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Preparations and crystal structures of $Sn(CH_2CH_2CO_2Me)_2(C_3S_5)$ and $[Q][Sn(CH_2CH_2CO_2Me)(C_3S_5)_2]$ (Q = NEt_4 or 1,4-dimethylpyridinium, C_3S_5 = 4,5-disulfanyl-1,3-dithiole-2-thionate)

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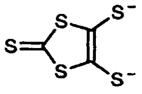
The compounds $Sn(CH_2CH_2CO_2Me)_2(C_3S_5)$ **1** (R = Me or Pr^i) and $[Q][Sn(CH_2CH_2CO_2Me)(C_3S_5)_2]$ **2** (Q = NEt_4 or 1,4-dimethylpyridinium; C_3S_5 = 4,5-disulfanyl-1,3-dithiole-2-thionate) have been prepared and characterised by solution and solid-state NMR spectroscopy. A crystal structure determination of **1** (R = Me) revealed it to be a monomeric six-co-ordinate, distorted-octahedral complex with chelating $MeO_2CCH_2CH_2$ groups and *trans*-carbon atoms [Sn–O(C) 2.629(7) Å]. The $MeO_2CCH_2CH_2$ group in **2**, both in solution and in the crystal, is monodentate: the tin centres in the anions of both complexes **2** were shown to have structures closer to rectangular pyramids than to trigonal bipyramids. There were, however, slight differences in the solid-state structures of the anions, particularly in regard to the separations of the Sn and carbonyl oxygen atoms; Sn • • • O intramolecular distances are 4.84(1) and 3.371(4) Å in **2** (Q = NEt_4) and **2** (Q = 1,4-dimethylpyridinium) respectively. There were also differences in the packing of the anions.

The term 'estertin' has been coined for compounds containing the moiety $RO_2CCH_2CH_2Sn$. The ready formation of $SnCl_3(CH_2CH_2CO_2R)$ and $SnCl_2(CH_2CH_2CO_2R)_2$ and their use as precursors of potentially valuable organotin-based poly(vinyl chloride) (pvc) stabilisers have generated much study.[1] While the commercial application of estertin mercaptides as pvc stabilisers has yet to be achieved, the study of estertin species continues to attract attention, mainly as a consequence of their co-ordination chemistry. Of particular interest has been the ability of the $RO_2CCH_2CH_2$ unit to act as a chelating ligand by utilising the carbonyl oxygen as an additional donor centre.[2–13] Related compounds studied include $SnCl_3(CH_2CH_2CH_2CO_2Et)$[14] and $[SnCl_3(CH_2CHMeCO_2Bu)(OPPh_3)]$.[4] Table 1 provides details of the crystal structures of a variety of estertin compounds. As can be seen, complexes with either mono- or bi-dentate $RO_2CCH_2CH_2$ groups exist. As part of a study[15–18] of main-group compounds containing the ligand $C_3S_5^{2-}$ (4,5-disulfanyl-1,3-dithiole-2-thionate), we have investigated the compounds $Sn(CH_2CH_2CO_2R)(C_3S_5)$ **1** (R = Me or Pr^i) and $[Q][Sn(CH_2CH_2CO_2R)(C_3S_5)_2]$ **2** (Q = NEt_4 or 1,4-dimethylpyridinium), including the crystal structures of **1** (R = Me), **2** (Q = NEt_4) and **2** (Q = 1,4-dimethylpyridinium).

Experimental

Infrared spectra were recorded on a Philips Analytical PU9800 Fourier-transform spectrometer, solution NMR spectra on a Bruker 250 MHz instrument (a 5 s pulse delay was employed in the acquisition of the ^{13}C spectra) and solid-state NMR spectra at the EPSRC solid-state NMR service, based at the University of Durham.

The compounds $SnCl_2(CH_2CH_2CO_2R)_2$ (R = Me or Pr^i) were obtained from reactions between anhydrous hydrogen chloride, tin and the appropriate $RO_2CCH{=}CH_2$ according to a published procedure,[1] as was $SnCl_3(CH_2CH_2CO_2Me)$ from anhydrous HCl, anhydrous $SnCl_2$ and $MeO_2CCH{=}CH_2$. The zinc salts $[NEt_4]_2[Zn(C_3S_5)_2]$ (m.p. 186–188 °C) and $[4\text{-}MeC_5H_4NMe]_2[Zn(C_3S_5)_2]$ (m.p. 231–233 °C) were produced from carbon disulfide, sodium, zinc sulfate and $[NEt_4]Br$ or $[4\text{-}MeC_5H_4NMe]I$, using a general procedure.[19]



$C_3S_5^{2-}$

Preparations

$Sn(CH_2CH_2CO_2Me)_2(C_3S_5)$ 1 (R = Me). Solutions of $SnCl_2(CH_2CH_2CO_2Me)_2$ (1.00 g, 2.76 mmol) in acetone and $[NEt_4]_2[Zn(C_3S_5)_2]$ (0.995 g, 1.38 mmol) in acetone (20 cm^3) were mixed. The reaction mixture was left for 1 h and filtered. The filtrate was rotary evaporated and the solid residue recrystallised from acetone to give the required product as orange crystals (0.63 g, 47%), m.p. 102–104 °C (Found: C, 27.1; H, 2.8. $C_{11}H_{14}O_4S_5Sn$ requires C, 27.0; H, 2.9%). IR (KBr, cm^{-1}): 2951–2919, 1674 (C=O), 1460, 1439, 1358, 1262, 1221, 1183, 1130, 1057, 1032, 953, 895, 748 and 687. NMR: ^1H (CD_3COCD_3), δ 1.93 [t, 4 H, $J(^1H–^1H)$ = 7.3, $J(^{119}Sn–^1H)$ = 79.2, CH_2Sn], 3.00 [t, 4 H, $J(^1H–^1H)$ = 7.3, $J(^{119}Sn–^1H)$ = 132.1, CH_2CH_2Sn] and 3.81 (s, 6 H, Me); ^{13}C ($CDCl_3$, 62.9 MHz), δ 19.6 [$J(^{119}Sn–^{13}C)$ = 574.3, CH_2Sn], 28.8 [$J(^{119}Sn–^{13}C)$ = 45.4 Hz, CH_2CH_2Sn], 53.8 (MeO), 129.6 (C=C), 180.9 (C=O) and 210.3 (C=S); (solid state, 75.4 MHz), δ 19.4, 30.3, 53.9, 56.4, 56.7, 57.4, 130.3, 130.9, 131.1, 180.5, 181.9, 183.0 and 208.9; ^{119}Sn (93.3 MHz), δ 84.4 (in CD_3COCD_3), 87.7 (in CD_2Cl_2) and 11.8 (in C_5H_5N); (solid state, 111.9 MHz), δ 83.0 and 99.5

$Sn(CH_2CH_2CO_2Pr^i)_2(C_3S_5)$ 1 (R = Pr^i). This compound was prepared similarly to **1** (R = Me) from $SnCl_2(CH_2CH_2CO_2Pr^i)_2$ (0.422 g, 1.00 mmol) and $[NEt_4]_2[Zn(C_3S_5)_2]$ (0.360 g, 0.50 mmol) in acetone (total volume = 20 cm^3). The product was recrystallised from methanol as orange crystals, m.p. 125–129 °C (Found: C, 33.1; H, 4.1. $C_{15}H_{22}O_4S_5Sn$ requires C, 33.0; H, 4.1%). IR (KBr, cm^{-1}): 2977–2896, 1665 (C=O), 1466, 1451, 1423, 1399, 1379, 1327, 1262, 1223, 1132, 1125, 1103, 1055, 1034, 999, 925, 893, 766, 689 and 463. NMR (CD_3COCD_3): ^1H, δ 1.28 [d, 12 H, $J(^1H–^1H)$ = 6.2, Me_2CH],

Table 1 Selected structural details of estertin compounds in the solid state

Compound	Co-ordination number of tin	Sn–O/Å	Bite angle, O–Sn–C/°	ν(C=O)/cm^{-1}	Ref.
$SnCl_3(CH_2CH_2CO_2Me)$	Five C=O complexed	2.347(5)	77.2(3)	1658	2
$SnCl_3(CH_2CH_2CO_2Pr^i)$	Five C=O complexed	2.337(5)	78.0(3)	1650	3
$SnCl_3(CH_2CH_2CO_2R)(OPPh_3)$ R = $H_2C{=}CHCH_2$	Six C=O complexed	2.413(4)	76.4(2)		4
$SnCl_2\{HB(pz)_3\}(CH_2CH_2CO_2Me)$	Six C=O uncomplexed	4.04(1)	42.84	1730	5
$Sn(NCS)_2\{HB(pz)_3\}(CH_2CH_2CO_2Me)$	Six C=O uncomplexed	3.736(5)	49.29	1731	5
$SnCl_{3-n}(S_2CNMe_2)_n(CH_2CH_2CO_2Me)$					
$n = 2$	Six^a C=O uncomplexed			1724	6
$n = 1$	Six^a C=O complexed	2.436(6)	76.5(3)	1652	7
$Sn(S_2CNMe_2)(CH_2CH_2CO_2R)X_2$					
$X_2 = (SCH_2CH_2)_2O$, R = Me	Six^b C=O uncomplexed Tridentate X_2			1731	8
$X_2 = (OCH_2CH_2)_2NMe$, R = Et	Six^b C=O uncomplexed Tridentate X_2			1717	8
$[(MeO_2CCH_2CH_2)(Me_2NCS_2)SnS]_2$	Five^a C=O uncomplexed Bridging S	3.19		1730	9
$[Q][Sn(CH_2CH_2CO_2Me)(C_3S_5)_2]$					
Q = NEt_4	Five C=O uncomplexed			1721	This work
Q = $4\text{-}MeC_5H_4NMe$	Five C=O uncomplexed	3.371(4)	55.6(2)	1720	This work
$SnIPh_2(CH_2CH_2CO_2Me)$	Five C=O complexed	2.55(2)	73.4(6)	1684	10
$SnCl_2(CH_2CH_2CO_2Me)_2$	Six Both C=O complexed	2.524(4) 2.520(2)	73.3(2) 74.0(3)	1675	2
$SnCl(L)(CH_2CH_2CO_2Me)_2$					
L = $H_2B(pz)$	Six^c One C=O complexed	2.745(6)	68.9(2)	1689 1737	11
L = quinolin-8-olato	Six^c One C=O complexed	2.847(4)	65.7(3)	1712 1737	12
L = S_2CNMe_2	Five^c Both C=O uncomplexed	2.942(5) 3.154(6)	65.3 61.3	1725	11
$Sn(S_2CNMe_2)_2(CH_2CH_2CO_2Me)_2$	Seven^b One C=O complexed	2.751(5)	69.8(2)	1693 1730	13
$Sn(CH_2CH_2CO_2Me)_2(C_3S_5)$	Six Both C=O complexed	2.629(7)	72.7(3)	1674	This work
$[(MeO_2CCH_2CH_2)_2SnS]_3$	Four Both C=O uncomplexed Bridging S			1713	9

^{a} Bidentate S_2CNMe_2. ^{b} Bidentate S_2CNMe_2, but with one weak and one strong bond. ^{c} Bidentate L.

1.90 [t, 4 H, $J(^1H-^1H) = 7.2$, $J(^{119}Sn-^1H) = 80.3$, $COCH_2$], 2.97 [t, 4 H, $J(^{119}Sn-^1H) = 132.4$, $J(^1H-^1H) = 77.3$, CH_2Sn] and 5.07 [spt, 2 H, $J(^1H-^1H) = 6.2$, $CHMe_2$]; ^{13}C (62.9 MHz), δ 20.6 [$J(^{119}Sn-^{13}C) = 590.8$ Hz, CH_2Sn], 21.7 (Me_2CH), 71.9 (COCH), 130.0 (C=C), 181.0 (C=O) and 210.4 (C=S) (the signals for CH_2Sn were masked by solvent absorptions); ^{119}Sn (93.3 MHz), δ 80.4.

$[NEt_4][Sn(CH_2CH_2CO_2Me)(C_3S_5)_2]$ 2 (Q = NEt_4). A mixture of $SnCl_3(CH_2CH_2CO_2Me)$ (0.312 g, 1.00 mmol) and $[NEt_4]_2[Zn(C_3S_5)_2]$ (0.719 g, 1.00 mmol) in MeOH (20 cm^3) was agitated in an ultrasonic bath for 30 min. The reaction mixture was filtered and the orange solid collected and recrystallised from MeOH as orange needles, m.p. 76–77 °C (Found: C, 29.9; H, 3.7; N, 2.0. $C_{18}H_{27}NO_2S_{10}Sn$ requires C, 29.7; H, 3.7; N, 1.9%). IR (KBr, cm^{-1}): 2980–2945, 1721 (C=O), 1445, 1391, 1331, 1210, 1171, 1059, 995, 905, 895, 461 and 457. NMR: ^1H (CD_3COCD_3), δ 1.41 [t, 12 H, $J(^1H-^1H) = 7.3$, NCH_2CH_3], 1.96 [t, 2 H, $J(^1H-^1H) = 7.1$, $J(^{119}Sn-^1H) = 71.6$, CH_2Sn], 2.87 [t, 2 H, $J(^1H-^1H) = 7.2$, $J(^{119}Sn-^1H) = 163.3$, CH_2CH_2Sn], 3.50 [q, 8 H, $J(^1H-^1H) = 7.2$, NCH_2] and 3.68 (s, 3 H, MeO); ^{13}C (CD_3COCD_3, 62.9 MHz), δ 7.6 (NCH_2CH_3), 31.3 [$J(^{119}Sn-^{13}C) = 636.4$, CH_2Sn], 52.3 (OMe), 52.9 (t, J = 6.3 Hz, NCH_2), 130.4 (C=C), 175.7 (C=O) and 208.2 (C=S) (the $SnCH_2$ absorption was masked by the solvent absorptions); (solid state, 75.4 MHz), δ 8.9, 18.1, 31.0, 33.5, 53.4, 60.7, 126.7, 130.9, 176.7, 203.5 and 204.8; ^{119}Sn (CD_3COCD_3, 93.3 MHz), δ 5.7; (solid state, 118.9 MHz), δ 32.5.

$[4\text{-}MeC_5H_4NMe][Sn(CH_2CH_2CO_2Me)(C_3S_5)_2]$ 2 (Q = 1,4-dimethylpyridinium). The compound $SnCl_3(CH_2CH_2CO_2Me)$ (1.32 g, 4.20 mmol) was added to a suspension of $[4\text{-}MeC_5H_4NMe]_2[Zn(C_3S_5)_2]$ (1.42 g, 2.10 mmol) in acetone (100 cm^3). The reaction mixture was stirred vigorously for 30 min, filtered and the filtrate evaporated. The brown solid residue was washed well with water and recrystallised from acetone. The required compound was obtained as a red-brown crystalline solid (1.10 g, 74.0%), m.p. 149–150 °C (Found: C, 29.3; H, 2.4; N, 2.0. $C_{17}H_{17}NO_2S_{10}Sn$ requires C, 28.9; H, 2.4; N, 2.0%). IR (KBr, cm^{-1}): 3048, 1720 (C=O), 1437 and 748. NMR: ^1H (CD_3COCD_3), δ 1.95 [t, 2 H, $J(^1H-^1H) = 7.2$,

$J(^{119}Sn–^{1}H)$ = 73.6, CH_2Sn], 2.75 (s, 3 H, Me), 2.88 [t, 2 H, $J(^{1}H–^{1}H)$ = 7.2, $J(^{119}Sn–^{1}H)$ = 169, CH_2CH_2Sn], 3.69 (s, 3 H, MeO), 4.58 (s, 3 H, MeN), 8.09 [d, $J(^{1}H–^{1}H)$ = 6.6, aryl H] and 8.96 [d, $J(^{1}H–^{1}H)$ = 6.6 Hz, aryl H]; ^{13}C (solid state, 75.4 MHz), δ 24.5 (Me), 29.0 (br, $Sn\mathit{CH}_2\mathit{CH}_2$), 51.5 (NMe), 54.2 (MeO), 126.7 (aryl C^3), 128.2 (C=C), 134.8 (C=C), 144.7 (aryl C^2), 157.3 (aryl C^4), 176.1 (C=O), 204.7 (C=S) and 206.0 (C=S); ^{119}Sn (CD_3COCD_3, 93.3 MHz), δ 6.2; (solid state, 111.9 MHz), δ 57.3.

Exchange reaction

A solution of $SnEt_2(C_3S_5)$ (30 mg, 0.087 mmol) [$\delta(^{119}Sn)$ 165.6] and $SnCl_2(CH_2CH_2CO_2Me)_2$ (30 mg, 0.087 mmol) [$\delta(^{119}Sn)$ −67.7] was made up in CD_3COCD_3 (1 cm^3) and was allowed to equilibriate for 2 h. The ^{119}Sn NMR spectrum indicated the presence in solution of $SnEt_2(C_3S_5)$ [$\delta(^{119}Sn)$ 164.2], $SnCl_2Et_2$ [$\delta(^{119}Sn)$ = 28.1], $Sn(CH_2CH_2CO_2Me)_2(C_3S_5)$ [$\delta(^{119}Sn)$ 85.0] and $SnCl_2(CH_2CH_2CO_2Me)_2$ [$\delta(^{119}Sn)$ −67.8]. Exchange also occurred in the reverse direction between $SnCl_2Et_2$ and $Sn(CH_2CH_2CO_2Me)_2(C_3S_5)$.

Addition reaction

To a solution of $Sn(CH_2CH_2CO_2Me)_2(C_3S_5)$ (40 mg, 0.10 mmol) in CD_3COCD_3 (1 cm^3) was added an excess of NEt_4Br (1 mmol); the solution was left for 30 min and the ^{119}Sn NMR spectrum obtained. The resulting product gave $\delta(^{119}Sn)$ −49.8.

Crystal structure determinations

Compounds 1 (R = Me) and 2 (Q = NEt_4). X-Ray diffraction data were obtained from suitable crystals on a Nicolet P3 four-circle diffractometer using Mo-Kα radiation (λ = 0.710 69 Å). Cell dimensions were determined using 14 reflections at θ 10.1–14.2°. Data collection used 2θ scan rates of 5.33 (I_p < 150) to 58.6 (I_p > 2500)° min^{-1}, where I_p is the prescan intensity. Scan widths were 2θ 2.4–2.7°. The programs SHELXS 86[20a] and SHELX 76[20b] were used for structure solution (Patterson methods) and refinement (on *F*), respectively. Refinement was by full-matrix least squares. All non-H atoms were refined anisotropically for compound **1** (R = Me), while for **2** (Q = NEt_4) only Sn, S and O were so refined; all other atoms were refined isotropically. For **1** (R = Me) the H atoms were placed in calculated positions with C–H 0.95 Å and refined riding upon the C to which they were attached with separate common group U_{iso} values for the methylene and methyl H; the C(6) methyl group was refined as a rigid body. For **2** (Q = NEt_4) the H atoms were placed in calculated positions with C–H 0.95 Å and refined riding upon the C to which they were attached with separate group U_{iso} values for each of the tin–alkyl methylene and methyl, amine–methylene and methyl groups; in addition the methyl groups involving C(10), C(12), C(14), C(16) and C(18) were refined as rigid bodies. No absorption corrections were made.

Computations were performed on the SUN SPARCserver (UNIX operating system) of the Computing Centre of the University of Aberdeen. Data collection and structure refinement parameters are in Table 2.

Compound 2 (Q = 1,4-dimethylpyridinium). X-Ray diffraction data were collected by the EPSRC Crystallography Service, Cardiff, using Mo-Kα radiation. The structure was refined (on *F*) by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions with C–H 1.00 Å. The first phasing model was refined[21] using SIR 88 and both completed by Fourier refinement and refined[22] using CRYSTALS PC. Computations were performed on a Viglen Genie P590 Pentium personal computer with CRYSTALS PC running under the Salford Software Services memory manager DBOS. Absorption corrections were not made.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Compounds 1

Compounds **1**, precipitated directly from acetone solutions of $[NEt_4]_2[Zn(C_3S_5)_2]$ and $SnCl_2(CH_2CH_2CO_2R)_2$ (R = Me or Pr^i) (1 : 2 mol ratio), equation (1). In contrast, direct reactions

$$2\,SnCl_2(CH_2CH_2CO_2R)_2 + [NEt_4]_2[Zn(C_3S_5)_2] \longrightarrow [NEt_4]_2[ZnCl_4] + 2\,Sn(CH_2CH_2CO_2R)_2(C_3S_5) \quad (1)$$

involving simple $SnCl_2R'_2$ compounds [R'_2 = Et_2, Bu_2, C_8H_{17}, Ph_2 or Ph(Me)] and $[Q]_2[Zn(C_3S_5)_2]$ led to the formation of salts $[Q][SnClR'_2(C_3S_5)]$ (Q = onium cation).[23] Compounds **1** were obtained as orange crystalline solids. Suitable crystals of **1** (R = Me) were obtained for X-ray crystallography.

Crystal structure of 1 (R = Me). The fractional atom coordinates are given in Table 3, bond lengths and angles in Table 4. The molecular structure and numbering system are shown in Fig. 1. The packing of the molecules in the unit cell is illustrated in Fig. 2. The compound is monomeric, with a crystallographic two-fold axis along the C=S bond, through the tin atom. The tin atom is six-co-ordinated, being bonded to the two carbonyl oxygen atoms, two S and two C atoms. The geometry at tin is best described as distorted octahedral with *trans* carbon atoms. The Sn–O bond length of 2.629(7) Å is considerably less than the sum of the van der Waals radii,

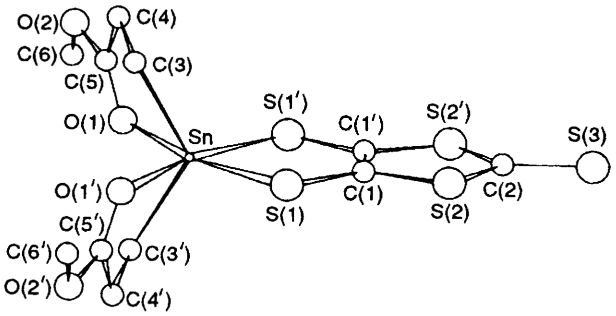


Fig. 1 Molecular structure and numbering scheme for compound **1** (R = Me). Symmetry relation: I 1 − *x*, *y*, ½ − *z*

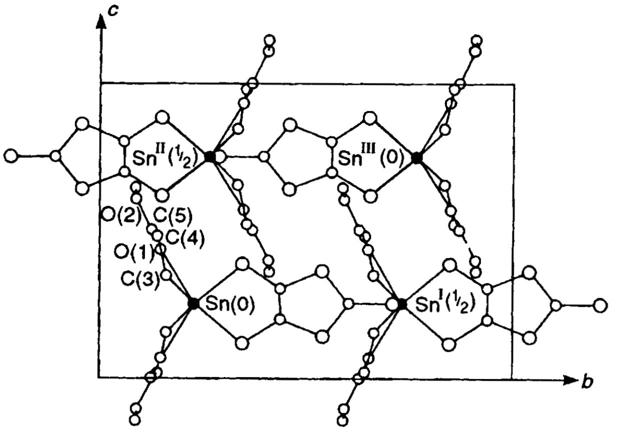


Fig. 2 Projection of the crystal structure of compound **1** (R = Me) onto the *bc* plane. The heights of the tin atoms, relative to *a*, are indicated. Symmetry relation: I ½ + *x*, ½ + *y*, ½ − *z*; II ½ − *x*, ½ − *y*, ½ + *z*; III −*x*, 1 − *y*, 1 − *z*

Table 2 Data collection and structure refinement parameters

Compound	**1** (R = Me)	**2** (Q = NEt_4)	**2** (Q = 4-MeC_5H_4NMe)
Formula	$C_{11}H_{14}O_4S_5Sn$	$C_{18}H_{27}NO_2S_{10}Sn$	$C_{17}H_{17}NO_2S_{10}Sn$
M	489.24	728.75	706.62
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Pbcn*	$P\bar{1}$	$P\bar{1}$
a/Å	10.608(4)	11.793(5)	7.895(5)
b/Å	15.338(9)	12.385(6)	11.313(8)
c/Å	10.992(6)	12.336(8)	15.435(6)
α/°		116.63(4)	106.77(4)
β/°		103.34(4)	96.87(4)
γ/°		102.37(4)	97.72(6)
U/Å^3	1788(2)	1459(1)	1290(1)
Z	4	2	2
D_c/Mg m^{-3}	1.817	1.658	1.82
μ/mm^{-1}	2.00	1.58	1.79
F(000)	968	736	704
Crystal size/mm	0.6 × 0.4 × 0.3	0.45 × 0.4 × 0.4	—
Maximum |*h*| (|*k*|, |*l*|)	12 (18, 13)	14 (14, 14)	8 (12, 18)
Reflections measured	1849	5171	5329
No. unique reflections	1464	4940	4485
R_{int}	0.020	0.006	0.006
No. observed reflections	1156	4448	3478
Criterion $F > n\sigma(F)$, *n*	4	4	3
No. parameters refined	102	213	280
Weighting scheme coefficients	0.0044[a]	0.018 93[a]	8.51, −0.781, 6.36[b]
R	0.064	0.049	0.0428
R′	0.074	0.062	0.0494
Minimum (maximum) Δρ/e Å^{-3}	−0.73 (1.79)	−1.07 (1.81)	−0.67 (1.15)

[a] In $w = 1/[\sigma^2(F) + aF^2]$. [b] A three-term Chebyshev series with the coefficients given.

Table 3 Atomic coordinates (×10^4) for non-hydrogen atoms of compound **1** (R = Me) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sn	0	2308.5(7)	2500
S(1)	848(2)	3463(2)	1163(2)
S(2)	721(2)	5394(2)	1401(2)
S(3)	0	7094(3)	2500
O(1)	−1106(6)	1502(5)	4320(6)
O(2)	−528(7)	911(4)	6054(5)
C(1)	333(8)	4378(6)	1975(8)
C(2)	0	6027(9)	2500
C(3)	1395(9)	1640(7)	3455(10)
C(4)	1063(10)	1425(9)	4796(9)
C(5)	−298(9)	1292(6)	4994(10)
C(6)	−1821(11)	894(8)	6438(11)

Table 4 Bond lengths (Å) and angles (°) for compound **1** (R = Me)

S(1)–Sn	2.471(2) × 2	C(3)–Sn	2.084(9) × 2
O(1)–Sn	2.629(7) × 2		
C(1)–S(1)	1.750(9)	C(1)–S(2)	1.731(9)
C(2)–S(2)	1.729(8) × 2	C(2)–S(3)	1.636(14)
C(5)–O(1)	1.178(11)	C(5)–O(2)	1.326(11)
C(6)–O(2)	1.435(13)	C(1^I)–C(1)	1.354(16)
C(4)–C(3)	1.552(14)	C(5)–C(4)	1.474(13)
C(3)–Sn–S(1)	113.2(3) × 2	O(1)–Sn–S(1)	162.3(2) × 2
S(1^I)–Sn–S(1)	88.42(8)	C(3^I)–Sn–S(1)	108.2(3) × 2
O(1^I)–Sn–S(1)	73.9(2) × 2	O(1)–Sn–C(3)	72.7(3) × 2
C(3^I)–Sn–C(3)	121.0(4)	O(1^I)–Sn–C(3)	80.5(3) × 2
O(1^I)–Sn–O(1)	123.8(2)	C(1)–S(1)–Sn	99.1(3)
C(2)–S(2)–C(1)	98.4(5)	C(6)–O(2)–C(5)	116.2(8)
C(1^I)–C(1)–S(1)	126.7(6)	C(1^I)–C(1)–S(2)	115.8(7)
S(2)–C(1)–S(1)	117.5(5)	S(3)–C(2)–S(2)	124.2(4) × 2
S(2^I)–C(2)–S(2)	111.6(5)	C(5)–O(1)–Sn	106.4(6)
C(4)–C(3)–Sn	114.9(7)	C(5)–C(4)–C(3)	113.1(8)
O(2)–C(5)–O(1)	122.6(9)	C(4)–C(5)–O(1)	125.6(9)
C(4)–C(5)–O(2)	111.8(9)		

Symmetry operation: I $-x, y, \frac{1}{2} - z$.

ca. 3.6 Å, but is longer than a covalent Sn–O single bond (*ca.* 2.0 Å). It is comparable to those determined in the chelated $SnCl_2(CH_2CH_2CO_2R)_2$ compounds,[2,3] see Table 1; for comparison with values in other estertin compounds, see Table 1. The planar C_3S_5 ligand is coplanar with the tin and carbonyl atoms. The Sn–S bond length [2.471(2) Å] is similar to the sum of the covalent bond radii, 2.44 Å. The bite angle of this ligand is 88.4(1)°.

Spectroscopic study. In contrast to the conclusion from X-ray crystallography, the solid-state ^{119}Sn NMR spectrum of a microcrystalline sample of compound **1** (R = Me) indicated two slightly different six-co-ordinate tin environments [δ(^{119}Sn) 83.0 and 99.5, in an approximate peak-height ratio of 2 : 3]. The solid-state ^{13}C NMR spectrum also suggested the presence of more than one molecular arrangement; four sharp signals can be detected for the MeO group [δ(^{13}C) 53.9, 56.4, 56.7 and 57.4], three for the olefinic carbons (δ 131.1, 130.9 and 130.3), three C=O signals (δ 180.5, 181.9 and 183.0) and a main and a shoulder peak for the C=S units. The signals for the $SnCH_2CH_2$ carbon atoms are particularly broad and are centred at δ *ca.* 19 and 30.

The solid-state NMR and X-ray diffraction data indicate that compound **1** (R = Me) exists in polymorphic forms. The crystal used in the X-ray diffraction study was slowly grown from acetone solution and must represent just one of these forms. Confirmation of different crystal forms was provided by the powder diffraction pattern of the bulk sample employed for solid-state NMR spectroscopy: this did not conform to that calculated from the X-ray crystallography data. At this stage we have been unable to grow suitable crystals of other forms of **1** (R = Me) for X-ray study.

In the solution NMR spectra of compound **1** (R = Me) the tin and carbon atoms all gave single chemical shifts; the δ(^{119}Sn) value in solution was essentially the same in chlorocarbon solvents, *e.g.* 87.7 in CD_2Cl_2, as in the weakly co-ordinating CD_3COCD_3 (84.4): however, in the more strongly co-ordinating solvent, pyridine, δ(^{119}Sn) was 11.8. Both carbonyl groups remain completely co-ordinated in chlorocarbon and acetone solutions, and remain partially co-ordinated even in pyridine solution. The values of ν(C=O) in the IR spectra are 1689 and 1732 (in pyridine) and 1687 cm^{-1} (in CH_2Cl_2), compared to the value of 1674 cm^{-1} in the solid state.

The value of ν(C=O) for an unco-ordinated carbonyl group, *e.g.* as in $MeO_2CCH_2CH_3$, is *ca.* 1740 cm^{-1}. The co-ordination by the carbonyl group(s) is also broken on addition of an excess of NEt_4Br to solutions of **1** (R = Me). This is shown by the resulting tin-containing product having $\delta(^{119}Sn)$ −49.8 (in acetone solution) and ν(C=O) 1727 cm^{-1} (in CH_2Cl_2 solution).

The C_3S_5 ligand can be transferred between diorganotin centres, equation (2). An equilibrium is set up, with an approximate value of 4 for the equilibrium constant, *K*.

$$SnEt_2(C_3S_5) + SnCl_2(CH_2CH_2CO_2Me)_2 \overset{K}{\rightleftharpoons} SnCl_2Et_2 + Sn(CH_2CH_2CO_2Me)_2(C_3S_5) \quad (2)$$

Compounds 2

Compounds **2** were readily obtained from $SnCl_3(CH_2CH_2CO_2Me)$ and the appropriate zinc salt, equation (3). Both

$$[Q]_2[Zn(C_3S_5)_2] + SnCl_3(CH_2CH_2CO_2Me) \longrightarrow [Q][Sn(CH_2CH_2CO_2Me)(C_3S_5)_2] + [Q][ZnCl_3] \quad (3)$$

compounds **2** (Q = NEt_4) and **2** (Q = 1,4-dimethylpyridinium) gave crystals suitable for crystallographic study.

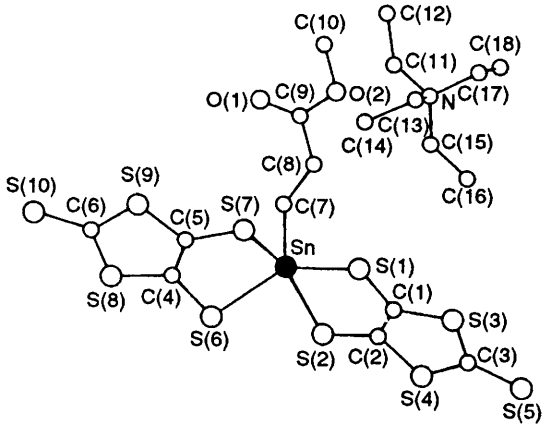


Fig. 3 The atom numbering scheme for compound **2** (Q = NEt_4)

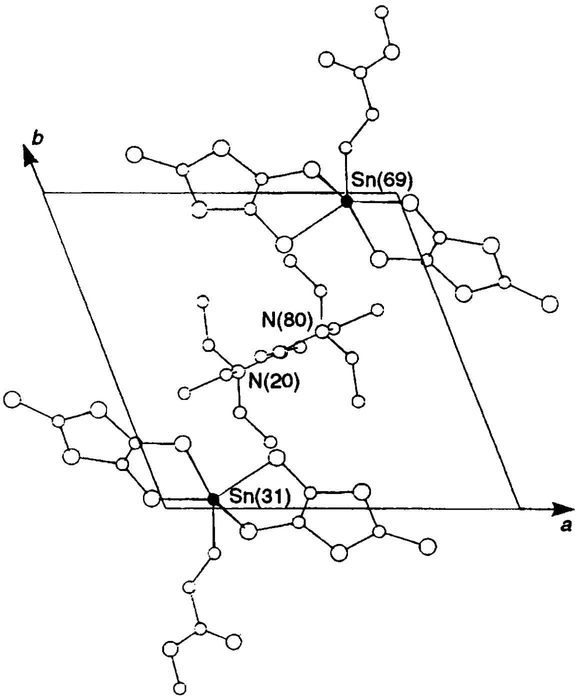


Fig. 4 The unit cell of compound **2** (Q = NEt_4) viewed down *c*. The edges *a* and *b* are shown in projection. Heights of Sn and N, in units of *z*/100, are indicated

Crystal structures. Fraction atom coordinates and bond lengths and angles for **2** (Q = NEt_4) are given in Tables 5 and 6, those for **2** (Q = 1,4-dimethylpyridinium) in Tables 7 and 8. The structure of **2** (Q = NEt_4) was evaluated at ambient temperature (*ca.* 25 °C), while that of **2** (Q = $4\text{-}MeC_5H_4NMe$) was determined at 120 K. Both complexes exist as ionic species. The anion $[Sn(CH_2CH_2CO_2Me)(C_3S_5)_2]^-$ exhibits slight structural differences in the two complexes. Figs. 3 and 5 portray the atomic arrangements and numbering systems, and the packings in the two complexes are shown in Figs. 4 and 6.

In the anion of compound **2** (Q = NEt_4) the estertin group acts as a monodentate ligand, with the carbonyl oxygen being directed away from the tin atom [Sn···O 4.84(1) Å]; consequently the tin centre is five-co-ordinated and has a geometry between rectangular pyramidal and trigonal bipyramidal. The extent of the distortion from trigonal-bipyramidal geometry is calculated to be 63%, using the dihedral-angle method, developed by Holmes and co-workers.[24] Similar structures were established for $[NBu_4][SnR(C_3S_5)_2]$ **3** (R = Bu or Ph).[16] Both the C_3S_5 ligands in the anion of **2** (Q = NEt_4) are asymmetrically bonded to tin, particularly for one of them. The Sn–S bond lengths are 2.582(1) and 2.475(2) Å [Δ(Sn–S) = 0.107 Å] from one ligand, and 2.511(2) and 2.477(1) Å [Δ(Sn–S) = 0.034 Å] from the other. The two S atoms [S(7) and S(2)] which make the longest bonds to Sn are in the quasi-axial sites with a S(2)–Sn–S(7) angle of 155.4(1)°. The bite angles of the C_3S_5 ligands are 83.4(1) and 87.9(1)°. The closest interanionic S···S contact involves S(3)···S(7^I) (I −*x*, −*y*, 2 − *z*) 3.605(2) Å; this is the only such contact which is less than the sum of the van der Waals radii (3.70 Å).

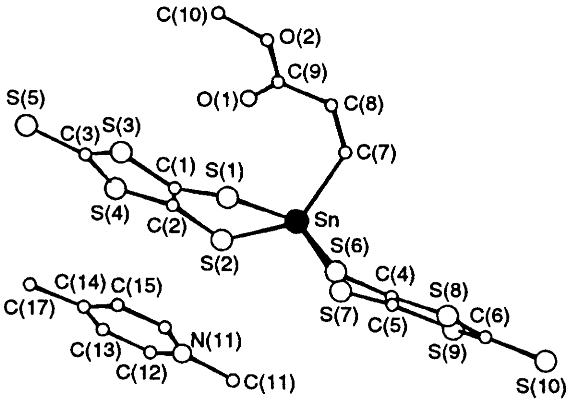


Fig. 5 The atom numbering scheme for compound **2** (Q = $4\text{-}MeC_5H_4NMe$)

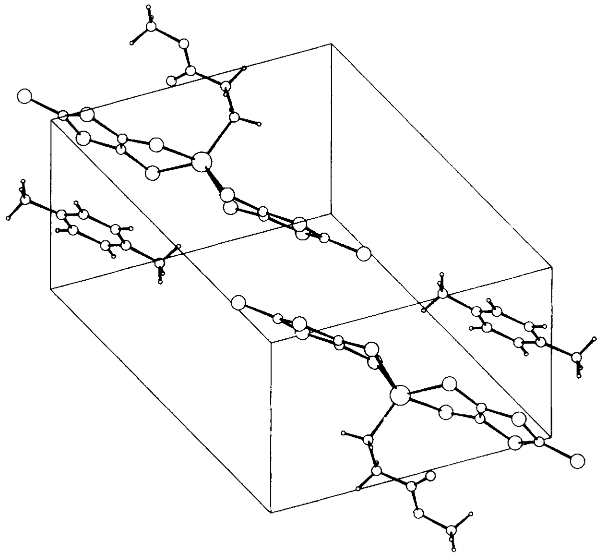


Fig. 6 The packing diagram for compound **2** (Q = $4\text{-}MeC_5H_4NMe$)

Table 5 Atomic coordinates ($\times 10^4$) for non-hydrogen atoms with e.s.d.s in parentheses for compound **2** (Q = NEt_4)

Atom	*X/a*	*Y/b*	*Z/c*
Sn	−1477.3(3)	−272.7(3)	6906.2(3)
S(1)	276(1)	−307(2)	8432(1)
S(2)	−1211(2)	−2068(2)	5064(1)
S(3)	2077(2)	−1650(2)	7882(2)
S(4)	790(2)	−3154(2)	5107(2)
S(5)	3101(3)	−3473(3)	6255(2)
S(6)	−3735(3)	−1623(2)	5722(2)
S(7)	−2135(2)	734(2)	8883(2)
S(8)	−5757(1)	−529(2)	5963(2)
S(9)	−4451(2)	1415(2)	8668(2)
S(10)	−7006(2)	1209(2)	7278(2)
C(1)	723(5)	−1396(5)	7293(5)
C(2)	122(5)	−2096(5)	5970(5)
C(3)	2047(6)	−2793(6)	6400(7)
C(4)	−4289(5)	−498(6)	6689(6)
C(5)	−3642(5)	441(5)	7959(5)
C(6)	−5803(5)	731(5)	7305(6)
C(7)	−930(6)	1430(6)	6793(6)
C(8)	177(6)	2507(6)	8001(7)
C(9)	308(6)	3834(6)	8221(6)
C(10)	1553(10)	5740(10)	8537(11)
O(1)	−512(5)	4246(6)	8267(10)
O(2)	1400(4)	4479(4)	8375(6)
N	3603(4)	4364(5)	1999(4)
C(11)	3040(6)	5203(6)	1623(6)
C(12)	3345(7)	6577(7)	2716(7)
C(13)	3234(9)	4270(10)	3059(10)
C(14)	1813(11)	3675(12)	2602(12)
C(15)	3196(7)	3071(7)	760(7)
C(16)	3734(8)	2134(8)	933(8)
C(17)	5032(8)	5003(8)	2601(8)
C(18)	5593(12)	5148(13)	1713(13)

The carbonyl oxygen atom in compound **2** (Q = 4-MeC_5H_4NMe) is directed towards the tin atom, but the tin–oxygen separation [3.371(4) Å] is still outside the accepted range of Sn–O bond lengths (*ca.* 2.95 Å). The tin atom is thus considered to be also five-co-ordinate with the geometry about tin best described as being between trigonal bipyramidal and rectangular pyramidal. The distortion from a trigonal bipyramid is calculated to be 70%. The range of Sn–S bond lengths is small, being from 2.484(1) to 2.527(1) Å, with values of Δ(Sn–S) = 0.039 and 0.018 Å for the two C_3S_5 ligands. The two S atoms [S(7) and S(1)] which make the longest bonds to tin are also in the quasi-axial positions with the S(1)–Sn–S(7) angle equal to 149.94(6)°. The bite angles of the C_3S_5 ligands are 84.09(4) and 86.65(4)°.

In contrast to the situation in compound **2** (Q = NEt_4), there are several interanionic $S\cdots S$ contacts in **2** (Q = 4-MeC_5H_4NMe) within the sum of the van der Waals radii of 3.70 Å: $S(3)\cdots S(3^{I})$ (I $2-x, y, 2-z$) [3.404(3) Å], $S(9)\cdots S(9^{II})$ (II $2-x, 1-y, 1-z$) [3.556(3) Å], $S(4)\cdots S(8^{III})$ (III $x-1, y-1, z$) [3.558(2) Å] and $S(7)\cdots S(9^{II})$ [3.636(2) Å]. Thus the two anions pack differently in the two ionic complexes. Different anion–anion interactions were also[18] revealed by X-ray crystallography for the two complexes $[Q][Sb(C_3S_5)_2]$ (Q = NEt_4 or 4-MeC_5H_4NMe).

Solid-state spectral data. The solid-state NMR $\delta(^{119}Sn)$ values for compounds **2** (Q = 4-MeC_5H_4NMe) and **2** (Q = NEt_4) are 57.3 and 32.5, respectively. These values reflect the slight differences in the environments of tin in the two anions, in particular the different separations between the carbonyl groups and the tin atoms in the two anions. The values of ν(C=O) in the IR spectra of **2** (Q = NEt_4) and **2** (Q = 4-MeC_5H_4NMe) in the solid state are essentially the same (1721 and 1720 cm^{-1}, respectively) and are as expected for non-co-ordinated ester groups.

Table 6 Bond lengths (Å) and angles (°) for compound **2** (Q = NEt_4)

S(1)–Sn	2.477(1)	S(2)–Sn	2.511(2)
S(6)–Sn	2.475(2)	S(7)–Sn	2.582(1)
C(7)–Sn	2.147(6)	C(1)–S(1)	1.737(5)
C(2)–S(2)	1.723(6)	C(1)–S(3)	1.750(5)
C(3)–S(3)	1.725(7)	C(2)–S(4)	1.746(6)
C(3)–S(4)	1.710(7)	C(3)–S(5)	1.644(7)
C(4)–S(6)	1.747(6)	C(5)–S(7)	1.735(6)
C(4)–S(8)	1.739(6)	C(6)–S(8)	1.715(6)
C(5)–S(9)	1.749(6)	C(6)–S(9)	1.731(6)
C(6)–S(10)	1.649(6)	C(2)–C(1)	1.360(8)
C(5)–C(4)	1.351(8)	C(8)–C(7)	1.510(9)
C(9)–C(8)	1.506(9)	O(1)–C(9)	1.188(8)
O(2)–C(9)	1.281(8)	O(2)–C(10)	1.447(11)
C(11)–N	1.523(8)	C(13)–N	1.513(10)
C(15)–N	1.507(8)	C(17)–N	1.531(9)
C(12)–C(11)	1.517(9)	C(14)–C(13)	1.527(14)
C(16)–C(15)	1.507(10)	C(18)–C(17)	1.459(14)
S(2)–Sn–S(1)	87.84(6)	S(6)–Sn–S(1)	133.63(6)
S(6)–Sn–S(2)	84.48(6)	S(7)–Sn–S(1)	85.13(6)
S(7)–Sn–S(2)	155.39(6)	S(7)–Sn–S(6)	83.42(6)
C(7)–Sn–S(1)	111.4(2)	C(7)–Sn–S(2)	107.8(2)
C(7)–Sn–S(6)	114.5(2)	C(7)–Sn–S(7)	96.7(2)
C(1)–S(1)–Sn	98.8(2)	C(2)–S(2)–Sn	98.0(2)
C(3)–S(3)–C(1)	98.1(3)	C(3)–S(4)–C(2)	98.6(3)
C(4)–S(6)–Sn	97.3(2)	C(5)–S(7)–Sn	95.0(2)
C(6)–S(8)–C(4)	98.4(3)	C(6)–S(9)–C(5)	98.8(3)
S(3)–C(1)–S(1)	117.6(3)	C(2)–C(1)–S(1)	126.9(4)
C(2)–C(1)–S(3)	115.5(4)	S(4)–C(2)–S(2)	116.9(3)
C(1)–C(2)–S(2)	127.8(4)	C(1)–C(2)–S(4)	115.2(4)
S(4)–C(3)–S(3)	112.6(4)	S(5)–C(3)–S(3)	123.5(4)
S(5)–C(3)–S(4)	123.9(4)	S(8)–C(4)–S(6)	118.3(3)
C(5)–C(4)–S(6)	125.0(5)	C(5)–C(4)–S(8)	116.6(5)
S(9)–C(5)–S(7)	119.9(3)	C(4)–C(5)–S(7)	125.7(5)
C(4)–C(5)–S(9)	114.4(4)	S(9)–C(6)–S(8)	111.8(3)
S(10)–C(6)–S(8)	123.3(4)	S(10)–C(6)–S(9)	124.9(4)
C(8)–C(7)–Sn	111.1(4)	C(9)–C(8)–C(7)	113.3(6)
O(1)–C(9)–C(8)	123.3(6)	O(2)–C(9)–C(8)	113.2(6)
O(2)–C(9)–O(1)	123.5(6)	C(10)–O(2)–C(9)	115.0(6)
C(13)–N–C(11)	111.4(5)	C(15)–N–C(11)	106.8(5)
C(15)–N–C(13)	113.7(6)	C(17)–N–C(11)	109.8(5)
C(17)–N–C(13)	105.0(5)	C(17)–N–C(15)	110.3(5)
C(12)–C(11)–N	116.7(6)	C(14)–C(13)–N	110.7(8)
C(16)–C(15)–N	114.2(6)	C(18)–C(17)–N	114.0(8)

Solution spectral data. All the spectral data point to non-co-ordinated ester groups in solution, *e.g.* for compound **2** (Q = NEt_4) the value for $\delta[^{13}C(CO)]$ is 175.7 in acetone: values for non-co-ordinated carbonyl groups in estertin species in solution are generally between δ 174 and 176. The $\delta[^{13}C(CO)]$ values for co-ordinated carbonyl groups are at lower field, *e.g.* for $Sn(CH_2CH_2CO_2Me)_2(C_3S_5)$ and $SnCl_2(S_2CNMe_2)(CH_2CH_2CO_2Me)$ are δ 180.9 and 181.0, respectively.

The $\delta(^{119}Sn)$ values in acetone solution for compound **2** (Q = NEt_4) and **2** (Q = 4-MeC_5H_4NMe) are the same (6.0 ± 0.3); the anions clearly have the same average structure in solution. The difference between the solid-state and solution $\delta(^{119}Sn)$ values for **2** (Q = 4-MeC_5H_4NMe) [$\Delta(\delta^{119}Sn)$ = 51.8] is greater than the corresponding differences for **2** (Q = NEt_4) [$\Delta\delta(^{119}Sn)$ = 26.8] and $[NBu_4][SnR(C_3S_5)_2]$ **3** (R = Bu or Ph) (10.6 and 12.5).[16] Differences of *ca.* 10–20 ppm are expected to arise merely from the change of phase; the difference of 51.8 ppm for **2** (Q = 4-MeC_5H_4NMe) is indicative of some structural change at tin on dissolution.

Structure comparisons of estertin compounds

With appropriate numbers of donor atoms, the estertin compounds exhibit a tendency to become six-co-ordinated in the solid state, although in the case of $Sn(S_2CNMe_2)_2(CH_2CH_2CO_2Me)_2$ if weak interactions are also considered the co-ordination number becomes even higher at seven, see Table 1. Exceptions to six- (and seven-) co-ordinate complexes are four-co-ordinate $[(MeO_2CCH_2CH_2)_2SnS]_3$[9] and the five-co-ordinate species, $SnCl(S_2CNMe_2)(CH_2CH_2CO_2Me)_2$ **4**,[11] $[(MeO_2CCH_2CH_2)(Me_2NCS_2)SnS]_2$,[9] and the anionic complexes **2**. In all these co-ordinatively unsaturated species the $RO_2CCH_2CH_2$ group remains unidentate. Clearly the tin centre is not sufficiently electron deficient to attract the carbonyl units. The two complexes $SnCl_2(CH_2CH_2CO_2Me)_2$ **5**[2] and **1** (R = Me) have similar octahedral geometries at tin. If the Sn–O bond lengths [2.522 (in **5**) and 2.629 Å (in **1**)] can be taken as indications of the strengths of the tin–oxygen interactions, then it appears that the C_3S_5 ligand is less electron withdrawing than is the combination of the two chloride ions.

For complexes in which the estertin group is clearly chelating (*i.e.* those in which the intramolecular Sn–O distance is less than 2.9 Å), the bite angle of the $RO_2CCH_2CH_2$ group is found to correlate with the Sn–O bond length, Fig. 7. The five-membered chelate rings in these complexes adopt envelope conformations. The oxygen atoms of the carbonyl groups in **4** and **2** (Q = 4-MeC_5H_4NMe) are directed towards the tin atoms but the tin–oxygen separations, 2.942(5) and 3.154(6) Å, are outside the limit normally accepted for Sn–O bonding. However, even for these compounds, the Sn···O and O···Sn–C data also fit the correlation, see Fig. 7. Furthermore, in the compounds $SnX_2\{HB(pz)_3\}(CH_2CH_2CO_2Me)$ (X = NCS or Cl; pz = pyrazol-1-yl) the Sn···O separations are considerably greater,[6] 3.736(5) (X = NCS) and 4.04(1) Å (X = Cl), but

Table 7 Atomic coordinates (× 10^4) for non-hydrogen atoms with e.s.d.s in parentheses for compound **2** (Q = 4-MeC_5H_4NMe)

Atom	*X/a*	*Y/b*	*Z/c*
Sn	10 172.2(5)	3 157.6(3)	7 180.9(2)
S(1)	10 949(2)	2 720(1)	8 678(1)
S(2)	8 948(2)	885(1)	6 516.0(9)
S(3)	9 074(2)	720(1)	9 286.1(9)
S(4)	7 403(2)	−830(1)	7 485.6(9)
S(5)	6 707(2)	−1 647(1)	9 107(1)
S(6)	13 201(2)	4 389(1)	7 578.0(8)
S(7)	10 601(2)	2 904(1)	5 544.9(9)
S(8)	14 527(2)	6 233(1)	6 640.7(9)
S(9)	12 234(2)	5 002(1)	4 937.4(9)
S(10)	14 718(2)	7 309(1)	5 094(1)
O(1)	6 678(5)	2 895(3)	8 217(2)
O(2)	6 911(6)	4 383(4)	9 556(3)
N(11)	13 302(6)	180(4)	6 822(3)
C(1)	9 561(7)	1 273(5)	8 384(3)
C(2)	8 759(7)	558(4)	7 543(3)
C(3)	7 679(7)	−640(5)	8 646(4)
C(4)	13 122(7)	4 888(5)	6 604(3)
C(5)	12 063(7)	4 285(5)	5 790(3)
C(6)	13 885(7)	6 238(5)	5 528(4)
C(7)	8 434(8)	4 485(5)	7 401(4)
C(8)	8 139(8)	4 961(5)	8 391(4)
C(9)	7 164(7)	3 951(5)	8 692(3)
C(10)	5 928(9)	3 481(6)	9 892(4)
C(11)	14 001(8)	969(5)	6 289(4)
C(12)	12 224(8)	−904(5)	6 374(3)
C(13)	11 600(8)	−1 693(5)	6 846(4)
C(14)	12 060(7)	−1 368(5)	7 780(4)
C(15)	13 128(8)	−234(6)	8 223(3)
C(16)	13 730(8)	529(5)	7 744(4)
C(17)	11 444(9)	−2 249(6)	8 290(4)

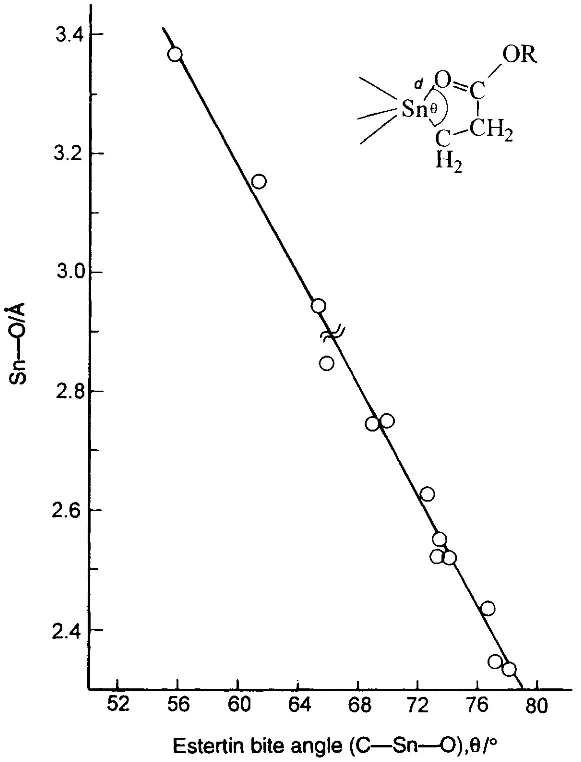


Fig. 7 Plot of the Sn–O bond length against the C–Sn–O bite angle for estertin compounds

Table 8 Bond lengths (Å) and angles (°) for compound **2** (Q = 4-MeC_5H_4NMe)

Sn–S(1)	2.523(1)	S(4)–C(2)	1.751(5)	S(10)–C(6)	1.646(5)	C(4)–C(5)	1.357(7)
Sn–S(2)	2.484(1)	S(4)–C(3)	1.725(5)	O(1)–C(9)	1.190(6)	C(7)–C(8)	1.523(8)
Sn–S(6)	2.509(1)	S(5)–C(3)	1.660(5)	O(2)–C(9)	1.332(6)	C(8)–C(9)	1.506(7)
Sn–S(7)	2.527(1)	S(6)–C(4)	1.750(5)	O(2)–C(10)	1.450(7)	C(12)–C(13)	1.384(8)
Sn–C(7)	2.151(6)	S(7)–C(5)	1.728(5)	N(11)–C(11)	1.474(7)	C(13)–C(14)	1.370(8)
S(1)–C(1)	1.748(5)	S(8)–C(4)	1.741(5)	N(11)–C(12)	1.340(7)	C(14)–C(15)	1.375(8)
S(2)–C(2)	1.746(5)	S(8)–C(6)	1.734(6)	N(11)–C(16)	1.350(7)	C(14)–C(17)	1.504(8)
S(3)–C(1)	1.745(5)	S(9)–C(5)	1.725(6)	C(1)–C(2)	1.342(7)	C(15)–C(16)	1.364(8)
S(3)–C(3)	1.721(5)	S(9)–C(6)	1.725(6)				
S(1)–Sn–S(2)	86.65(4)	C(2)–S(4)–C(3)	97.6(2)	S(2)–C(2)–C(1)	126.2(4)	S(9)–C(6)–S(10)	124.1(3)
S(1)–Sn–S(6)	83.74(4)	Sn–S(6)–C(4)	96.4(2)	S(4)–C(2)–C(1)	116.0(4)	Sn–C(7)–C(8)	114.2(4)
S(2)–Sn–S(6)	133.42(5)	Sn–S(7)–C(5)	96.1(2)	S(3)–C(3)–S(4)	112.7(3)	C(7)–C(8)–C(9)	112.3(5)
S(1)–Sn–S(7)	149.94(6)	C(4)–S(8)–C(6)	98.3(2)	S(3)–C(3)–S(5)	123.1(3)	O(1)–C(9)–O(2)	123.9(5)
S(2)–Sn–S(7)	82.00(4)	C(5)–S(9)–C(6)	98.6(3)	S(4)–C(3)–S(5)	124.2(3)	O(1)–C(9)–C(8)	124.3(5)
S(6)–Sn–S(7)	84.09(4)	C(9)–O(2)–C(10)	115.4(4)	S(6)–C(4)–S(8)	119.2(3)	O(2)–C(9)–C(8)	111.7(4)
S(1)–Sn–C(7)	107.3(2)	C(11)–N(11)–C(12)	118.8(4)	S(6)–C(4)–C(5)	124.9(4)	N(11)–C(12)–C(13)	120.4(5)
S(2)–Sn–C(7)	119.1(2)	C(11)–N(11)–C(16)	121.3(4)	S(8)–C(4)–C(5)	115.9(4)	C(12)–C(13)–C(14)	120.4(5)
S(6)–Sn–C(7)	107.3(2)	C(12)–N(11)–C(16)	119.9(5)	S(7)–C(5)–S(9)	118.8(3)	C(13)–C(14)–C(15)	117.8(5)
S(7)–Sn–C(7)	102.6(2)	S(1)–C(1)–S(3)	116.7(3)	S(7)–C(5)–C(4)	125.9(4)	C(13)–C(14)–C(17)	120.5(5)
Sn–S(1)–C(1)	96.7(2)	S(1)–C(1)–C(2)	127.5(4)	S(9)–C(5)–C(4)	115.3(4)	C(15)–C(14)–C(17)	121.7(5)
Sn–S(2)–C(2)	98.0(2)	S(3)–C(1)–C(2)	115.7(4)	S(8)–C(6)–S(9)	111.8(3)	C(14)–C(15)–C(16)	120.9(5)
C(1)–S(3)–C(3)	98.0(2)	S(2)–C(2)–S(4)	117.8(3)	S(8)–C(6)–S(10)	124.1(3)	N(11)–C(16)–C(15)	120.6(5)

still for these complexes the Sn···O and O···Sn–C data [42.8 (X = Cl) and 49.3° (X = NCS)] also fall on the linear plot.

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References

1 R. E. Hutton and V. Oakes, *Adv. Chem. Ser.*, 1976, **157**, 123; R. E. Hutton, J. W. Burley and V. Oakes, *J. Organomet. Chem.*, 1978, **156**, 369.

2 P. G. Harrison, T. J. King and M. A. Healey, *J. Organomet. Chem.*, 1979, **182**, 17.

3 R. A. Howie, E. S. Paterson, J. L. Wardell and J. W. Burley, *J. Organomet. Chem.*, 1986, **304**, 301.

4 M. Gielen, H. Pan and E. R. T. Tiekink, *Bull. Soc. Chim. Belg.*, 1993, **102**, 447.

5 O.-S. Jung, J. H. Jeong and Y. S. Sohn, *J. Organomet. Chem.*, 1990, **399**, 235.

6 O.-S. Jung, J. H. Jeong and Y. S. Sohn, *Acta Crystallogr., Sect. C*, 1990, **46**, 31.

7 O.-S. Jung, J. H. Jeong and Y. S. Sohn, *Polyhedron*, 1989, **8**, 1413.

8 O.-S. Jung, J. H. Jeong and Y. S. Sohn, *Organometallics*, 1991, **10**, 761.

9 O.-S. Jung, J. H. Jeong and Y. S. Sohn, *Polyhedron*, 1989, **8**, 2557.

10 P. Harston, R. A. Howie, G. P. McQuillan, J. L. Wardell, E. Zanetti, S. M. S. V. Doidge-Harrison, N. S. Stewart and P. J. Cox, *Polyhedron*, 1991, **10**, 1085.

11 O.-S. Jung, J. H. Jeong and Y. S. Sohn, *Organometallics*, 1991, **10**, 2217.

12 S. W. Ng, C. Wei, V. G. Kumar Das, J. P. Charland and F. E. Smith, *J. Organomet. Chem.*, 1989, **364**, 343.

13 S. W. Ng, C. Wei, V. G. Kumar Das, G. B. Jameson and R. J. Butcher, *J. Organomet. Chem.*, 1989, **365**, 75.

14 R. A. Howie, E. S. Patterson, J. L. Wardell and J. W. Burley, *J. Organomet. Chem.*, 1983, **259**, 71.

15 S. M. S. V. Doidge-Harrison, R. A. Howie, J. T. S. Irvine, G. M. Spencer and J. L. Wardell, *J. Organomet. Chem.*, 1991, **414**, C5.

16 S. M. S. V. Doidge-Harrison, R. A. Howie, J. T. S. Irvine, G. M. Spencer and J. L. Wardell, *J. Organomet. Chem.*, 1992, **436**, 23.

17 S. M. S. V. Doidge-Harrison, R. A. Howie, J. T. S. Irvine and J. L. Wardell, *Polyhedron*, 1992, **11**, 2223.

18 S. M. S. V. Doidge-Harrison, J. T. S. Irvine, G. M. Spencer, J. L. Wardell, M. Wei, P. Ganis and G. Vialle, *Inorg. Chem.*, 1995, **34**, 4581.

19 L. Valade, J. P. Legros, M. Bousseau and M. Garbaukas, *J. Chem. Soc., Dalton Trans.*, 1985, 783.

20 G. M. Sheldrick, (*a*) *Acta Crystallogr., Sect. A*, 1990, **46**, 467; (*b*) SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

21 M. C. Burla, M. Camalli, G. Cascarino, C. Giacovazzo, G. Polidori, R. Spagno and D. Viterbo, *J. Appl. Crystallogr.*, 1989, **22**, 389.

22 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, *CRYSTALS User Guide*, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1985.

23 G. M. Spencer, Ph.D. Thesis, University of Aberdeen, 1994.

24 R. O. Day, J. M. Holmes, S. Shafieezad, V. Chandrasekhar and R. R. Holmes, *J. Am. Chem. Soc.*, 1988, **110**, 5377.

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