Synthesis and Characterization of Tin(IV) and Organotin(IV) 1,4-Dimethylpiperazine-2,5-dione (Cyclosarcosylsarcosine) Adducts†

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The complexes [{$SnCl_4(L)$}$_n$] **1**, ($SnBuCl_3(L)_2$] **2** and [{$SnR_2Cl_2(L)$}$_n$] (R = Me **3** or Ph **4**) [L = cyclosarcosylsarcosine (1,4-dimethylpiperazine-2,5-dione)] have been prepared and structurally characterized in the solid state by means of ^{119}Sn Mössbauer spectroscopy, the determination of lattice dynamics by temperature-dependent ^{119}Sn Mössbauer spectroscopy and by vibrational studies. The structure of complex **4** has been determined by X-ray crystallography and consists of infinite zigzag polymeric chains of *trans*-diphenyltin(IV) bridged by ketonic oxygen atoms. Each tin(IV) atom is surrounded by two carbons [Sn–C 2.129(7), 2.146(8) Å; C–Sn–C 160.1(3)°], two chlorides [Sn–Cl 2.450(2) Å, Cl–Sn–Cl 98.5(1)°] and two oxygen atoms [Sn–O 2.370(6), 2.468(6) Å; O–Sn–O 86.1(2)°]. Tin-119 Mössbauer and vibrational data are discussed in terms of the crystal structure and the proposed structures. From the variable-temperature Mössbauer effect, the Debye temperatures for **1**–**4** were determined to be 144, 102, 128 and 123 K respectively.

Octahedral tin(IV) complexes are potential anti-tumour and -viral agents[1] and a number have been shown to be active. Six-co-ordination in organotin(IV) chemistry is widely observed in mono- and di-organotin(IV) compounds, but less so in tri-organotin(IV) derivatives, which possess diminished acceptor strengths.[2] Diorganotin(IV) derivatives appear to be the most active.[3] The mechanism of the activity of these complexes requires an understanding of their structure and isomerism. In attempts to correlate the anti-tumour activity with structure, it has been generally assumed that the organic ligand would facilitate the transport of the complex across cell membranes, while the anti-tumour activity would be exerted by the dissociated diorganotin(IV) moieties.[4]

The interaction of metal cations and cyclic peptides is closely related to the activities of cyclic peptide antibiotics and are of great relevance to the understanding of the transport mechanism of metal cations through a biological membrane by complexation. The simplest cyclic peptide cyclosarcosylsarcosine or 1,4-dimethylpiperazine-2,5-dione (L) forms complexes with metal cations such as copper, lithium, barium and silver.[5] An ill defined adduct of $SnCl_4$ with the related 3,6-diisobutylpiperazine-2,5-dione has also been reported.[5] Special types of bis(2,6-dioxopiperazine) compounds have been extensively researched and successfully applied as anti-tumour, anti-metastatic and cardioprotective agents.[6]

Continuing our interest in the area of tin and organotin heterocyclic compounds and interactions in biological molecules,[7] adducts of $SnCl_4$, $SnBuCl_3$ and SnR_2Cl_2 (R = Me or Ph) with 1,4-dimethylpiperazine-2,5-dione have been isolated and characterized by variable-temperature Mössbauer and IR spectroscopies. The crystal structure of the polymer [{$SnPh_2Cl_2(L)$}$_n$] is also reported. To the best of our knowledge there have been no previous structural reports on ($SnPh_2Cl_2O_2$)$_n$ complexes.

Experimental

Tin(IV) chloride and the organotin compounds were purchased from Aldrich and Fluka and used without further purification. Solvents were purified by the usual methods. Physical and characterization measurements were carried out by published procedures.[7–9] Mössbauer spectra were collected between 20 and 293 K using a constant acceleration spectrometer and $BaSnO_3$ source at room temperature. The spectrometer was calibrated with a natural iron foil at room temperature using a ^{57}Co–Rh source. Measurements below room temperature were obtained using a Displex 202 closed cycle refrigerator system. The temperature control was better than ± 1 K. Spectra were fitted using Lorentzian lines by a least-squares minimization program. The C, H and N analyses were performed by the Microanalytical service of the University of Padova. Melting points listed are uncorrected. Melting points and microanalytical data are given in Table 1.

Preparation.—[{$SnCl_4(L)$}$_n$] **1**. To a solution of L (0.484 g, 3.4 mmol) in benzene (25 cm^3) was added $SnCl_4$ (0.443 cm^3, 1.7 mmol) and the reaction mixture refluxed for 3 h under a Dean–Stark trap. The solution was cooled and the resulting white solid filtered off, washed with dry benzene and recrystallized from benzene. The final product was dried *in vacuo* over silica gel and redried at 80 °C for 1 h *in vacuo* over P_4O_{10}. Yield 93%.

[$SnBuCl_3(L)_2$] **2**. To a solution of L (0.341 g, 2.4 mmol) in benzene (25 cm^3) and dimethylformamide (dmf), (10 cm^3) was added $SnBuCl_3$ (0.667 g, 2.4 mmol). The reaction mixture was heated gently for 12 h under a Dean–Stark trap. The clear solution was rotatory evaporated to a small volume, chilled and triturated with diethyl ether to give a white solid. This was filtered off and washed with diethyl ether and dried as before. Yield 81%.

[{$SnMe_2Cl_2(L)$}$_n$] **3**. To a solution of L (0.362 g, 2.5 mmol) in benzene (30 cm^3) was added $SnMe_2Cl_2$ (0.64 g, 2.5 mmol). The reaction mixture was heated gently for 12 h under a Dean–Stark

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Elemental analyses, melting points and molar conductivity data for tin complexes

Compound	Analysis[a] (%) C	H	N	Sn	Cl	M.p./°C	Λ_M[b]/S cm^2 mol^{-1}
[{SnCl$_4$(L)}$_n$]	18.10 (17.90)	2.70 (2.50)	7.00 (6.95)	29.50 (29.50)	35.40 (35.20)	261	8.5
[SnBuCl$_3$(L)$_2$]	31.95 (31.90)	5.05 (4.85)	8.85 (9.30)	20.80 (21.00)	19.10 (18.80)	74	8.0
[{SnMe$_2$Cl$_2$(L)}$_n$]	26.50 (26.55)	4.60 (4.45)	7.75 (7.75)	33.05 (32.80)	19.55 (19.60)	145	6.6
[{SnPh$_2$Cl$_2$(L)}$_n$]	44.35 (44.50)	4.35 (4.15)	5.75 (5.75)	24.25 (24.40)	14.70 (14.60)	179	6.4

[a] Calculated values in parentheses. [b] Values of molar conductance for *ca.* 10^{-3} mol dm^{-3} solutions in dmf at 25 °C.

Table 2 Summary of crystal and intensity collection data

Formula	$C_{18}H_{20}Cl_2N_2O_2Sn$
M	485.97
a/Å	18.540(1)
b/Å	13.7243(7)
c/Å	15.2431(8)
U/Å^3	3878.54
Z	8
D_c/Mg m^{-3}	1.664
D_m/Mg m^{-3}	1.65
Space group	*Pbca*
Crystal dimensions/mm	0.07 × 0.24 × 0.29
λ(Mo-Kα)/Å	0.71073
μ/cm^{-1}	14.75
Max. absorption correction factor	1.19
Data collected	4268
Data unique	3814
Data used [3σ(F_o)]	2587
Range of h	0–22
Range of k	0–16
Range of l	−18 to 0
Weighting	Unit weights
F(000)	1396
No. of refined parameters	287
$\lvert\Delta/\sigma\rvert_{max}$	0.030
$\Delta\rho_{max}$/e Å^{-3}	0.601
$\Delta\rho_{min}$/e Å^{-3}	−0.564
Goodness of fit	3.96
R (observed)	0.0435
R (all data)	0.0812
R' (observed)	0.0487
R' (all data)	0.0781

Goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N - P)]^{\frac{1}{2}}$, P = number of parameters, N = number of observed reflections; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 3 Positional parameters (× 10^4) of the non-H atoms with estimated standard deviations in parentheses

Atom	x	y	z
Sn	1653.2(3)	1671.2(4)	1817.8(3)
Cl(1)	1700(2)	3085(2)	2798(1)
Cl(2)	710(1)	2249(2)	819(2)
C(1)	977(4)	782(6)	2613(5)
C(2)	547(4)	1217(7)	3255(6)
C(3)	133(5)	656(9)	3821(6)
C(4)	134(5)	−326(8)	3746(6)
C(5)	545(5)	−774(8)	3129(6)
C(6)	972(5)	−213(6)	2561(6)
C(7)	2557(4)	2118(6)	1036(5)
C(8)	3191(5)	2428(6)	1427(6)
C(9)	3789(5)	2651(6)	902(7)
C(10)	3756(5)	2535(7)	8(6)
C(11)	3125(5)	2269(6)	−382(6)
C(12)	2512(5)	2065(6)	125(5)
O(1)	2630(3)	942(5)	2700(3)
O(2)	3285(3)	−239(4)	5951(3)
N(1)	3469(3)	431(4)	3666(4)
N(2)	2446(3)	312(5)	5013(4)
C(13)	3666(4)	22(7)	4509(6)
C(14)	3105(4)	20(5)	5201(5)
C(15)	2210(4)	540(7)	4117(5)
C(16)	2798(4)	646(5)	3451(5)
C(17)	4048(5)	540(8)	3021(6)
C(18)	1874(5)	324(7)	5678(5)

trap. The same procedure as in preparation **1** was then repeated. Yield 84%.

[{SnPh$_2$Cl$_2$(L)}$_n$] **4**. Equimolar quantities of L (0.265 g, 1.9 mmol) and SnPh$_2$Cl$_2$ (0.64 g, 1.9 mmol) were dissolved separately in ethanol (25 cm^3) and then mixed. The reaction solution was stirred for 12 h at 35 °C and the resulting white solid filtered off, washed with ethanol and dried as before. Yield 48%.

Crystals of [{SnPh$_2$Cl$_2$(L)}$_n$] suitable for crystal-structure analysis were obtained by slow evaporation of a concentrated solution of the complex in tetrahydrofuran (thf).

Crystal-structure Determination of Complex **4**.—A white prismatic crystal with approximate dimensions 0.07 × 0.24 × 0.29 mm was mounted in air. Measurements were made on a P2 Nicolet diffractometer upgraded by Crystal Logic using zirconium-filtered Mo-Kα radiation. Unit-cell dimensions were determined and refined using the angular settings of 21 automatically centred reflections in the range 11 < 2θ < 21°. Intensity data were recorded using a 2θ scan to $2\theta_{max}$ = 52° with scan speed 3.0 ° min^{-1} and scan range 2.3° plus $\alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and absorption corrections were applied using Crystal Logic software.

Symmetry equivalent data were averaged to give 3814 independent reflections from a total of 4268 collected. The structure was solved by direct methods using SHELXS 86 and refined by full-matrix least-squares techniques with SHELX 76[10] using 2587 reflections with $F > 3\sigma(F)$ and 287 refined parameters. All hydrogen atoms (except those of the methyl groups) were located by difference maps and their positions refined isotropically. All non-hydrogen atoms were refined anisotropically.

The maximum and minimum residual peaks in the final difference map were 0.601 and −0.564 e Å^3. The largest shift/e.s.d. in the final cycle was 0.030.

Other details are given in Table 2. Non-hydrogen atomic coordinates and bond lengths and angles are given in Tables 3 and 4, respectively

Table 4 Bond distances (Å) and angles (°)

Sn–Cl(1)	2.450(2)	C(8)–C(9)	1.40(1)
Sn–Cl(2)	2.450(2)	C(9)–C(10)	1.37(1)
Sn–C(1)	2.129(7)	C(10)–C(11)	1.36(1)
Sn–C(7)	2.146(8)	C(11)–C(12)	1.40(1)
Sn–O(1)	2.468(6)	O(1)–C(16)	1.254(9)
Sn–O(2)	2.370(6)	O(2)–C(14)	1.243(8)
C(1)–C(2)	1.40(1)	N(1)–C(13)	1.45(1)
C(1)–C(6)	1.37(1)	N(1)–C(16)	1.320(9)
C(2)–C(3)	1.39(1)	N(1)–C(17)	1.46(1)
C(3)–C(4)	1.35(1)	N(2)–C(14)	1.319(9)
C(4)–C(5)	1.36(1)	N(2)–C(15)	1.467(9)
C(5)–C(6)	1.40(1)	N(2)–C(18)	1.47(1)
C(7)–C(8)	1.38(1)	C(13)–C(14)	1.48(1)
C(7)–C(12)	1.39(1)	C(15)–C(16)	1.50(1)
Cl(1)–Sn–Cl(2)	98.5(1)	C(8)–C(7)–C(12)	119.8(8)
Cl(1)–Sn–C(1)	97.3(2)	C(7)–C(8)–C(9)	119.5(8)
Cl(2)–Sn–C(1)	96.8(2)	C(8)–C(9)–C(10)	120.4(9)
Cl(1)–Sn–C(7)	94.9(2)	C(9)–C(10)–C(11)	120.1(8)
Cl(2)–Sn–C(7)	96.9(2)	C(10)–C(11)–C(12)	120.7(8)
C(1)–Sn–C(7)	160.1(3)	C(7)–C(12)–C(11)	119.2(9)
Cl(1)–Sn–O(1)	87.8(2)	Sn–O(1)–C(16)	144.2(5)
Cl(2)–Sn–O(1)	173.5(2)	C(13)–N(1)–C(16)	123.0(6)
C(1)–Sn–O(1)	83.7(2)	C(13)–N(1)–C(17)	116.8(6)
C(7)–Sn–O(1)	81.1(2)	C(16)–N(1)–C(17)	120.2(6)
Cl(1)–Sn–O(2)	173.9(2)	C(14)–N(2)–C(15)	122.9(6)
C(1)–Sn–O(2)	82.5(2)	Cl(2)–Sn–O(2)	87.5(2)
O(1)–Sn–O(2)	86.1(2)	C(7)–Sn–O(2)	83.7(2)
Sn–C(1)–C(2)	119.3(6)	C(14)–N(2)–C(18)	121.5(6)
Sn–C(1)–C(6)	122.9(6)	C(15)–N(2)–C(18)	115.2(6)
C(2)–C(1)–C(6)	117.7(8)	N(1)–C(13)–C(14)	117.1(7)
C(1)–C(2)–C(3)	120.9(9)	O(2)–C(14)–N(2)	122.5(7)
C(2)–C(3)–C(4)	120.0(9)	O(2)–C(14)–C(13)	117.8(7)
C(3)–C(4)–C(5)	120.6(9)	N(2)–C(14)–C(13)	119.7(7)
C(4)–C(5)–C(6)	119.8(9)	N(2)–C(15)–C(16)	115.8(7)
C(1)–C(6)–C(5)	121.0(9)	O(1)–C(16)–N(1)	122.2(7)
Sn–C(7)–C(8)	120.8(6)	O(1)–C(16)–C(15)	118.0(7)
Sn–C(7)–C(12)	119.4(7)	N(1)–C(16)–C(15)	119.8(6)

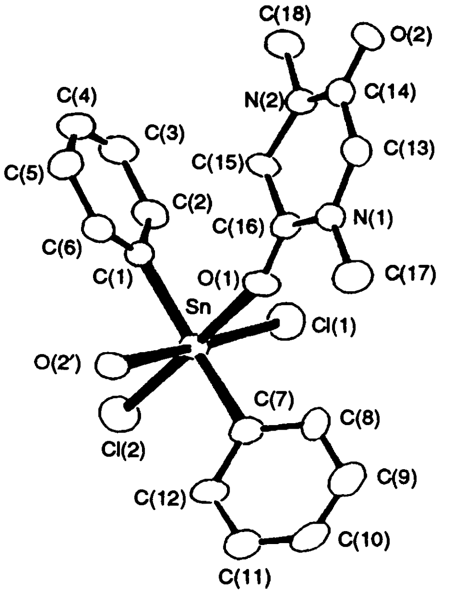

Fig. 1 Structure of [{SnPh$_2$Cl$_2$(L)}$_n$] **4**, showing the atomic labelling scheme

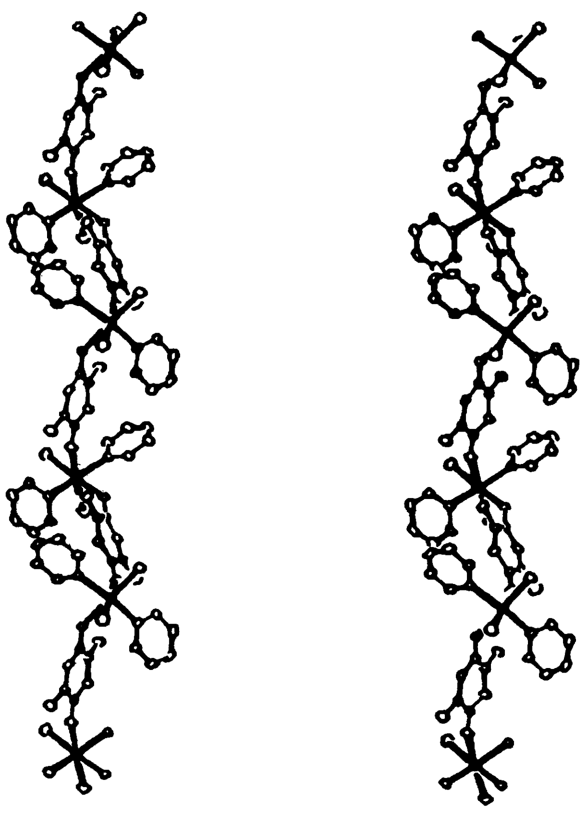

Fig. 2 Structure of the polymeric infinite chain

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

The tin adducts **1**–**4** are prepared by direct reaction between the starting materials in protic or aprotic solvents or solvent mixtures and at ratios in the range 1:1–1:2. It is noteworthy that L reacts in a different manner with $SnCl_4$, SnR_2Cl_2 (R = Me or Ph) and $SnBuCl_3$ to give 1:1 and 1:2 adducts respectively. No complexes with the deprotonated form of the ligand could be obtained. All the attempts (reaction in pH 7 media or reaction with the organotin oxide) met with failure. Failure to isolate triorganotin adducts of L can be explained by the diminished acceptor strength of SnR_3X.

Structure of [{SnPh$_2$Cl$_2$(L)}$_n$] **4**.—The atom labelling scheme and polymeric nature of the structure of compound **4** are shown in Figs. 1 and 2 respectively. The tin atoms are surrounded by two *trans*-phenyl groups, two *cis* rings (L) and two *cis*-chlorine atoms in a distorted-octahedral arrangement. The octahedra form infinite chains and the crystalline structure is built up by packing these one-dimensional chains in a parallel fashion with no intermolecular bonding between adjacent chains. The polymeric chains are generated by bridging L molecules. The ligand bridges two Sn^{IV}Ph$_2$ centres with different bond strengths indicating that the two oxygens O(1) and O(2) are inequivalent.

The co-ordination polyhedron is distorted as the C–Sn–C bond angle is 160.1(3)° and the two Cl–Sn–O bond angles are 173.5(2) and 173.9(2)° respectively. Steric and electronic factors may be responsible for the major bond angle deviations. In the base plane the Cl–Sn–Cl bond angle [98.5(1)°] is larger (up to 12°) than the corresponding Cl(1)–Sn–O(1) [87.8(2)°] and O(1)–Sn–O(2) [86.1(2)°] angles.

The Sn–O bond lengths are 2.370(6) and 2.468(6) Å compared to the sum of the covalent bond radii of tin and oxygen of 2.06 Å, although a value of 1.940(1) Å has been determined for $(SnMe_3)_2O$.[11] Intramolecular Sn···O bond distances in the range 2.263(6)–3.071(2) Å have been reported to indicate Sn–O bonding.[12] The two Sn–Cl bonds are equivalent and significantly shorter than the corresponding values of *ca.* 2.60 Å found in many octahedral Sn^{IV} complexes.[13]

A comparison of selected molecular dimensions in compound **4** with those in related compounds is given in Table 5. The Sn–C bond lengths are, however, comparable to reported Sn–C bond lengths and are longer than the corresponding Sn–C(Me) and Sn–C(Bu) distances in compound **5** [2.101(5), 2.103(5) Å] and in **6** [2.05(1), 2.13(1) Å]. The Sn–Cl distance in compound **4** [2.450(2) Å] is marginally shorter than the corresponding distance in **5** [2.485(1), 2.496(9) Å], and, in conjunction with the lengthening of the Sn–C bond in the phenyl derivative, reflects a decrease in the 5s content of the Sn–C(Ph) bonds over the Sn–Cl bonds. This is reflected not only in the decrease in the C–Sn–C angle from 166.6(2)° in **5** to 160.1(3)° in **4**, but also in a decrease in the isomer shifts (i.s.) parameter from 1.64 mm s^{-1} for **5** to 1.29 mm s^{-1} for **4**.[9] Another factor should also contribute to the difference in the i.s. values, *i.e.*, the positive inductive effect of the phenyl group compared to the negative inductive effect of the methyl group.

The bond lengths in the ring of L indicate a delocalization of electron density over the N–C bonds. The N(2)–C(14) bond length [1.319(9) Å] is close to the aromatic N–C bond length [1.340(1) Å] in pyridine;[14] C(15)–N(2) and C(15)–C(16) distances are close to a single bond. The difference in the strengths of the Sn–O(1) and Sn–O(2) bonds is reflected in the corresponding C(16)–O(1) [1.254(9) Å] and C(14)–O(2) [1.243(8) Å] bond distances. Some of the charge on the C=O double bond is transfered to the Sn–O bond.

Cunningham *et al.*[15] determined the crystal structure of a pyrazine (pyz)-polymer similar to **4**, [$\{SnPh_2Cl_2(pyz)\}_n$] (*trans*-Ph_2, *cis*-Cl_2 and *cis*- N_2), which develops through very weak *cis*-N–C–N bonds and shows major bond angle deviations with respect to ideal octahedral geometry [C–Sn–C 137.7(2), N–Sn–N 117.9(3)°]. Their complex crystallizes together with the binuclear five-co-ordinated tin complex [$(SnPh_2Cl_2)_2(pyz)$]. A previous structure report of a $(SnMe_2Cl_2O_2)_n$ complex was made by Randaccio.[16] The one-dimensional polymeric chain in all *trans* [$\{SnMe_2Cl_2(H_2salen)\}_n$] contains *N,N'*-ethylenebis(salicylideneimine) (H_2salen) acting as a bridge between linear (*trans*) dimethyltin units.

Table 5 Comparison of selected molecular dimensions of **4** with those of [$SnMe_2Cl_2(L'')_2$] **5** and [$SnBu_2Cl_2(L'')_2$] **6** (ref. 9)*

Bond distances (Å)	**4**	**5**	**6**
Sn–C	2.129(7)	2.101(5)	2.05(1)
	2.146(8)	2.103(5)	2.13(1)
Sn–O	2.370(6)	2.401(2)	2.497(6)
	2.468(6)	2.434(2)	2.527(7)
Sn–Cl	2.450(2)	2.485(1)	2.460(3)
	2.450(2)	2.496(9)	2.466(3)
Bond angles (°)			
C–Sn–C	160.1(3)	166.6(2)	155.2(5)
Cl–Sn–Cl	98.5(1)	94.41(3)	92.09(8)
O–Sn–O	86.1(2)	87.83(8)	86.4(4)

*Where L'' is 2-imidazolidone.

The steric hindrance of the *N*-methyl group of L prevents $Sn^{IV}R_2$ co-ordinating to the amide nitrogen and the fairly large electric dipole moment of L (1.13 D; D ≈ 3.33564 × 10^{-30} cm)[17] might be the principal driving force for the complexation. The *cis*-chlorine and *cis*-oxygen atoms make a large contribution to the overall dipole moment of the *trans* isomer.

Infrared Spectra.—Characteristic IR bands[9,18–20] for the complexes prepared are given in Table 6. The weak bands at 3060–3020 cm^{-1} which appear in all the compounds are assigned to the $\nu(CH_3)$ and $\nu(CH_2)$ stretching motions, while the band at 2870 cm^{-1} in L is assigned to $\nu(N–CH_3)$.

The carbonyl stretching frequency appears as a broad strong band at 1660 cm^{-1} in L and shifts by 15 cm^{-1} in the complexes indicating interaction between the tin and oxygen atoms.

The ν(Sn–C) frequencies are assigned according to the literature values. The ν(Sn–O) frequency is difficult to assign owing to its proximity to and overlapping with the strong ν(Sn–Cl) band. Strong ν(Sn–Cl) far-IR bands suggest a *cis*-Cl_2 octahedral structure for **3** and **4** and C_{2v} symmetry (*mer* isomer) for **2**. Representations $2A_1 + B_2$ appear for the $SnCl_3$ stretching modes.

Mössbauer Spectra.—Tin-119 Mössbauer measurements have been made at various temperatures between 20 and 293 K. Table 7 presents the hyperfine parameters of the spectra obtained at 20 K. The isomer shifts for the new compounds are lower than those of the corresponding uncomplexed tin(IV), consistent with adduct formation and the consequent decrease in covalency of the tin bonding. The isomer shift is a measure of the total electron density at the tin nucleus and is sensitive to the electronegativities of the atoms bonded to tin.

The two diorganotin complexes display similar Mössbauer hyperfine parameters. Therefore similar configurations for both complexes in the solid state are assumed. The decrease in i.s. and quadrupole splitting (q.s.) of [$\{SnR_2Cl_2(L)\}_n$] on replacing methyl by phenyl groups reflects the greater electron-releasing power of the former, resulting in greater electron density around the tin in the methyl compound and decreasing asymmetry of the electron cloud about the tin atom in the phenyl compound as the difference in the polarity of the Sn–C and Sn–ligand bonds is reduced. The observed C–Sn–S bond angle in compound **4** closely agrees with the predicted value of 161° based on Mössbauer data. From the point-charge approach[21] the equation q.s. = $4[R]\,(1\text{-}3\sin^2\theta\cos^2\theta)^{\frac{1}{2}}$ gives an estimate of θ, where $180-2\theta$ is the R–Sn–R bond angle and the partial q.s. (p.q.s.) contributions, [R] ($=\frac{1}{2}e^2Q_R$), for ligands other than R groups are considered to be negligible. A C–Sn–C bond angle of 171° for the dimethyltin derivative is calculated. By

Table 6 Characteristic IR bands (cm^{-1}) for L and its complexes

Assignment	L	**1**	**2**	**3**	**4**
$\nu(N–CH_3)$	2870m	2890w	2870m	2930m	2920w
$\nu(CH_3)$, $\nu(CH_2)$	3020w	3060vw	3020w	3020w	3060w
	2970w	2950m	2950w	2980w	2030w
	2920m		2930ms	2940w	2970w
ν(C=O)	1660vs (br)	1645s	1645s	1645vs	1645vs
$\delta(CH_3)$, $\delta(CH_2)$	1445ms	1425mw	1465w	1435m	1430m
	1400ms	1410s	1435s	1400s	1405mw
$\delta(N–CH_3)$	1340s	1360s	1360vs	1358vs	1345s
δ(C=O)	410s	460s	410mw	430s	420m
ν(Sn–C)			390m	585s	285w
				522m	
ν(Sn–Cl)		340vs	310ms	290sh	310w
			270vs	270s	270s
			260s		

Table 7 Mössbauer spectral parameters[a]

Compound	i.s./mm s^{-1}	q.s./mm s^{-1}	Γ^{b}/mm s^{-1}
1	0.31	1.01	1.05
$SnCl_4 \cdot 2Et_2O$[c]	0.45	1.1	
$SnCl_4 \cdot 2MeOH$[c]	0.43	0.70	
$SnCl_4 \cdot pyz$[d]	0.38	0.6	
2	0.92	2.05	1.01
$[SnMeCl_3(L'')_2]$[e]	0.95	1.62	0.96
3	1.45	4.08	1.14
4	1.29	3.65	1.04

[a] Measured at 20 K. Isomer shift (i.s.) relative to room temperature $Ba^{119}SnO_3$. Estimated errors between 0.02 and 0.03 mm s^{-1} in the last significant figure. [b] Full width at half-maximum. [c] Ref. 21. [d] Ref. 22. [e] L″ = 2-imidazolidone.

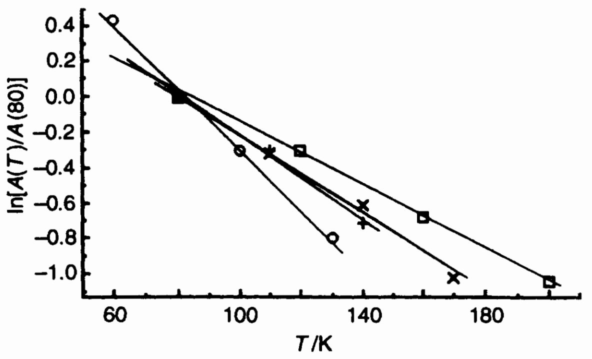

Fig. 3 Temperature dependence of the Mössbauer spectral areas for **1** (□), **2** (○), **3** (+) and **4** (×). Slopes of the best fit straight lines (-10^2 dln$A$/dT, K^{-1}): **1**, 0.82; **2**, 1.70; **3**, 1.10 and **4**, 1.20

using the point-charge model for **4**, a value of −0.075 mm s^{-1} is calculated for the p.q.s of L in an octahedral environment.

As expected for the monobutyl derivative **2**, the substitution of an organic group by a chlorine atom is reflected in the evident decrease of the i.s. with respect to **3** and **4**. The values of i.s. and q.s. observed for compound **2** compare favourably with these reported for the monobutylchloride adducts[23] which have octahedral structures. This suggests that a similar co-ordination may exist around tin in **2**. The p.q.s. value calculated for the ligand gives a q.s. value (2.13 mm s^{-1}) close to the experimental value for a structure with three chlorines and a ligand on the equatorial plane. The two other possible structures also give values (1.98 mm s^{-1}) close to the experimental value. The IR spectrum of **2**, however, exhibits three bands in the tin–halogen stretching region consistent with the former structure.

A fairly large q.s. was observed for the tin tetrachloride adduct **1** (1.01 mm s^{-1}). A measurable q.s. suggests *trans*-octahedral Sn^{IV} halide structures with oxygen in the *trans* position.[24] Yeats *et al.*[22] have suggested that the observation of q.s. for $SnX_4L'_2$ species in which L′ is an oxygen donor reflects a weaker donor interaction for the L–Sn as opposed to the X–Sn bond. A strong donor interaction in $SnCl_4 \cdot 2Me_2SO$ (Sn–O bond distances 2.17 and 2.10 Å) does not give q.s., whereas a weaker donor interaction in $SnCl_4 \cdot 2POCl_3$ (bond distances 2.25 and 2.30 Å) shows a q.s. of 1.12 mm s^{-1}.[22] Nitrogen is thought to be a better donor than analogous oxygen derivatives. Thus, the 1 : 2 derivative $SnCl_4 \cdot 2pyz$ does not show q.s., whereas the 1 : 1 derivative $SnCl_4 \cdot pyz$, which probably has bridging pyz groups and hence a weaker interaction does.[25] In the presence of a weak interaction between a donor and acceptor steric and structural effects are mainly responsible for the value of the q.s.[23]

The results of the variable-temperature Mössbauer study are depicted in Fig. 3.[26] The Mössbauer recoil-free fraction, f, for harmonic systems is given by $f = \exp(-k^2\langle x^2\rangle)$, where $\langle x^2\rangle$ is the component of the mean square vibrational amplitude of the emitting atom in the direction of the Mössbauer gamma ray. For thin absorbers f is linearly related in a Debye model to the area under the resonance $A(T)$, and its temperature dependence in the high-temperature limit[27] can be written as equation (1),

$$A(T) \propto f = \exp[-6E_R\, T/K\,\theta_D{}^2] \text{ for } T > \theta_{\frac{D}{2}} \quad (1)$$

where E_R is the Mössbauer recoil energy, K is the Boltzmann constant and θ_D is the Debye temperature of the solid. A plot of ln$A(T)$ *vs.* T gives a straight line of slope $\alpha = -\mathrm{dln}A(T)/\mathrm{d}T$, characterizing the tightness with which the tin atom is bound into the lattice and hence the degree of molecular association. In the present study Mössbauer spectra above 60 K have been used and the corresponding slopes obtained through a least-squares fit. The goodness of the fit is determined by the correlation coefficient r which in all cases was better than −0.996.

For compound **2**, between 60 and 130 K the slope of -1.7×10^{-2} K^{-1} is typical of non-interacting lattice units (-1.60×10^{-2} to -1.96×10^{-2} K^{-1}).[26] For the diorganotin complexes the slopes are identical, within experimental error. Furthermore, the i.s. and q.s. data indicate that we are dealing with very similar lattice dynamics in the two cases. The slopes of the diorganotin adducts (-1.1×10^{-2} and -1.2×10^{-2} K^{-1}) indicate a zigzag polymeric octahedral configuration with bidentate bridged ligation.[26,28] The lowest negative value of -0.82×10^{-2} K^{-1} is observed for compound **1**. Strong intermolecular interactions give small negative values of about -0.9×10^{-2} K^{-1} for strongly bonded polymeric lattices.[29] The most rigid lattices (-0.7×10^{-2} to -0.9×10^{-2} K^{-1}) are based upon a rod-like architecture.[26,30]

Taking into account the recoil energy of ^{119}Sn ($E_R = 2.58 \times 10^{-3}$ eV; eV ≈ 1.60×10^{-19} J T^{-1})[31] the Debye temperatures 144, 102, 128 and 123 K were calculated for complexes **1**–**4** respectively.

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