds we assign as amino-coordinated, except for Cy₃Sn(glygly), lends support to the suggestion of an intermolecularly associated structure. This situation should be contrasted with that found in Cy₃Sn(isoleu), drawn from the class of those compounds not amino coordinated, whose Mossbauer spectrum at 77°K is shown in Figure 2, in which the ρ value is also ca. 2.1 but where no Goldanskii-Karyagin effect is seen. This contrast is also illustrated in Me₃Sn(glygly) which exhibits measurable asymmetry and Cy₃Sn(glygly) which exhibits none. Only large line intensity differences, such as that seen in Figure 1, have been used in this interpretation, whose importance should not be stressed unduly.

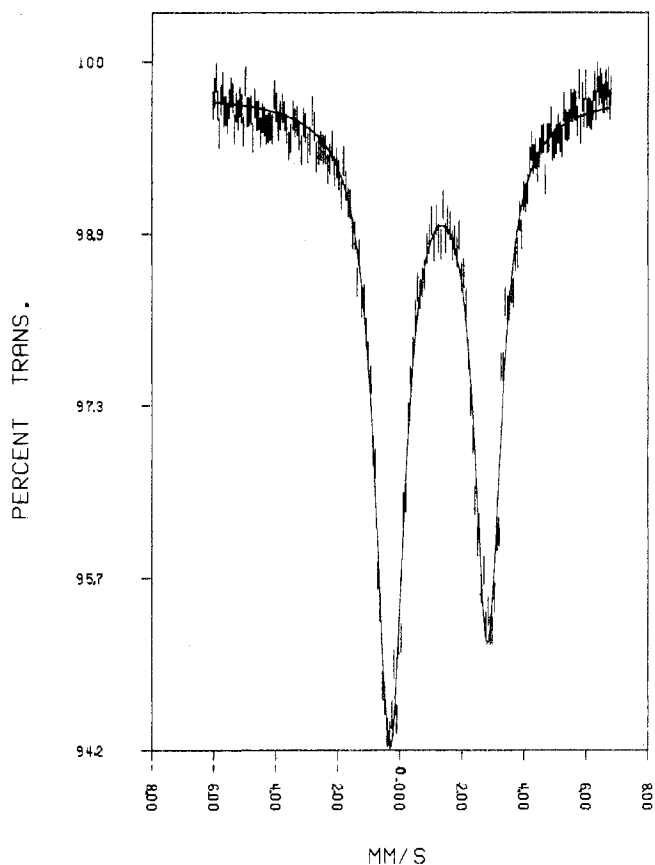


Figure 1. Mossbauer spectrum of $\text{Me}_3\text{Sn}(\text{gly})$ at 77°K vs. $\text{Ba}^{119\text{m}}\text{SnO}_3$.

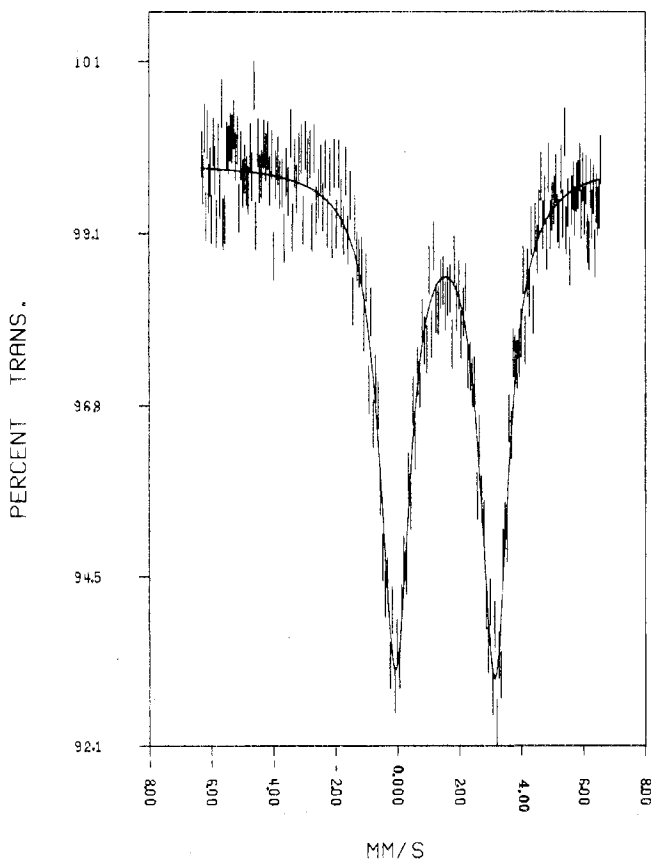


Figure 2. Mossbauer spectrum of $\text{Cyh}_3\text{Sn}(\text{isoleu})$ at 77°K vs. $\text{Ba}^{119\text{m}}\text{SnO}_3$.

Mass Spectrometric Results. Information concerning the associated nature of organotin compounds may be deduced from mass spectrometric studies. Table VII²⁷ lists the mass spectrometric data for the hydroxides and carbonates of trimethyl- and tricyclohexyltin.

Trimethyltin hydroxide, which adopts a polymeric solid-state structure,^{6,15,26} exhibits an intense peak at m/e 329 which can be formulated on the basis of high-resolution data as $\text{Me}_3\text{SnOSnMe}_2^+$. Tricyclohexyltin hydroxide likewise gives a peak at m/e 669 which on the basis of high-resolution data can be formulated as $\text{Cyh}_3\text{SnOSnCyh}_2^+$. The peak in this case, however, is far less intense, but the data clearly confirm the polymeric nature of Cyh_3SnOH .

Trimethyltin hydroxide is known to take up carbon dioxide quite readily,²⁸ and so the mass spectra of the analogous carbonates were also examined. Both trimethyltin hydroxide and carbonate have the m/e 329 ion, $\text{Me}_3\text{SnOSnMe}_2^+$, as most abundant. In the cyclohexyl compounds, on the other hand, the ions assigned as $\text{Cyh}_3\text{SnOSnCyh}_2^+$ (669), $\text{Cyh}_2\text{-SnOSnCyh}_2^+$ (586), $\text{Cyh}_2\text{SnOSnCyh}^+$ (503), and $\text{Cyh}_2\text{SnOH}^+$ (302) in the spectrum of Cyh_3SnOH do not appear in the spectrum of the carbonate but are replaced by peaks which can be assigned to $\text{Cyh}_3\text{Sn}(\text{Cyh}_2\text{Sn})\text{CO}_2^+$ (697), $(\text{Cyh}_2\text{Sn})_2\text{-CO}^+$ (598), $(\text{CyhSn})_2\text{CO}_3^+$ (464), CyhSnOSnH_2^+ (339) and SnOSnH^+ (255). In both cyclohexyltin compounds CyhSn^+ (202) is the most abundant ion. Doubly charged ions are common in the spectrum of $(\text{Me}_3\text{Sn})_2\text{CO}_3$, and the amount of CO_2^+ is significant, while in the cyclohexyl analog doubly charged ions are not observed, and the release of CyhO is a principal process in fragmentation.

The comparison between the methyl and cyclohexyl spectra reflects the greater availability of hydrogen from cyclohexyl groups during fragmentation to give species such as SnH^+ (120).

It was hoped that the associated nature of some of the amino acid and dipeptide derivatives would reveal itself in the mass spectral data, but as seen in Tables VIII²⁷ and IX,²⁷ neither the parent molecular ions nor ions of higher mass are seen. The P-R^+ ion peaks where $\text{R} = \text{Me}$ or Cyh are potentially useful in establishing the identity of the compounds. The most abundant tin-bearing ions are Me_3Sn^+ (164) and CyhSn^+ (202) for their respective derivatives. The ions CO_2^+ and NH_2R^+ are observed, with the latter occasionally the most abundant ion in the spectrum.

Structural Conclusions

Compounds with Amino Coordination. Strong carboxylate group oxygen interaction is ruled out in these twelve compounds on the basis of high stretching frequency values. Presence of both symmetric and asymmetric infrared and Raman $\nu(\text{SnC}_3)$ bands for the methyltin compounds rules out precisely planar Me_3Sn groups. Large Mossbauer quadrupole splitting values confirm higher coordination at tin and ambient-temperature and line intensity asymmetry data suggest a polymeric structure for all but the $\text{Cyh}_3\text{Sn}(\text{glygly})$ derivative. The combination of these data specifies a five-coordinated, presumably trigonal-bipyramidal structure with oxygen and a nitrogen atom from an adjacent molecule occupying axial positions. This arrangement is the conven-

(27) Tables VII-X will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1552.

(28) R. Okawara and K. Yasuda, *J. Organometal. Chem.*, **1**, 356 (1964).

tional, axially most electronegative structure universally found in organotin chemistry.⁶ This structural type requires for monomeric amino acid derivatives axial bridging by a single amino acid ligand which is impossible, even in the β -ala derivative. The axial positions can, however, be spanned by the glygly ligand, but the ambient-temperature Mossbauer spectrum for $\text{Me}_3\text{Sn}(\text{glygly})$ specifies a polymeric structure.

With reference to the analogous organotin carboxylates, it is surprising that with the introduction of an amino group into the carboxylate ligand, the strong intermolecular bridging of the carboxylate group⁶ is apparently replaced by that of the amine nitrogen atom, despite the generally acknowledged greater affinity of tin for oxygen.

The three amino-coordinated cyclohexyltin compounds have as a common feature that the NH_2 group is at a terminal position, linked through a CHR group in which R = hydrogen. Nonbonded interactions will obviously play a larger role in the Cyh_3Sn series as can be seen in the disruption of the amino coordination in the α -amino acid derivatives except the glycinate.

Possible Structures for $\text{Cyh}_3\text{Sn}(\text{glygly})$. The QS value for tricyclohexyltin glycyglycinate (3.45) falls outside the range occupied by the other amino-coordinated compounds (3.08–3.28 mm/sec), and the doublet spectrum shows no Goldanskii-Karyagin line asymmetry, unlike in the other amino-coordinated compounds. Direct comparison can be drawn with the trimethyltin analog where there is pronounced Goldanskii-Karyagin line intensity asymmetry in the doublet spectrum (QS = 3.14 mm/sec). In addition, the amide carbonyl frequency is lowered from the $\text{Me}_3\text{Sn}(\text{glygly})$ value of 1683 to 1658 cm^{-1} in the tricyclohexyltin analog. The mass effect is not strong enough to account for this lowering, as may be seen by comparing the decrease of the carbonyl asymmetric stretching frequencies of $\text{Me}_3\text{Sn}(\text{gly})$ (1630 cm^{-1}), $n\text{-Bu}_3\text{Sn}(\text{gly})$ (1625 cm^{-1}), and $\text{Cyh}_3\text{Sn}(\text{gly})$ (1620 cm^{-1}). The observed decrease of 25 cm^{-1} in $\nu(\text{C}=\text{O})$ in the glycyglycinato ligand can be compared to similar shifts which are observed in *N,N*-dimethylformamide (DMF) on complexation to tin halides. In this case $\nu(\text{C}=\text{O})$ in DMF shifts from 1685 to 1650 cm^{-1} on forming $\text{SnCl}_4 \cdot 2\text{DMF}$,²⁹ where a larger shift in the stretching frequency is expected since the tetrachloride is a stronger Lewis acid than the Cyh_3Sn dipeptide. Coordination through the amide nitrogen atom would be expected to produce frequency shifts in the opposite direction. The melting point of the Cyh_3Sn derivative (126–127° dec) is also much lower than that of the Me_3Sn analog (171–172°).

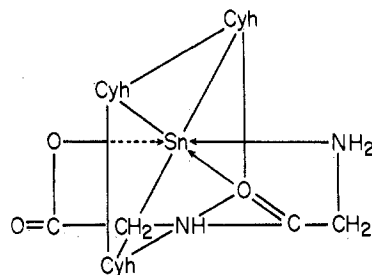
We interpret these data in terms of a structure in which both the amide group carbonyl oxygen and terminal amino group nitrogen atoms of the glycyglycinato ligand are involved in coordination to tin to create a hexacoordinated arrangement. Symmetrical, fused-ring chelation through the amide group nitrogen atom as has been established in the five-coordinated glycyglycinatocopper(II) trihydrate by X-ray study^{12a} can be ruled out on the basis of the amide carbonyl infrared shift to lower frequency, as can similar utilization of amide group nitrogen coordination in the dimeric tripeptide derivative sodium glycyglycyglycinatocopper(II) monohydrate whose structure is also known.³⁰

No triorganotin complexes with hexacoordination at tin have been authenticated.^{6,15} Trimethyltin nitrate monohydrate was proposed to contain hexacoordinated tin, but

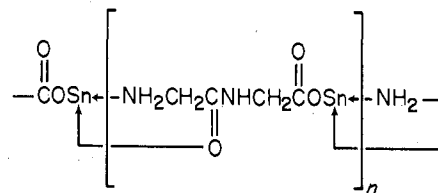
(29) E. W. Randall, C. M. S. Yoder, and J. J. Zuckerman, *Inorg. Chem.*, **5**, 2240 (1966).

(30) H. C. Freeman, J. C. Schoone, and J. G. Sime, *Acta Crystallogr.*, **18**, 381 (1965).

X-ray study shows a trigonal-bipyramidal arrangement of the axially most electronegative type.³¹ Dipyrindinium triphenyltrichlorostannate³² and tetramethylammonium triethyltrichlorostannate³³ are also formulated as hexacoordinated, but no structural data are yet available. Octahedral complexes of the formula R_3SnL_3 have available two kinds of configuration, meridional (ligands of the same kind arranged in a T shape) and facial (ligands of the same type occupying one face of the octahedron). The quadrupole splitting parameter from ¹¹⁹mSn Mossbauer spectra can readily distinguish these two possibilities. Calculations based upon a point-charge model predict zero quadrupole splitting for the facial arrangement,³⁴ and X-ray study has confirmed that the tin atom in the compound $[(\text{Cl}_3\text{SnOPCl}_3^+)(\text{O}_2\text{PCl}_2^-)]_2$ is part of a slightly distorted facially arranged octahedral moiety. The small QS values of 0.30 (at 298°K) and 0.75 mm/sec (at 77°K)³⁵ are consistent with this structure. Based upon data from a wide range of organotin complexes,²³ meridionally substituted, octahedral triorganotin derivatives of amino acids were predicted to exhibit QS values of approximately 3.5 mm/sec.³⁴ We interpret the QS of $\text{Cyh}_3\text{Sn}(\text{glygly})$ (=3.45 mm/sec) in terms of a meridional O_h structure, assuming that the oxygen and nitrogen donor atoms produce similar partial electric field gradients along their coordinate axes to tin. Such a meridional octahedral arrangement could adopt a monomeric unsymmetrical chelated structure of five- and seven-membered fused rings as shown by



or, alternatively, a structure in which each tin atom is bonded to the terminal nitrogen and amide carbonyl oxygen atom of the dipeptide ligand of a second molecule



Such an arrangement is found in the tripeptide derivative glycyglycyglycinatocopper(II) chloride sesquihydrate in which an infinite chain of copper-peptide units is found.³⁶ Cyclic dimeric or oligomeric structures with this arrangement are also possible. Lack of solubility prevented molecular weight determination, and the absence of Goldanskii-Karyagin line intensity asymmetry in the Mossbauer spectrum and of mass spectral fragments higher in mass than the

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parent molecular ion is negative evidence. The problem must await crystallographic study for solution.

Compounds Lacking Amino Coordination. We now deal with the five compounds, all tricyclohexyl derivatives, which have not been discussed so far.

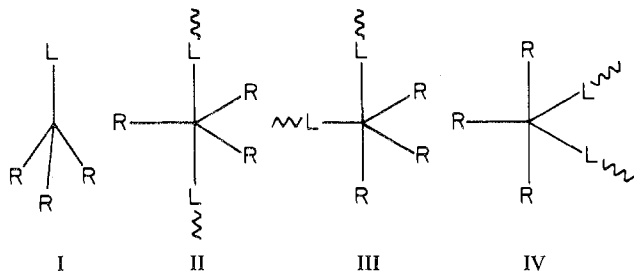
Infrared tin-carbon stretching frequency data have helped to establish that the geometry of the trimethyltin and tricyclohexyl groups cannot be precisely planar or T shaped.

Turning to the infrared data for the carboxylate group, among the compounds lacking amino coordination, Cy_3Sn -(-ala), -(leu), and -(isoleu) exhibit ν_{asym} and $\Delta\nu(\text{O}=\text{C}=\text{O})$ values which compare closely to those for the corresponding zwitterionic solid HAA's, which suggests interaction between the carboxylate carbonyl oxygen atom and tin in these three compounds. The remaining two Cy_3Sn derivatives (but and val) lack carboxylate bridging on the basis of the same arguments and low QS and ρ values in the Mossbauer spectra. These two compounds must clearly be monomeric, four-coordinated species.

It has been shown on the basis of the extension of a molecular orbital model which correlates QS data with stereochemistry³⁷ that in organotin compounds of the type R_3SnL where R is an organic group and L is a potentially bridging ligand, the ratio of QS values of

$$1 : \frac{4}{3} : \frac{2\sqrt{13}}{9} : \frac{4\sqrt{7}}{9} = 1 : 1.333 : 0.801 : 1.176$$

is given for structures I-IV.³⁸ Taking Cy_3Sn (but) and -(val)



as monomers of structure I, the following predicted QS values are obtained for each structural type: II, 3.2-3.7; III, 1.9-2.2; IV, 2.8-3.3. On this basis the axially most electronegative type of arrangement (II) can be ruled out in the three Cy_3Sn derivatives exhibiting carboxylate coordination, since even the highest of the QS values, that for the isoleu compound, falls more completely within the range assigned to structure IV, which is analogous to that taken by Cy_3Sn acetate (their QS values are identical within experimental error). The melting point of Cy_3Sn (isoleu) (54-57°) is similarly low as in the acetate (mp 61-63°) as well. Cy_3Sn (ala) and -(leu) then most likely adopt structures III and IV, respectively.

Stereochemical Rationale. As has been pointed out above, the three amino-coordinated tricyclohexyltin compounds have the CH_2NH_2 terminal unit in common. Model studies show that substituents on the carbon next to the amino group (the α carbon) will not hinder intramolecular association (chelation), since they can be directed away from the three cyclohexyl groups, whereas in intermolecular association (polymerization) the substituents on the adjacent carbon are brought into close contact with the three cyclohexyl groups. Thus a bulky substituent on the α carbon would be expected to disrupt polymerization, but not chelation, and only pointed ligand groups such as CH_2NH_2 can achieve

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(38) M. G. Clark, private communication, 1972.

intermolecular coordination with the Cy_3Sn moiety.

Hence, we find that in the Cy_3Sn series only the gly and β -ala derivatives can adopt the polymerized structure, whereas in the Me_3Sn series not even a bulky *sec*-butyl group on the α carbon (isoleu) serves to disrupt polymerization. Apparently, substitution of groups, R, larger than the proton on the α carbon effectively eliminates the amino-bridged structures as the most stable for the Cy_3Sn derivatives. In at least two cases, with R = ethyl (but) and isopropyl (val), the crowding is so severe that no additional coordination of tin of any kind is possible, and simple, four-coordinated monomers result. For R = *sec*-butyl (isoleu) a structure is adopted in which carboxylate association is apparently possible between equatorial positions on the trigonal bipyramid, which may be through chelation in a monomeric species similar to that found in Cy_3Sn acetate.¹⁶ For R = methyl (ala) and isobutyl (leu) carboxylate-coordinated structures involving axial and equatorial positions for ala and two equatorial positions for leu are adopted which probably also involve intramolecular association (chelation).

Experimental Section

Melting points were measured on a Thomas-Hoover capillary melting point apparatus (Arthur H. Thomas Co.) and were uncorrected. Carbon, hydrogen, and nitrogen analyses were performed by Instranal Laboratory, Inc., Rensselaer, N. Y., except those of the compound trimethyltin glycinate which were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Tin was analyzed as tin(IV) oxide through the action of nitric and sulfuric acids.

Our cam-drive, constant-acceleration Mossbauer spectrometer and curve-fitting procedures have been described in detail.³⁹ Mossbauer spectra were calibrated against an NBS 5-mil β -tin foil as having an absolute value of 2.56 mm/sec (lit.⁴⁰ 2.56 ± 0.01 mm/sec). SnTe which has been suggested as the isomer shift standard for tin has a value of 3.43 ± 0.06 mm/sec (lit.⁴⁰ 3.43 ± 0.02 mm/sec) on this basis.

Six trimethyltin compounds were studied from 650 to 450 cm^{-1} as listed in Table IV using a Jarrell-Ash 25-300 Raman spectrometer equipped with a helium-neon laser source. The conditions used for running the samples were as follows: He-Ne source, 6328 Å; source intensity, 50 mW; slit, 4 cm^{-1} ; time constant, 2 sec; sensitivity, 1×10^2 ; scanning speed, 0.5 in./min; gear, $20\text{ cm}^{-1}/0.5\text{ in.}$

Mass spectra were obtained from an AEI-MS-902 mass spectrometer operating at an ionization energy of 70 eV, an accelerating voltage of 8 kV, and a source temperature of about 200°. A program (in Fortran V) written for the UNIVAC 1108 computer was used for the analysis of the mass spectral fragments containing polyisotopic elements.

Infrared and far-infrared spectra were recorded on Beckman IR-12 and Beckman IR-11 infrared spectrophotometers calibrated with indene, polystyrene film, and water vapor. The far-infrared spectra and some infrared spectra were expanded to be able to read to $\pm 1\text{ cm}^{-1}$, but due to the broad nature of the bands, it is judged that $\pm 5\text{ cm}^{-1}$ is a more reasonable error limit for the solid state. Prominent infrared absorptions of the compounds prepared as Nujol and/or halocarbon oil mulls are listed in Table X.²⁷

The triorganotin derivatives of amino acids and dipeptides were synthesized by azeotropic distillation of water from benzene solutions of triorganotin hydroxides (or bis(triorganotin) oxides) and the acids. *N,N*-Dimethylformamide was added for the synthesis of trimethyltin glycinate, trimethyltin alaninate, and tributyltin glycinate. Trimethyltin hydroxide (M and T Chemicals) was purified by sublimation at room temperature *in vacuo* using a liquid nitrogen cooled cold finger. The syntheses of the compounds studied are described by the following typical procedures.

Trimethyltin Glycinate.⁴¹ Trimethyltin hydroxide (5.40 g, 0.03

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(40) J. G. Stevens and V. E. Stevens, "Mossbauer Effect Data Index, Covering the 1970 Literature," Plenum Press, New York, N. Y., 1972.

(41) Preliminary X-ray data ($\text{Cu K}\alpha$) have been gathered for this compound held in nitrogen-filled Lindemann glass capillary tubes. The tetragonal crystals are of unit cell dimensions $a = b = 7.839$, $c = 14.659$ Å, with four molecules per unit cell. The calculated density is 1.78 g/cm^3 , and the measured density is 1.73 g/cm^3 (pycnometer). The space group is $P4_1$ or $P4_3$.

mol) and glycine (2.25 g, 0.03 mol) were combined with 50 ml of DMF in 150 ml of dry benzene. Nitrogen gas was used to flush a system consisting of the reaction flask with contents, a Dean-Stark trap filled with benzene, and a water-cooled condenser before starting the reaction by heating the heterogeneous benzene suspension. After 2 hr, about 0.6 ml of water had been collected (theoretical 0.54 g). The hot solution was filtered under nitrogen to give a clear light yellowish filtrate. Some crystallization took place on cooling. The solution was concentrated on a rotary evaporator, and the crystals were filtered under nitrogen and washed with petroleum ether (80% yield).

Tributyltin Glycinate. Bis(tributyltin) oxide (4.25 g, 0.01 mol) and glycine (1.50 g, 0.02 mol) were combined with 7 ml of DMF in 150 ml of benzene. The reaction was carried out as described above. After 4 hr 0.19 ml of water had been collected (theoretical 0.18 g). The hot solution was filtered under nitrogen, and benzene was evaporated on a rotary evaporator. The small amount of solid formed in the remaining DMF solution was filtered and washed with petroleum ether (35% yield).

Tricyclohexyltin Glycinate. DMF was not used in this synthesis. Following a similar procedure as above, tricyclohexyltin hydroxide (0.02 mol) and glycine (0.02 mol) gave water (0.33 ml; theoretical 0.36 ml) and the product in 48% yield after 6 hr.

Deuteration of Glycine. Glycine (ca. 5 g) was dissolved in 99.8% D₂O in a stoppered flask and left at room temperature for 1 month. Addition of excess acetone precipitated the deuterated glycine (94% yield).

Deuteration of L- α -Isoleucine. Isoleucine (2.7 g) was partially dissolved in 99.8% D₂O at room temperature, left for 2 weeks in a stoppered flask, and then warmed for 2 days during which time all solids dissolved. Crystallization took place on cooling. The remaining deuterium oxide was evaporated *in vacuo* to yield the deuterated isoleucine (2.6 g).

Bis(tricyclohexyltin) Carbonate. Tricyclohexyltin hydroxide (1 g) was dissolved in 100 ml of dry benzene, and carbon dioxide was bubbled through the solution overnight. Bis(tricyclohexyltin) carbonate (mp 195–197°) remained after the solvent was evaporated. *Anal.* Calcd: C, 55.80; H, 8.36; Sn, 29.81. Found: C, 54.80; H, 8.38; Sn, 29.69.

Bis(trimethyltin) Carbonate. Carbon dioxide was bubbled overnight through a solution of trimethyltin hydroxide (1 g) in 100 ml of benzene. The solid isolated was infusible above 210° (lit.⁴² mp >200°).

(42) H. Sato, *Bull. Chem. Soc. Jap.*, 40, 410 (1967).

The amino acid and dipeptide derivatives studied were purified by recrystallization from hot benzene solution, except the following compounds which were purified by sublimation: trimethyltin glycinate, trimethyltin glycyglycinate, and tributyltin glycinate (sublimed using a cold finger at -78° with a maximum oil bath temperature of 150, 165, and 160, respectively, under a pressure of 0.1, 0.005, and 0.02 Torr, respectively).

The single crystals of trimethyltin glycinate used for X-ray study were grown by sublimation using a pointed cold finger kept at -78° with an oil bath temperature of 140–150° and at a pressure of 90 Torr.

Registry No. Trimethyltin hydroxide, 39700-41-9; tricyclohexyltin hydroxide, 39700-42-0; bis(tributyltin)oxide, 56-35-9; glycine, 56-40-6; DL-alanine, 302-72-7; DL- α -aminobutyric acid, 2835-81-6; DL-valine, 516-06-3; DL-leucine, 328-39-2; L-isoleucine, 73-32-5; β -alanine, 107-95-9; glycyglycine, 556-50-3; Me₃Sn(gly), 39700-30-6; Me₃Sn(ala), 39700-31-7; Me₃Sn(but), 39700-32-8; Me₃Sn(val), 39700-33-9; Me₃Sn(leu), 39700-34-0; Me₃Sn(isoleu), 39700-35-1; Me₃Sn(β -ala), 39700-36-2; Me₃Sn(glygly), 39700-37-3; Bu₃Sn(gly), 39700-38-4; Cyh₃Sn(gly), 39700-39-5; Cyh₃Sn(ala), 39699-39-3; Cyh₃Sn(but), 39678-69-8; Cyh₃Sn(val), 39678-70-1; Cyh₃Sn(leu), 39699-40-6; Cyh₃Sn(isoleu), 39699-41-7; Cyh₃Sn(β -ala), 39700-40-8; Cyh₃Sn(glygly), 39708-58-2; bis(tricyclohexyltin) carbonate, 39678-71-2; bis(trimethyltin) carbonate, 16469-60-6; carbon dioxide, 124-38-9.

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Electron Paramagnetic Resonance Investigations of Photosensitive Transition Metal Oxalates. Copper-Doped K₂Pd(C₂O₄)₂·2H₂O

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In a general study of photosensitive materials, an epr investigation of a single crystal of K₂Pd(C₂O₄)₂·2H₂O substitutionally doped with the paramagnetic cupric ion has been carried out at ambient temperature. The magnetic data were analyzed using a spin Hamiltonian which included the quadrupole term. An evaluation of the bonding parameters for the included copper complex revealed that in the ground state the unpaired electron is confined to the d_{x²-y²} metal orbital. However, in the excited state there is significant delocalization of unpaired electron density into the oxalate ligand π orbitals. A mechanism for the observed photoconductivity of the host material is proposed.

Introduction

Some interest has been shown recently in the solid-state photochemistry of transition metal-oxalate complexes.¹⁻⁴

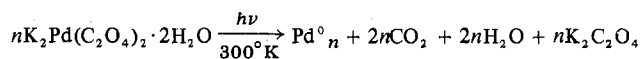
(1) H. E. Spencer and M. W. Schmidt, *J. Phys. Chem.*, 74, 3472 (1970).

(2) H. E. Spencer, *J. Phys. Chem.*, 73, 2316 (1969).

(3) H. E. Spencer and M. W. Schmidt, *J. Phys. Chem.*, 75, 2986 (1971).

(4) W. G. McDugle, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., 1972, No. INOR 67.

Potassium bis(oxalato)palladium(II) dihydrate (KOPD) is known to be photosensitive and the following overall reaction scheme has been proposed to account for the formation of aggregated palladium atoms during exposure of the solid material⁵



(5) H. E. Spencer and J. E. Hill, *Photogr. Sci. Eng.*, 16, 234 (1972).