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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XXIII *. ESTERTIN DERIVATIVES. STRUCTURAL AND SPECTROSCOPIC STUDIES

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Summary

The crystal and molecular structures of three 'estertin' derivatives, $Cl_3SnCH_2CH_2CO_2Me$, $Cl_2Sn[CH_2CH_2CO_2Me]_2$ and $Cl_2Sn[CH_2CH_2CONH_2]_2$, are reported. Crystals of $Cl_3SnCH_2CH_2CO_2Me$ are orthorhombic, space group $P2_12_12_1$, with a 9.2981, b 10.5389, and c 10.0885 Å; those of Cl_2Sn-$[CH_2CH_2CO_2Me]_2$ are monoclinic, space group $P2_{1/c}$, with a 8.0107, b 15.9104, c 13.4109 Å, and β 131.0044°; and those of $Cl_2Sn[CH_2CH_2CONH_2]_2$ are also monoclinic, space group C_c, with a 9.1314, b 12.8672, c 13.0317 Å, and β 126.6032°. Crystals of $Cl_3Sn(CH_2CH_2CO_2Me)$ and $Cl_2Sn[CH_2CH_2CO_2Me]_2$ both consist of discrete molecules, but extensive intermolecular hydrogen-bonding occurs in crystals of $Cl_2Sn[CH_2CH_2CONH_2]_2$. Intramolecular carbonyl oxygen-to-tin coordination occurs in all three compounds.

Vibrational and mass spectra are also reported, and are assigned in accordance with the determined structures.

Tin-119 Mössbauer studies demonstrate that it is possible to investigate the nature of organotin additives to PVC by this method. Preliminary investigations show that $Bu_2Sn(IOTG)_2$ ** added to PVC undergoes only partial IOTG for chlorine exchange at the milling stage, but is completely converted to Bu_2SnCl_2 after thermal degradation. Both $BuAcSn(IOTG)_3$ and $BuAcSn(\beta MeOct)_3$** undergo complete sulphur ligand for Cl exchange during the milling process giving $BuAcSnCl_3$ as the species detected. Degradation to some unidentified organotin species occurs on heating.

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* For part XXII see ref. 12.

** IOTG = *iso*-octythioglycollate, βMeOct = $SCH_2CH_2OCOC_7H_{15}$.

Introduction

The formation of β-carbonyl-substituted ethyltin compounds by the reactions of tin metal or tin (II) halides with a carbonyl-substituted alkene in the presence of hydrogen halide, a method devised by Burley, Hutton and Oakes [1], has facilitated the preparation of a new series of 'Estertin' stabilisers for PVC plastics. The syntheses, which appear to take place in a wide variety of solvents and over a large temperature range, may be summarised by the equations:

$$Sn + 2\,HX + 2\,R_2C{=}CR_2 \rightarrow X_2Sn(CR_2{-}CR_2H)_2 \qquad (1)$$

$$SnX_2 + HX + R_2C{=}CR_2 \rightarrow X_3SnCR_2{-}CR_2H \qquad (2)$$

X = Cl, Br, I.

where at least one of the groups R must be a carbonyl function (ester, ketone, amide, etc.). The mechanisms of the reactions were initially proposed to involve the intermediate formation of the halogenostannanes, X_3SnH and X_2SnH_2, but more recent investigations by Bulten [2] have indicated the intermediacy of $H_2SnCl_4 \cdot nEt_2O$ in both.

In this paper we report the structures of three estertin derivatives, as well as vibrational, mass spectral, and tin-119 Mössbauer data. Preliminary results of a Mössbauer study of estertin thiolate compounds in PVC are also presented.

Experimental

1. Syntheses

(i) Bis(β-carbomethoxyethyl)tin dichloride

The procedure used was essentially similar to that outlined by Hutton and Oakes [1]. To a stirred suspension of tin powder (3.5 g, 0.03 mol) in dry THF (15 cm^3) was added methyl acrylate (5.5 cm^3, 0.06 mol). Anhydrous hydrogen chloride gas was then passed through the mixture for ca. 2 h maintaining the temperature at ca. 20°C using a water bath. The white precipitate formed was washed with dry THF (3 × 10 cm^3) to remove any organotin trichloride. Extraction of the residue with hot chloroform (30 cm^3), and subsequent slow crystallisation yielded a highly crystalline sample of bis(β-carbomethoxyethyl)tin dichloride, mp. 132—133°C (lit. [1] 132°C). Found: C, 26.42; H, 4.14; Cl, 18.62%. $C_8H_{14}Cl_2O_4Sn$ calcd.: C, 26.37; H, 3.84; Cl, 19.30%.

(ii) β-Carbomethoxyethyltin trichloride

A similar procedure was adopted for the preparation of this compound using anhydrous tin(II) chloride (4.7 g, 0.025 mol) and methyl acrylate (2.25 cm^3, 0.025 mol) in dry toluene (20 cm^3). Anhydrous hydrogen chloride was passed through the solution for 1 h, when the solvent was removed under vacuum. Extraction and re-crystallisation from hot toluene yielded white crystalline β-carbomethoxyethyltin trichloride, mp. 71—72°C (lit. [1] 70°C). Found: C, 12.54; H, 1.90; Cl, 28.14%. $C_4H_7Cl_3O_2Sn$ calcd.: C, 12.55; H, 1.83; Cl, 27.85%.

(iii) Other compounds

All other compounds were provided by Dr. J.W. Burley of AKZO Chemie (UK) Ltd, and recrystallised where necessary.

2. *X-ray diffraction studies*

(i) *β-Carbomethoxyethyltin trichloride*

A crystal of approximate dimensions 0.3 × 0.3 × 0.5 mm was loaded into a Lindemann capillary and used for the initial photography and subsequent intensity data.

Crystal data: $C_4H_7Cl_3O_2Sn$, M = 312.29, Orthorhombic, a 9.2981, b 10.5389, c 10.0885 Å, V 988.59 Å^3, Z = 4, $F(000)$ = 592, μ(Mo-K_α) = 33.45 cm^{-1}, space group $P2_12_12_1$ by systematic absences ($h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$).

Cell measurements and data collection: The space group and initial cell parameters were determined from oscillation and zero- and first-layer Weissenberg photographs using a Nonius-Weissenberg Camera. Relative intensities up to $\theta = 27.5°$ were collected using Mo-K_α radiation (λ 0.71069 Å) on a Hilger and Watts Y290 four-circle automatic diffractometer. Accurate cell parameters were obtained by least squares refinement using ca. 23 reflections. Systematically absent reflections and reflections with $I < 3\sigma(I)$ were discarded reducing the total number of reflections from 1365 to 1198. Intensity corrections were made for Lorentz and polarization effects, but none were made for absorption due to the low value of μ.

Structure determination and refinement: The positional parameters of the tin atom were determined using a three dimensional Patterson synthesis. These coordinates were then used to phase the initial structure factor calculations. Subsequent alternate Fourier syntheses and least-squares isotropic refinement yielded the positions of the remaining light atoms. The final stages of the refinement were carried out with the atoms varying anisotropically, and when the R value reached convergence of 0.042, a weighting scheme based on the Chebychev series to five terms

$$w = \frac{1}{A(0)\,T(0)\,(X) + A(1)\,T(1)\,(X) + \ldots + A(n-1)\,T(n-1)\,(X)}$$

where $A(n)$ is the coefficient of the nth term and $X = F_0/F_{0(\max)}$, was employed to minimise $\Sigma(F_0 - F_c)$ [4] over all reflections. The coefficients used were 791.49, 1350.07, 854.89, 379.59 and 94.37. After a further four cycles of full matrix, anisotropic least-squares refinement, a final R value of 0.0332 was obtained. Calculations were performed using the CRYSTALS [3] suite of programmes The scattering factors used were those neutral atoms. [4] Final fractional atomic coordinates and anisotropic thermal parameters are listed in Tables 1 and 2, respectively. Intramolecular bond lengths and angles are given in Table 3, and least-squares planes data are collected in Table 4. Fig. 1 shows the molecular geometry and atomic labelling, and a projection of the unit cell onto the bc plane is illustrated in Fig. 2.

(ii) *Bis(β-carbomethoxyethyl)tin dichloride*

A very similar procedure to that above was adopted using a crystal of approximate dimensions 0.3 × 0.3 × 0.4 mm mounted in a Lindemann capillary.

Crystal data: $C_8H_{14}O_4Cl_2Sn$, M = 363.81, Monoclinic, a 8.0107, b 15.9104, c 13.4109 Å, β 131.0044°, V 1289.13 Å^3, Z = 4, $F(000)$ = 712, μ(Mo-K_α) =

TABLE 1

FINAL FRACTIONAL ATOMIC COORDINATES IN β-CARBOMETHOXYETHYLTIN (IV) TRICHLORIDE $Cl_3SnCH_2CH_2CO_2CH_3$

Atom	x/a	y/b	z/c
Sn(1)	0.18463(4)	0.02702(5)	0.22049(4)
Cl(1)	0.4036(2)	0.1007(3)	0.2639(3)
Cl(2)	0.2227(3)	—0.2165(2)	0.2038(3)
Cl(3)	0.1036(2)	0.0558(3)	0.4246(2)
O(1)	—0.0351(5)	—0.0340(6)	0.1707(5)
O(2)	—0.1966(6)	0.0346(7)	0.0435(6)
C(1)	0.1335(7)	0.1821(8)	0.0788(7)
C(2)	0.0038(9)	0.1560(1)	0.0202(8)
C(3)	—0.768(9)	0.0440(1)	0.0855(9)
C(4)	—0.2840(9)	—0.0660(1)	0.1060(1)

Estimated standard deviations in parentheses

$23.96\ cm^{-1}$. Space group $P2_{1/c}$ by systematic absences ($0k0$) for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$).

Cell measurements and data collection: These were carried out as above collecting data up to $\theta = 25°$. Of 3109 reflections measured, those with $I < 3\sigma(I)$ were discarded leaving 2388 for the structure determination. Again corrections were made for Lorentz and polarization effects, but not for absorption.

Structure Determination and Refinement: This structure was also determined using an initial three-dimensional synthesis to locate the tin atom, followed by successive Fourier syntheses to locate the light atoms. Full-matrix, least-squares anisotropic refinement was carried out to an R value of 0.048, when a weighting scheme based on the Chebychev series in $T(n)(X)$ to give terms was used. The coefficients $A(0)$—$A(4)$, calculated to minimise $\Sigma(F_0 - F_c)$ [4] over all reflections used were 162.91, 246.44, 118.66, 42.08 and 14.33. A final R value of 0.046 was obtained after a further three cycles of full-matrix, least-squares anisotropic refinement. All calculations were performed as above. Final fractional

TABLE 2

FINAL ANISOTROPIC THERMAL PARAMETERS FOR β-CARBOMETHOXYETHYL TIN (IV) TRICHLORIDE

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Sn(1)	5.150(20)	5.580(20)	5.730(20)	1.350(20)	0.090(20)	0.00(20)
Cl(1)	5.120(9)	9.90(2)	10.20(2)	0.90(1)	—0.40(1)	—0.50(1)
Cl(2)	9.50(1)	5.80(1)	8.70(1)	1.10(1)	1.30(1)	1.40(1)
Cl(3)	7.10(1)	9.30(1)	5.90(1)	—0.30(1)	8.60(9)	—0.50(1)
O(1)	5.70(2)	6.10(3)	7.60(3)	1.90(3)	—1.60(2)	—0.40(3)
O(2)	6.90(3)	7.50(3)	9.60(4)	—0.60(3)	—3.20(3)	1.70(3)
C(1)	6.70(4)	7.10(4)	8.10(4)	3.20(3)	0.20(3)	0.00(3)
C(2)	8.20(5)	7.30(5)	6.50(4)	1.90(4)	—0.30(4)	1.10(5)
C(3)	5.90(4)	5.60(5)	6.10(5)	—1.10(4)	—0.80(4)	1.40(5)
C(4)	5.70(4)	8.20(6)	14.00(1)	0.40(6)	2.10(5)	0.50(4)

$U(ij)$ are of the form $10^2 \exp[-2\pi^2(h^2U(11)a^{*2} + k^2U(22)b^{*2} + l^2U(33)c^{*2} + 2hkU(12)a^*b^* + 2klU(23)b^*c^* + 2hlU(13)a^*c^*)]$. Standard deviations in parentheses.

TABLE 3

INTRAMOLECULAR BOND LENGTHS (Å) AND ANGLES (b) OF β-CARBOMETHOXYETHYLTIN-(IV) TRICHLORIDE

Bond lengths	
Sn(1)—Cl(1)	2.357(2)
Sn(1)—Cl(2)	2.303(2)
Sn(1)—Cl(3)	2.317(2)
Sn(1)—O(1)	2.347(5)
Sn(1)—C(1)	2.139(8)
C(1)—C(2)	1.47(1)
C(2)—C(3)	1.50(1)
C(3)—O(1)	1.23(1)
C(3)—O(2)	1.29(1)
C(4)—O(2)	1.45(2)
Angles	
Cl(1)—Sn(1)—Cl(2)	98.3(1)
Cl(1)—Sn(1)—Cl(3)	96.7(1)
Cl(2)—Sn(1)—Cl(3)	104.1(1)
Cl(1)—Sn(1)—O(1)	176.7(2)
Cl(1)—Sn(1)—C(1)	99.5(2)
Cl(2)—Sn(1)—O(1)	84.4(2)
Cl(2)—Sn(1)—C(1)	130.5(2)
Cl(3)—Sn(1)—O(1)	84.4(2)
Cl(3)—Sn(1)—C(1)	119.0(2)
O(1)—Sn(1)—C(1)	77.2(3)
Sn(1)—C(1)—C(2)	113.6(6)
C(1)—C(2)—C(3)	113.9(7)
C(2)—C(3)—O(1)	124.3(8)
C(2)—C(3)—O(2)	113.4(7)
O(1)—C(3)—O(2)	122.3(8)
Sn(1)—O(1)—C(3)	110.2(5)
C(3)—O(2)—C(4)	117.1(7)

Estimated standard deviations in parentheses.

TABLE 4

EQUATIONS OF THE MEAN PLANES THROUGH GROUPS OF ATOMS IN β-CARBOMETHOXYETHYL TIN (IV) TRICHLORIDE AND DEVIATIONS OF ATOMS FROM THE PLANES (Å)

PLANE 1. Sn(1), Cl(1), C(1), C(2), C(3), O(1), O(2), C(4).

Equation of the plane:

$3.22384x - 6.20558y - 7.0889z = -1.167$

Sn(1), 0.032; Cl(1), —0.027; C(1), —0.091; C(2), 0.066; C(3), 0.043; O(1), 0.055; O(2), 0.010; C(4), —0.088.

PLANE 2. Sn(1), Cl(2), Cl(3), C(1).

Equation of the plane:

$9.49338x + 2.67305y + 1.88094z = 1.998$

Sn(1), 0.242; Cl(2), —0.079; Cl(3), —0.067; C(1), —0.096.
Angle between plane 1 and plane 2 = 90.64°.

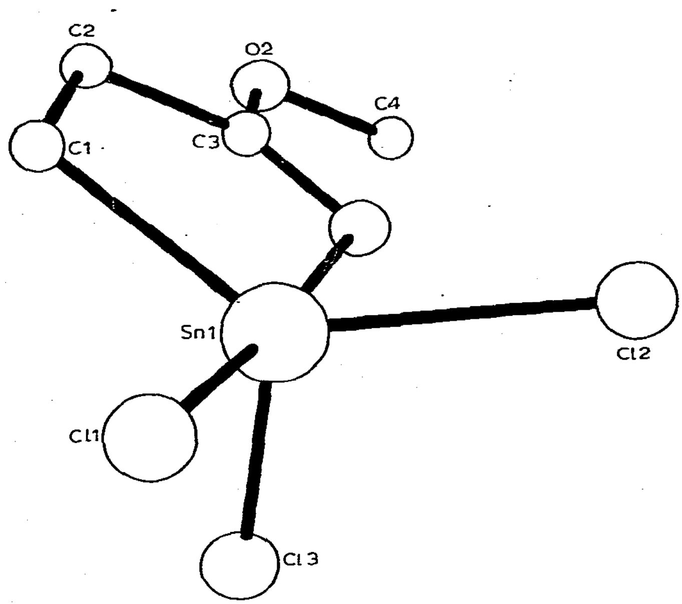

Fig. 1. The molecular structure and atomic labelling in $Cl_3SnCH_2CH_2CO_2Me$.

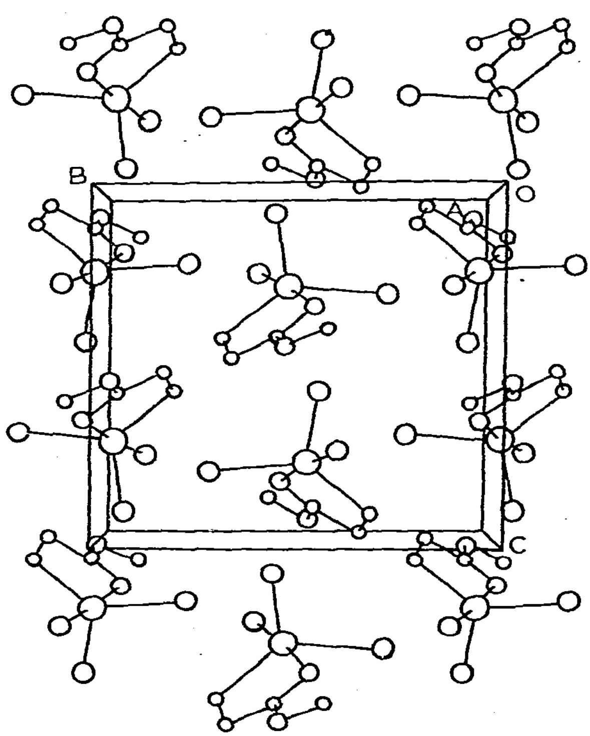

Fig. 2. Projection of the structure of $Cl_3SnCH_2CH_2CO_2Me$ onto the *bc* plane.

TABLE 5

FINAL FRACTIONAL ATOMIC COORDINATES IN BIS-(β-CARBOMETHOXYETHYL) TIN(IV) DICHLORIDE, $Cl_2Sn(CH_2CH_2CO_2CH_3)_2$.

Atom	x/a	y/b	z/c
Sn(1)	0.17179(6)	0.17907(2)	0.18179(3)
Cl(1)	0.4307(3)	0.0989(1)	0.1864(2)
Cl(2)	0.0891(4)	0.2811(1)	0.0220(2)
O(1)	−0.0814(8)	0.2608(3)	0.1960(5)
O(2)	−0.0664(7)	0.3725(3)	0.2985(4)
O(3)	0.229(10)	0.0744(4)	0.3432(7)
O(4)	0.0147(9)	−0.0033(3)	0.3579(6)
C(1)	0.3810(7)	0.2525(3)	0.3566(4)
C(2)	0.2633(7)	0.3302(3)	0.3502(4)
C(3)	0.024(1)	0.3162(4)	0.2760(6)
C(4)	−0.303(10)	0.3636(4)	0.2259(7)
C(5)	−0.108(10)	0.0978(5)	0.0714(7)
C(6)	−0.158(10)	0.0651(4)	0.1567(7)
C(7)	0.0478(9)	0.0462(3)	0.2945(6)
C(8)	0.208(10)	−0.0240(5)	0.4937(8)

Estimated standard deviations in parentheses.

atomic coordinates and anisotropic thermal parameters are listed in Tables 5 and 6, respectively. Intramolecular bond distances and angles are listed in Table 7. The molecular geometry and atomic numbering is shown in Fig. 3, and a projection of the unit cell onto the *bc* plane illustrated in Fig. 4. Planes data are given in Table 8.

(iii) Bis(β-amidoethyl)tin dichloride

The sample of bis(β-amidoethyl)tin dichloride, supplied by Dr. J.W. Burley,

TABLE 6

FINAL ANISOTROPIC THERMAL PARAMETERS FOR BIS-(β-CARBOMETHOXYETHYL) TIN (IV) DICHLORIDE

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Sn(1)	4.90(20)	4.60(20)	4.85(20)	0.14(20)	3.45(20)	0.23(20)
Cl(1)	6.85(9)	8.30(1)	7.80(1)	1.56(9)	5.78(9)	2.42(8)
Cl(2)	10.10(1)	5.12(8)	7.20(1)	1.48(7)	6.30(1)	0.87(8)
O(1)	5.80(2)	6.00(2)	5.90(3)	−1.50(2)	3.90(2)	−0.60(2)
O(2)	7.70(2)	5.60(2)	7.00(2)	−1.20(2)	5.50(2)	−0.50(2)
C(3)	4.90(3)	6.70(4)	5.80(4)	0.70(3)	3.40(3)	−0.60(3)
O(4)	6.10(3)	6.20(3)	6.40(3)	0.60(2)	4.60(3)	−0.40(2)
C(1)	5.70(2)	6.10(2)	5.60(2)	−1.20(2)	2.80(2)	−0.30(2)
C(2)	5.70(2)	6.20(2)	6.60(2)	−2.00(2)	3.90(2)	−1.10(2)
C(3)	6.40(3)	4.80(3)	5.00(3)	−0.10(2)	4.10(3)	0.10(3)
C(4)	6.20(3)	8.80(3)	7.40(4)	−0.20(3)	4.90(3)	0.90(2)
C(5)	5.10(4)	4.50(4)	5.60(4)	−0.30(3)	3.30(3)	−0.30(3)
C(6)	5.20(3)	5.20(4)	7.20(3)	1.00(3)	4.20(3)	0.40(3)
C(7)	5.70(3)	4.00(3)	6.30(3)	0.10(2)	4.50(3)	0.40(3)
C(8)	6.40(4)	7.80(5)	6.30(4)	1.70(4)	4.20(3)	0.70(4)

$U(ij)$ are of the form: $10^2 \exp[-2\pi^2(h^2U(11)a^{\star 2} + k^2U(22)b^{\star 2} + l^2U(33)c^{\star 2} + 2hkU(12)a^{\star}b^{\star} + 2klU(23)b^{\star}c^{\star} + 2hlU(13)a^{\star}b^{\star})]$. Estimated standard deviations in parentheses.

TABLE 7

INTRAMOLECULAR BOND LENGTHS (Å) AND ANGLES (°) OF BIS-(β-CARBOMETHOXYETHYL) TIN (IV) DICHLORIDE

Distances			
Sn(1)—Cl(1)	2.401(2)		
Sn(1)—Cl(2)	2.409(2)		
Sn(1)—C(1)	2.124(6)		
Sn(1)—C(5)	2.127(5)		
Sn(1)—O(1)	2.520(4)		
Sn(1)—O(3)	2.524(4)		
Cl(1)—C(2)	1.523(9)	C(5)—C(6)	1.531(8)
C(2)—C(3)	1.487(9)	C(6)—C(7)	1.491(9)
C(3)—O(1)	1.205(7)	C(7)—O(3)	1.220(7)
C(3)—O(2)	1.306(7)	C(7)—O(4)	1.307(7)
C(4)—O(2)	1.463(8)	C(8)—O(4)	1.457(8)

Angles	
Cl(1)—Sn(1)—O(1)	175.5(1)
Cl(1)—Sn(1)—Cl(2)	96.3(1)
Cl(1)—Sn(1)—C(5)	101.0(2)
Cl(1)—Sn(1)—O(3)	87.7(1)
Cl(1)—Sn(1)—C(1)	102.8(2)
Cl(2)—Sn(1)—C(1)	99.7(2)
Cl(2)—Sn(1)—C(5)	103.9(2)
Cl(2)—Sn(1)—O(3)	175.5(1)
Cl(2)—Sn(1)—O(1)	87.4(1)
O(1)—Sn(1)—C(1)	74.0(2)
O(1)—Sn(1)—C(5)	80.5(2)
O(1)—Sn(1)—O(3)	88.7(2)
O(3)—Sn(1)—C(1)	81.3(2)
O(3)—Sn(1)—C(5)	73.3(2)
C(1)—S(1)—C(5)	144.1(3)
Sn(1)—C(1)—C(2)	111.9(4)
C(1)—C(2)—C(3)	113.3(5)
C(2)—C(3)—O(1)	123.2(5)
C(2)—C(3)—O(2)	114.2(5)
O(1)—C(3)—O(2)	122.5(6)
C(3)—O(2)—C(4)	116.9(5)
Sn(1)—O(1)—C(3)	108.4(4)
Sn(1)—C(5)—C(6)	111.0(4)
C(5)—C(6)—C(7)	112.2(5)
C(6)—C(7)—O(3)	123.2(6)
C(6)—C(7)—O(4)	113.4(4)
O(3)—C(7)—O(4)	123.4(6)
C(7)—O(4)—C(8)	116.5(5)
Sn(1)—O(3)—C(7)	107.5(4)

Estimated Standard deviations in parentheses.

was air-stable (decomp. >260°C. Found: C, 21.49; H, 4.16; N, 8.36; Cl, 21.11%. $C_6H_{12}Cl_2N_2O_2Sn$ calcd.: C, 21.56; H, 3.59; Cl, 21.26%; N, 8.38.), and a suitable crystal (approximate dimensions 0.3 X 0.3 X 0.2 mm) was mounted in a Lindemann capillary.

TABLE 8

EQUATIONS OF THE MEAN PLANES THROUGH GROUPS OF ATOMS IN BIS-(β-CARBOMETHOXY-ETHYL) TIN (IV) DICHLORIDE, AND DEVIATION OF ATOMS FROM THE PLANES (Å)

PLANE 1. Sn(1), Cl(1), C(1), O(3), C(5).

equation of the plane:

$-1.12287x' + 11.87909y' - 5.34819z' = 0.203$

Sn(1), 0.759; Cl(1), —0.508; C(1), 0.461; O(3), —1.411; C(5), 0.698.

PLANE 2. Sn(1), Cl(1), Cl(2), O(3), O(1).

equation of the plane:

$2.87599x' + 8.83637y' + 4.43250z' = 2.887$

Sn(1), —0.005; Cl(1), 0.051; Cl(2), 0.049; O(3), —0.050; O(1), 0.052.

PLANE 3. Sn(1), Cl(2), C(5), O(1), C(1).

equation of the plane:

$4.95338x' - 11.04934y' - 1.71743z' = -2.203$

Sn(1), 0.763; Cl(2), —0.500; C(5), 0.467; O(1), —1.419; C(1), 0.689.

Angle between plane 1 and plane 2 = 97.09°

Angle between plane 1 and plane 3 = 147.61°

Angle between plane 2 and plane 3 = 83.55°

Equations are of the form $px' + qy' + rz' = s$ where x', y' and z' are orthogonal coordinates related to the monoclinic coordinates by: $x' = x + z \cos\beta$, $y' = y$ and $z' = z \sin\beta$ (7)

Crystal data: $C_6H_{12}Cl_2N_2O_2Sn$, $M = 333.89$, Monoclinic, a 9.1314, b 12.8672, c 13.0317 Å, β 126.6032°, V 1229.196 Å^3, $Z = 4$, $F(000) = 648$, μ(Mo-K_α) 24.94 cm^{-1}. Space group C_c by systematic absences (hkl for $h + k = 2n + 1$, $h0l$ for $l = 2n + 1$ ($h = 2n + 1$), $0k0$ for $k = 2n + 1$).

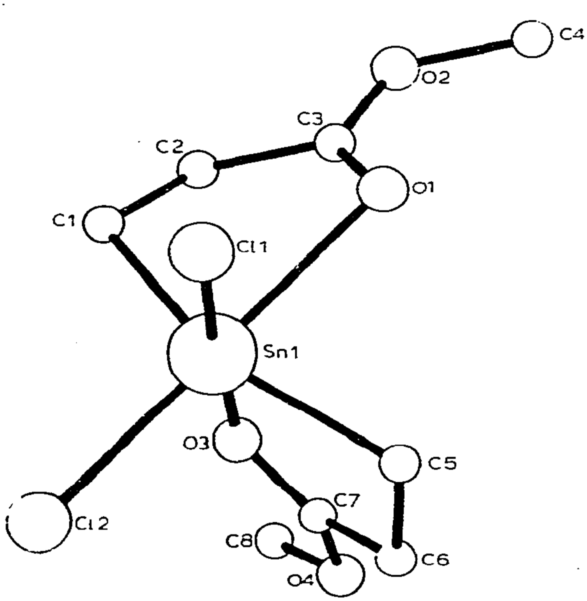

Fig. 3. The molecular structure and atomic labelling in $Cl_2Sn(CH_2CH_2CO_2Me)_2$.

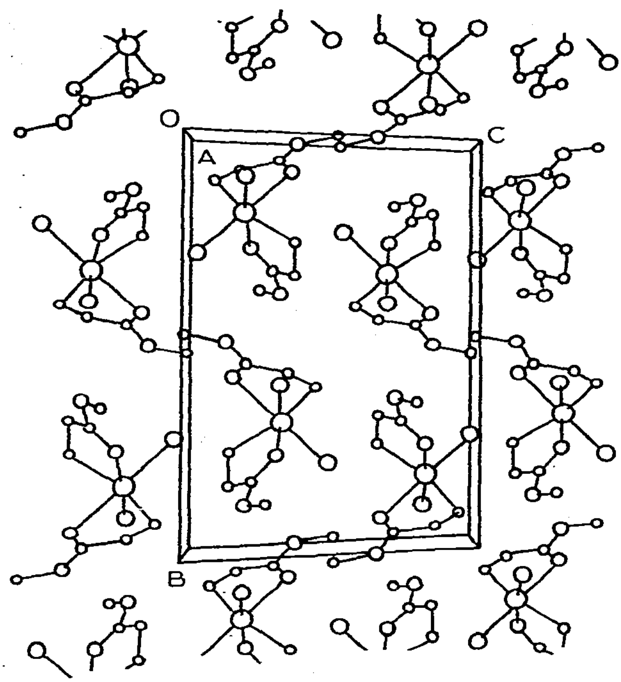

Fig. 4. Projection of the structure of $Cl_2Sn(CH_2CH_2CO_2Me)_2$ onto the *bc* plane.

Cell measurements and data collection: These were performed as before, relative intensities of 1472 independent reflections being collected up to $\theta = 25°$. Those with $I < 3\sigma(I)$ were discarded leaving 1024 for use in the structure determination.

Structure determination and refinement: Again a three dimensional Patterson synthesis was employed to locate the tin atom, and the remaining light atoms were located by successive Fourier syntheses. After full-matrix, least-squares anisotropic refinement, convergence was achieved at an R value of 0.029. The same type of Chebychev series weighting scheme as before (with coefficients 144.84, 219.39, 99.79, 22.75 and 1.86) was then employed, and further full-matrix, least-squares anisotropic refinement resulted in a final R value of 0.0268. Calculations were performed as before. Final fractional atomic coordinates, anisotropic thermal parameters, intramolecular bond distances and angle data, and least-squares planes data are listed in Tables 9—12, respectively. The molecular geometry and atomic numbering is shown in Fig. 5, and the projection of the unit cell onto the *ac* plane illustrated in Fig. 6.

3. *Spectroscopic Measurements*

Tin-119 Mössbauer spectra were collected at 77 K using a Harwell spectrometer calibrated with iron and β-tin foils. Data reduction to Lorentzian line shapes was achieved by usual least-squares methods.

Infrared spectra were recorded using a Perkin—Elmer 577 spectrophotometer. Raman spectra were obtained on a Cary 81 instrument using a He-Ne laser.

Mass spectra were obtained using a MS-902 instrument.

TABLE 9

FINAL FRACTIONAL ATOMIC COORDINATES IN BIS-(β-AMIDOETHYL) TIN (IV) DICHLORIDE, $Cl_2Sn(CH_2CH_2CONH_2)_2$

Atom	x/a	y/b	z/c
Sn(1)	0.0000	0.00672(3)	0.2500
Cl(1)	0.1844(8)	−0.1254(6)	0.4156(7)
Cl(2)	−0.1908(9)	−0.1184(6)	0.0756(8)
N(1)	0.397(2)	0.253(1)	0.436(1)
N(2)	−0.373(3)	0.265(1)	0.065(2)
O(1)	0.171(2)	0.141(1)	0.392(1)
O(2)	−0.170(2)	0.146(2)	0.117(2)
C(1)	0.279(2)	0.1732(9)	0.375(1)
C(2)	0.324(3)	0.123(2)	0.281(2)
C(3)	0.187(2)	0.036(1)	0.214(2)
C(4)	−0.191(3)	0.032(2)	0.297(2)
C(5)	−0.315(3)	0.122(2)	0.212(2)
C(6)	−0.297(3)	0.181(2)	0.127(2)

Standard deviations in parentheses.

TABLE 10

FINAL ANISOTOPIC THERMAL PARAMETERS FOR BIS-(β-AMIDOETHYL) TIN (IV) DICHLORIDE

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Sn(1)	4.60(30)	4.09(30)	5.34(30)	−0.13(90)	3.34(20)	−0.16(80)
Cl(1)	5.7(3)	6.2(3)	9.4(4)	3.7(3)	4.8(3)	2.2(2)
Cl(2)	5.5(3)	8.1(4)	7.1(3)	−2.6(3)	3.2(2)	−0.1(2)
N(1)	5.6(7)	7.7(9)	7.9(8)	−3.8(7)	4.3(7)	−2.0(7)
N(2)	7.0(1)	5.6(8)	1.1(1)	1.0(8)	6.0(1)	2.7(7)
O(1)	4.5(6)	5.3(8)	6.5(7)	−1.5(6)	4.1(6)	−1.5(5)
O(2)	9.0(1)	6.3(9)	9.0(10)	2.1(7)	7.1(9)	2.9(8)
C(1)	5.4(8)	3.1(5)	5.1(7)	−2.0(5)	3.9(7)	−1.9(5)
C(2)	14.0(2)	10.0(1)	9.0(1)	−3.0(1)	8.0(1)	−2.0(1)
C(3)	4.8(7)	5.3(7)	4.5(7)	0.3(5)	2.9(6)	1.8(6)
C(4)	8.0(1)	5.8(9)	10.0(1)	2.5(7)	8.0(1)	3.1(7)
C(6)	3.9(7)	10.0(2)	8.0(1)	−4.0(1)	3.9(8)	−0.3(8)

$U(ij)$ are of the form $10^2 \exp[-2\pi^2(h^2U(11)a^{\star 2} + k^2U(22)b^{\star 2} + l^2U(33)c^{\star 2} + 2hkU(12)a^\star b^\star + 2klU(23)b^\star c^\star + 2hlU(13)a^\star c^\star)]$. Standard deviations in parentheses.

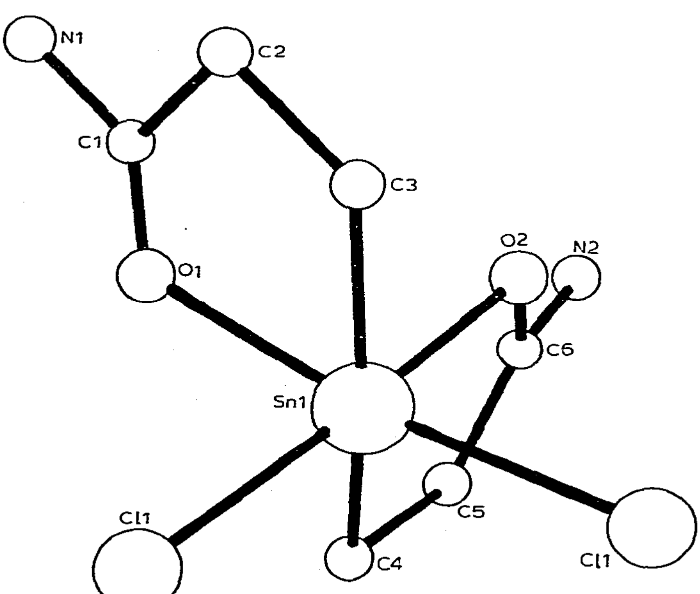

Fig. 5. Molecular structure and atomic labelling in $Cl_2Sn(CH_2CH_2CONH_2)_2$.

TABLE 11

INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLES (DEG.) OF BIS-(β-AMIDOETHYL) TIN (IV) DICHLORIDE

Bond lengths			
Sn(1)—Cl(1)	2.460(7)	N(1)—O(2′) = 3.04(3)	
Sn(1)—Cl(2)	2.464(7)		
Sn(1)—O(1)	2.327(16)		
Sn(1)—O(2)	2.321(18)	N(2′)—O(1) = 2.83(3)	
Sn(1)—C(3)	2.059(17)		
Sn(1)—C(4)	2.190(16)		
C(3)—C(2)	1.52(3)	C(4)—C(5)	1.52(3)
C(2)—C(1)	1.64(3)	C(5)—C(6)	1.43(3)
C(1)—N(1)	1.36(2)	C(6)—N(2)	1.28(3)
C(1)—O(1)	1.21(2)	C(6)—O(2)	1.32(3)

Bond Angles			
Cl(1)—Sn(1)—Cl(2)	95.5(1)		
Cl(1)—Sn(1)—C(3)	95.6(5)	Cl(2)—Sn(1)—C(3)	97.7(6)
Cl(1)—Sn(1)—O(1)	91.8(5)	Cl(2)—Sn(1)—O(1)	171.9(5)
Cl(1)—Sn(1)—O(2)	171.6(5)	Cl(2)—Sn(1)—O(2)	91.4(5)
Cl(1)—Sn(1)—C(4)	95.7(5)	Cl(2)—Sn(1)—C(4)	96.4(6)
C(3)—Sn(1)—O(1)	78.0(6)	C(4)—Sn(1)—O(2)	78.7(6)
C(3)—Sn(1)—O(2)	88.2(6)	C(4)—Sn(1)—O(1)	86.3(6)
Sn(1)—C(3)—C(2)	121(1)	Sn(1)—C(4)—C(5)	106(1)
C(3)—C(2)—C(1)	103(1)	C(4)—C(5)—C(6)	126(1)
C(2)—C(1)—N(1)	106(1)	C(5)—C(6)—N(2)	132(2)
C(2)—C(1)—O(1)	127(1)	C(5)—C(6)—O(2)	114(2)
N(1)—C(1)—O(1)	128(1)	N(2)—C(6)—O(2)	114(2)
C(1)—O(1)—Sn(1)	110(1)	C(6)—O(2)—Sn(1)	115(2)
C(4)—Sn(1)—O(1)	75.6(6)	O(1)—Sn(1)—O(2)	79.8(6)
C(4)—Sn(1)—C(3)	191(1)		

Standard deviations in parentheses.

TABLE 12

EQUATIONS OF THE MEAN PLANES THROUGH GROUPS OF ATOMS IN BIS-(β-AMIDOETHYL) TIN (IV) DICHLORIDE AND DEVIATIONS OF ATOMS FROM THE PLANES (Å)

PLANE 1. Sn(1), Cl(1), O(2), C(6), N(2), C(5), C(4), C(3).

equation of the plane:

$-1.59410x - 8.25039y - 6.46102z = -1.859$

Sn(1), 0.188; Cl(1), —0.085; O(2), 0.171; C(6), 0.022; N(2), —0.155; C(5), —0.013; C(4), —0.018; C(3), —0.114.

PLANE 2. Sn(1), Cl(1), Cl(2), O(1), O(2).

equation of the plane:

$8.81727x + 0.22689y - 10.21725z = -2.563$

Sn(1), 0.010; Cl(1), —0.086; Cl(2), 0.081; O(1), 0.098; O(2), —0.103.

PLANE 3. Sn(1), Cl(2), O(1), C(1), N(1), C(2), C(3), C(4).

equation of the plane:

$-1.83290x + 8.66639y - 5.88257z = -1.230$

Sn(1), —0.183; Cl(2), 0.108; O(1), —0.170; C(1), 0.015; N(1), 0.133; C(2), 0.051; C(3), —0.063; C(4), 0.108.

Angle between Plane 1 and Plane 2 = 89.20°
Angle between Plane 1 and Plane 3 = 82.25°
Angle between Plane 2 and Plane 3 = 89.85°

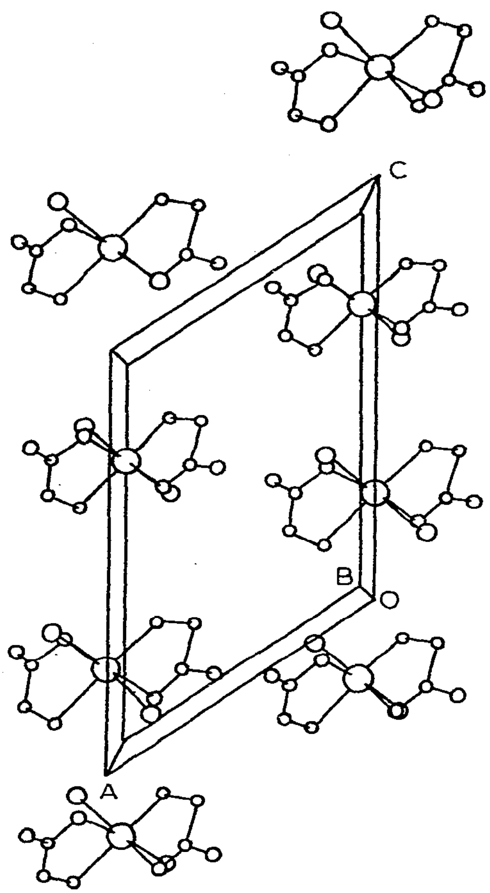

Fig. 6. Projection of the structure of $Cl_2Sn(CH_2CH_2CONH_2)_2$ onto the *ac* plane.

Results and discussion

Structural studies

No crystal structure of an organotin trichloride has yet been reported. β-Carbomethoxyethyltin trichloride, a somewhat less hygroscopic compound than an unsubstituted alkyl or aryltin analogue, contains five-coordinated tin via intramolecular coordination of the carbonyl group (Fig. 1). The geometry at tin is thus distorted trigonal bipyrimidal with the carbonyl oxygen and one chlorine atom occupying the axial positions, whilst the organic residue and the two remaining chlorine atoms are bonded at equatorial sites. Not unexpectedly, the $Sn—Cl_{ax}$ bond distance (2.357(2) Å) is somewhat longer than the $Sn—Cl_{eq}$ distances (2.303(2), 2.317(2) Å). The Sn—C distance is normal (2.129(8) Å), and the coordinate Sn—O bond distance (2.347(5) Å) is quite short, when compared with values of 2.332(6) Å for $Me_3SnCl \cdot (Ph_3PCHCOMe)$ [5] and 2.308(4) Å for $Ph_3Sn{\cdot}ONPh{\cdot}CO{\cdot}Ph$ [6].

Both bis(β-carbomethoxyethyl)tin dichloride and bis(β-amidoethyl)tin dichloride possess distorted octahedral geometries, with both substituted-ethyl ligands functioning as chelating groups (Figs. 3 and 5). In both compounds, the two chlorine atoms occupy *cis* positions, whilst the two carbon atoms are mutually *trans*. The oxygen atoms are therefore in *cis* positions. It is noteworthy that, in the β-amidoethyltin derivatives, of the two possible donor atoms, carbonyl oxygen and amido nitrogen, the oxygen atom is preferred for coordination to tin. Although very similar within each compound, the Sn—Cl bond distances of the amidoethyl derivatives are longer (2.462(7) Å) than those in the carbomethoxyethyl derivative (2.405(2) Å). Both are shorter than those of Ph_2SnCl_2·bipy (2.520(2) Å), [7] but longer than in Et_2SnCl_2 (2.385(3) Å) [8]. In $Cl_2Sn(CH_2CH_2CONH_2)_2$, the Sn—O bond distances are similar (2.324(18) Å) to that in $Cl_3SnCH_2CH_2CO_2Me$ (2.347(5) Å) and $Me_2Sn(ONMeCOMe)_2$ (2.377(5) Å) [9] but longer than in $Me_2Sn(ONHCOMe)_2$ (2.228(4) Å), in which intermolecular hydrogen-bonding occurs [10]. The Sn—O distances in $Cl_2Sn(CH_2CH_2CO_2Me)_2$ are significantly longer (2.522(4) Å) reflecting a considerably weaker coordinate bond. The Sn—C bond distances in $Cl_2Sn(CH_2CH_2CO_2Me)_2$ are slightly shorter (2.126(6) Å) than in Et_2SnCl_2 (2.132(13), 2.167(15) Å) [8], but those in the amidoethyl analogues are quite dissimilar (2.059(17) and 2.190(16) Å).

The bond distances within the carbomethoxyethyl residue of $Cl_3SnCH_2CH_2COMe$ and $Cl_2Sn(CH_2CH_2CO_2Me)_2$ are quite similar, with the C=O distances falling in the range 1.205(7)—1.227(10) Å. The Me—O distances are much longer (1.448(15)—1.463(8) Å) than the C(10)—O distances (1.290(10)—1.307(7) Å).

The distances within the two amidoethyl residues in $Cl_2Sn(CH_2CH_2CONH_2)_2$ are quite dissimilar. In one, the carbonyl distance is short (1.205(20) Å), and the C—N and C(:O)—C distances relatively long (1.355(20) and 1.638(26) Å, respectively). In the other the carbonyl distance is very long (1.321(25) Å), whereas the corresponding C—N and C(:O)—C distances are short (1.277(29) Å and 1.427(30) Å, respectively). The dissimilarity is most probably due to the presence of hydrogen-bonding involving the amide and carbonyl groups, the longer carbonyl and C—N distances being associated with a short (2.827 Å) C : O---H—N hydrogen bond, and the shorter carbonyl and C—N distances with the longer (3.043 Å) C : O---H—N hydrogen bond.

Vibrational spectra

The vibrational spectra of the two β-carbomethoxytin chlorides, $Cl_nSn(CH_2CH_2CO_2Me)_{4-n}$ (n = 2, 3), together with that of methyl acrylate, are listed in Table 13. As expected, the ν(C=C) vibration of the alkene at 1637 cm^{-1} is absent in the two tin derivatives. In addition, the carbonyl stretching band, at 1740 cm^{-1} in methyl acrylate, moves to 1650 cm^{-1} in $Cl_3SnCH_2CH_2CO_2Me$ and 1674 cm^{-1} in $Cl_2Sn(CH_2CH_2CO_2Me)_2$ indicative of carbonyl → tin coordination as shown by the crystallographic studies. The dissimilarity of the strength of these coordinate interactions, shown by the different Sn—O bond distances, is also reflected in the vibrational spectra: the carbonyl band being at much lower energy in the tin trichloride than the dichloride. In $Cl_2Sn(CH_2CH_2CONH_2)_2$, the carbonyl stretching mode occurs at 1651 cm^{-1} (Table 14). Tin—carbon and tin—chlorine stretching modes for all three compounds are also assigned.

TABLE 13

INFRARED AND RAMAN DATA FOR $Cl_3SnCH_2CH_2CO_2CH_3$ AND $Cl_2Sn[CH_2CH_2CO_2CH_3]_2$ (cm^{-1})

CH_2=$CHCO_2CH$ Infrared Liquid film	$Cl_3SnCH_2CO_2CH_3$ Infrared KBr disc	Nujol mull	Raman Solid	$Cl_2Sn[CH_2CH_2CO_2CH_3]_2$ Infrared KBr disc	Nujol mull	Raman Solid	Assignment
3033 (sh)							
3004m	3010w		3012m	3010w		3010m	
2962s	2962m		2966s	2950m		2963s	ν(C—H)
2918w	2930w		2932w	2930w		2930s	
2863w	2872w		2872s	2858w		2870w	
1740s	1650vvs	1650vvs	1652m	1674vs	1674vs	1683m	ν(C=O)
1650 (sh)							
1637m							ν(C=C)
1625 (sh)							
1444s	1448s	1460s	1451m	1442s	1442s	1464m	
1408s	1401m	1401m	1404m	1404m	1404m	1406m	
	1370s	1374s	1376w	1363s	1366s		
1280s	1272s	1272s		1270s	1270s		
1213s	1250 (sh)	1250 (sh)		1228vs	1228vs	1235m	ν(C—O)
1187 (sh)	1188w	1188w		1186m	1186m		
	1134w	1134w	1144m	1155vw	1155vw		
			1126m	1140 (sh)	1140 (sh)	1140w	
			1103m	1132m	1132m	1129m	
1073s	1047w	1047w		1031m	1031m		
992s							
975 (sh)	956m	956m	952w	957m	957m	952w	
				922w	922w		
858m	900w	902w	900m	892w	892w	890m	
817s	746 (sh)	730sh		757m	757m	750w	
668w	700m	704m		694m	694m		
	580vw	578vw	573m	592w	592w	584m	
		546vw	548m	553vw	553vw		ν(Sn—C)
				526vw	526vw		
	468w	470w	468m	467vw	467vw	463m	
	422 (sh)	422vw					
	404s	404s	398m				
	365s	376s		382m	382m	373m	
	350s	350s	345vs				ν(Sn—Cl)
	322s	324s	313vs	310s	310s		
				297vs	297vs	300vvs	
				288 (sh)	288s		
		254m	267w			267w	
			248w	240w	240w	246w	skeletal
						185m (br)	deformation
			138vs			133vs	modes.
			116m			117vs	
			105m				
			75w			77w	

Mass spectra

Mass spectral data for all three compounds are listed in Table 15. Both β-carbomethoxyethyltin derivatives exhibit weak parent ions, and in addition $Cl_3SnCH_2CH_2CO_2Me$ exhibited an unidentified low intensity fragment at $m/e = (P + 8)^+$. The fragmentation patterns of both compounds were similar, the major processes involving tin—carbon and tin—chlorine bond fission, although loss of a

TABLE 14

INFRARED AND RAMAN DATA FOR $Cl_2Sn(CH_2CH_2CONH_2)_2$ (cm^{-1})

CH_2=CHCONH$_2$ Infrared KBr disc	$Cl_2Sn(CH_2CH_2CONH_2)_2$ Infrared KBr disc	Raman Solid	Assignment
	3420s		ν(N—H)
3340vs (br)	3340s	3360m (br)	
3160vs (br)	3280w	3194w (br)	
	2985s	2935	
	2930m (sh)	2958s	ν(C—H)
		2919s	
2800w	2871m		
1660vs (br)	1651vvs	1672w	ν(C=O)
1605vs (br)	1625m		
	1547m		
		1474w	
1425vs	1450m	1438w	
		1428w	
		1409w	
1350s			
1280s	1282m	1297w	
	1266m	1256w	
	1169w		
1137m		1134w	
	1110s	1120s	
1051mw	1067m		
990m	979w		
962m	932w	906vw	
	884w		
841m		852w	
819s	820 (sh)		
	805m		
	775 (sh)		
700m (vbr)	724m	700w (br)	
	683s		
630m (vbr)	650m		
570m	579w	568s	
	537w		ν(Sn—C)
		478s	
	371s	344w	
315m	318vs	312m	ν(Sn—Cl)
		269vvs	
		229w	
		169w (sh)	
		150s	
		112s	
		56vs	
		34s	

(CO_2Me) fragment from the organic ligand leading to $[Cl_nSnCH_2CH_2]^+$ ions, particularly for $Cl_3SnCH_2CH_2CO_2Me$, is observed. Loss of a (MeO) fragment from one organic group in $Cl_2Sn(CH_2CH_2CO_2Me)_2$ also occurs. In both compounds, the most abundant ion is $[Cl_2SnCH_2CH_2COMe]^+$.

The fragmentation pattern of the β-amido-ethyltin derivative, $Cl_2Sn(CH_2CH_2CONH_2)_2$, again involved both tin—chlorine and tin—carbon bond

TABLE 15

MAJOR FRAGMENTS[a] IN THE MASS SPECTRUM OF $Cl_3SnCH_2CH_2CO_2CH_3$, $Cl_2Sn(CH_2CH_2CO_2CH_3)_2$ and $Cl_2Sn(CH_2CH_2CONH_2)_2$

m/e	Relative Intensity[b]	Assignment
$Cl_3SnCH_2CH_2CO_2CH_3$[c]		
319	4.7	
311	1.4	$Cl_3SnCH_2CH_2CO_2CH_3^+$
276	100.00	$Cl_2SnCH_2CH_2CO_2CH_3$
252	29.5	$Cl_3SnCH_2CH_2^+$
224	38.6	$SnCl_3^+$
217	14.0	$Cl_2SnCH_2CH_2^+$
189	26.6	$SnCl_2^+$
154	97.0	$SnCl^+$
147	24.2	$SnCH_2CH_2^+$
119	35.4	Sn^+
$Cl_2Sn(CH_2CH_2CO_2CH_3)_2$[d]		
363	1.5	$Cl_2Sn(CH_2CH_2CO_2CH_3)_2^+$
328	23.3	$ClSn(CH_2CH_2CO_2CH_3)_2^+$
297	1.4	$ClSn(CH_2CH_2CO_2CH_3)CH_2CH_2CO^+$
276	100.00	$Cl_2SnCH_2CH_2CO_2CH_3$
241	8.2	$ClSnCH_2CH_2CO_2CH_3^+$
219	4.1	
206	16.4	$SnCH_2CH_2CO_2CH_3^+$
186	8.2	$ClSnCH_2CH_2$
154	27.4	$SnCl^+$
119	10.9	Sn^+
$Cl_2Sn(CH_2CH_2CONH_2)_2$[e]		
333	0.37	$Cl_2Sn(CH_2CH_2CONH_2)_2^+$
299	29.63	$ClSn(CH_2CH_2CONH_2)(CH_2CH_2CONH_3)^+$
280	92.50	$ClSn(CH_2CH_2CONH_2)CH_2CH_2CN^+$
261	48.10	$Cl_2Sn(CH_2CH_2CONH_2)^+$
243	5.53	$Cl_2Sn(CH_2CH_2CN)$
226	20.46	$ClSn(CH_2CH_2CONH_2)^+$
208	7.48	$ClSn(CH_2CH_2CN)^+$
191	46.30	$Sn(CH_2CH_2CONH_2)^+$
154	100.00	$ClSn^+$
135	33.34	SnO^+
119	20.37	Sn^+

[a] Based on ^{119}Sn and ^{35}Cl. [b] Relative to the most intense tin containing fragment. [c] Spectrum obtained by direct injection at 130°C. [d] Spectrum obtained by direct injection at 190°C. [e] Spectrum obtained by direct injection at 190°C.

fission as major processes, although dehydration of the amidoethyl group to afford cyanoethyltin ions was also important.

Tin-119m Mössbauer Data

Tin-119*m* Mössbauer data for the three compounds under study as well as for several β-carbobutoxytin derivatives are listed in Table 16. All the spectra consisted of quadrupole split doublets. The I.S. and Q.S. for $BuAcSnCl_3$ and $(BuAc)_2SnCl_2$ are, not unexpectedly, similar to those of $Cl_3SnCH_2CH_2CO_2Me$ and $Cl_2Sn(CH_2CH_2CO_2Me)_2$ respectively, indicating a general structural similarity. The amidoethyltin compound, $Cl_2Sn(CH_2CH_2CONH_2)_2$, exhibits a lower I.S. and

TABLE 16

TIN-119*m* MOSSBAUER DATA FOR CARBONYL-SUBSTITUTED-ETHYLTIN COMPOUNDS

Compound [a]	I.S. [bc]	Q.S. [c]	Γ_1 [cd]	Γ_2 [c]	I_1/I_2
$MeAcSnCl_3$	1.00	2.18	1.01	1.01	1.01
$BuAcSnCl_3$	1.11	2.06	1.12	1.07	1.05
$BuAcSnCl_2(IOTG)$	1.26	2.68	0.95	1.02	1.02
$BuAcSnCl(IOTG)_2$	1.33	2.45	1.03	0.98	1.01
$BuAcSn(IOTG)_3$	1.39	1.64	0.89	0.89	1.00
$BuAcSnCl_2(\beta MeOct)$	1.26	2.32	1.00	1.12	1.01
$BuAcSnCl(\beta MeOct)_2$	1.30	2.15	1.08	1.02	0.99
$BuAcSn(\beta MeOct)_3$	1.38	1.48	0.98	0.87	0.98
$MeAc_2SnCl_2$	1.50	3.45	0.94	0.94	1.00
$BuAc_2SnCl_2$	1.45	3.44	1.06	1.01	1.02
$BuAc_2Sn(IOTG)_2$	1.48	2.16	0.87	0.87	0.99
$Bu_2Sn(IOTG)_2$	1.46	2.31	0.91	0.91	1.01
$AmAc_2SnCl_2$	1.39	3.71	0.90	0.90	0.98

[a] MeAc = $MeO{\cdot}C(:O){\cdot}CH_2CH_2$—; BuAc = $BuO{\cdot}C(:O){\cdot}CH_2CH_2$—; AmAc = $H_2N{\cdot}C(:O){\cdot}CH_2CH_2$—; IOTG = *iso*-octythioglycollate; βMeOct = $SCH_2CH_2OCOC_7H_{15}$. [b] Relative to $CaSnO_3$ = O. [c] Mm s^{-1}. [d] The subscripts 1 and 2 refer to the lower and higher velocity lines, respectively.

a higher Q.S. than $Cl_2Sn(CH_2CH_2CO_2Me)_2$ as a consequence of both the significantly shorter Sn—O bond distances and lower distortion from linearity of the C—Sn—C unit in the former.

As chlorine atoms are successively replaced by sulphur (IOTG and βMeOct) ligands, the isomer shift progressively increases. However, the quadrupole splitting at first increases and then decreases, the final low value of the quadrupole splitting for $BuAcSn(IOTG)_3$ (1.64 mm^{-1}) and $BuAcSn(\beta MeOct)_3$ (1.48 mm^{-1}) suggesting a four-coordinated structure for both. The isomer shifts of $BuAc_2SnCl_2$, $BuAc_2Sn(IOTG)_2$ and $Bu_2Sn(IOTG)_2$ are very similar, but the quadrupole splittings of the two latter compounds are much lower than of $BuAc_2SnCl_2$ (3.44 mm^{-1}). The close similarity of the data for the two IOTG derivatives strongly suggests that both possess similar structures, most probably tetrahedral.

The different isomer shift and quadrupole splitting value for the compounds demonstrates that each should be identifiable when present in a PVC matrix. In order to test this hypothesis, we have attempted to record spectra from PVC samples containing 1—2 per cent of various thiolatotin additives as stabilisers. PVC samples with three different organotin additives were investigated: Bu_2Sn-$(IOTG)_2$, $BuAcSn(IOTG)_3$, and $BuAcSn(\beta MeOct)_3$. Thermally degraded as well as freshly milled samples were studied. Although doublet spectra could be detected for all samples, several could not be quantified due to the weakness of the Mössbauer source. Several of the samples did, nevertheless, yield useful results, and a typical such spectrum is illustrated in Fig. 7. Although the signal-to-noise ratio in this spectrum is not particularly satisfactory, it does demonstrate that useful spectra can be recorded from PVC samples and the structure of the tin species present investigated, thus providing an insight into the mechanism of stabilisation. The useful data obtained are listed in Table 17, together with comparative data.

The isomer shift of freshly-milled $BuSn(IOTG)_2$-PVC was unchanged from that

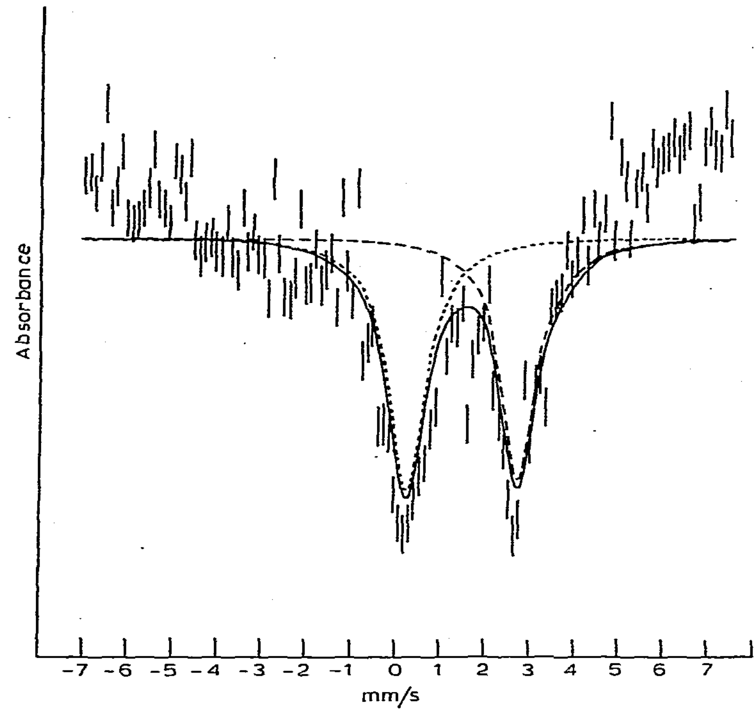

Fig. 7. Tin-119 Mössbauer spectrum of $Bu_2Sn(IOTG)_2$ in PVC.

of neat $Bu_2Sn(IOTG)_2$, although the quadrupole splitting increased somewhat (from 2.31 to 2.48 mm^{-1}). This would suggest that, in the freshly-milled PVC, only part of the available IOTG groups have been exchanged for chlorine, and the organotin species present is most probably $Bu_2SnCl(IOTG)$. Thermal degradation, however, substantially increases both the I.S. and the Q.S. to values which are close to those of Bu_2SnCl_2. At this stage, therefore, complete IOTG-for-chlorine exchange has taken place. Both the freshly-milled samples of BuAcSn-

TABLE 17

TIN-119*m* MOSSBAUER DATA FOR ORGANOTIN-STABILISED PVC SAMPLES TOGETHER WITH COMPARATIVE DATA

Sample	I.S. [a,b]	Q.S. [a]
PVC — $Bu_2Sn(IOTG)_2$		
— Freshly milled	1.48	2.48
— Thermally degraded	1.58	3.14
PVC — $BuAcSn(IOTG)_3$		
— Freshly milled	1.1	2.0
PVC — $BuAcSn(\beta MeOct)_3$		
— Freshly milled	1.09	1.98
— Thermally degraded	1.0	1.0
Bu_2SnCl_2 [c]	1.60	3.25

[a] Mm s^{-1}. [b] Relative to $CaSnO_3$ = O. [c] ref. 11.

$(IOTG)_3$-PVC and BuAcSn(βMeOct)$_3$-PVC exhibited spectra identical to that of $BuAcSnCl_3$, showing that, in these cases, complete sulphur for chlorine ligand exchange takes place in the milling process. The spectra from the thermally degraded samples were generally of lower quality, but no tin(II) species could be detected. The Q.S. values for the degraded samples was much lower ($\simeq$1.0 mm^{-1}) than that of the freshly-milled samples suggesting further degradation, possibly to mono-alkyltin oxides or sulphides.

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