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Some further studies of estertin compounds. Crystal structures of $[NEt_4][MeO_2CCH_2CH_2Sn(dmio)_2]$ (dmio = 1,3-dithiole-2-one-4,5-dithiolato) and $(MeO_2CCH_2CH_2)_2SnX_2[X_2 = I_2$, $(NCS)_2$ or Cl, Br]

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Abstract—Estertin compounds, $(MeO_2CCH_2CH_2)_2SnX_2$ [$X_2 = I_2$ (**2**); $X_2 = Br_2$ (**9**); X_2 = Cl,Br (**4**); or $X_2 = (NCS)_2$ (**3**)] have been obtained by halide exchange reactions of $(MeO_2CCH_2CH_2)_2SnCl_2$. Crystal structure determinations of **2**–**4** revealed chelating $MeO_2CCH_2CH_2$ units with distorted octahedral geometries at tin. The Sn—O bond lengths in the isothiocyanato complex, **3**, are shorter [2.390(11) to 2.498(12), mean 2.439 Å], with the chelate bite angles, C—Sn—O, larger [74.3(7) to 78.2(6), mean 76.0°] than those in the halide analogues **2** and **4** [Sn—O = 2.519(2) to 2.541(8), mean 2.530 Å; C—Sn—O 72.8(3) to 73.9(4), mean 73.3°]. ^1H, ^{13}C and ^{119}Sn NMR and IR spectra of **2**–**4** and **9** were determined in $CDCl_3$ solution: the NMR spectra of $(MeO_2CCH_2CH_2)_2SnX_2$ show the following trends: (i) both δ^1H_α and $\delta^{13}C_\alpha$, increase and (ii) both $^2J(Sn—H)$ and $^1J(Sn—C)$ decrease in the sequence $X_2 = (NCS)_2$, Cl_2, ClBr, Br_2 and I_2. The $MeO_2CCH_2CH_2$ and dmio groups (dmio = 1,3-dithiole-2-one-4,5-dithiolato) are all chelating groups in $(MeO_2CCH_2CH_2)_2Sn(dmio)$ (**5**). As shown by X-ray crystallography, the tin atom in the anion of solid $[Q][MeO_2CCH_2CH_2Sn(dmio)_2]$ **6** ($Q = NEt_4$) forms 5 strong bonds [to C and the 4 thiolato S atoms, Sn—S 2.459(2) to 2.559(2) Å], arranged in a near trigonal bipyramidal array. There is an additional intramolecular, but weaker, interaction with the carbonyl oxygen atom [Sn—O = 3.111(5) Å]; $\nu(C=O) = 1714\ cm^{-1}$ in solid **6** ($Q = NEt_4$). NMR spectra of **5** and **6** are also reported. © 1997 Elsevier Science Ltd

Keywords: estertin compounds; organotin complexes; crystallography; 1,3-dithiole-2-one-4,5-dithiolato (dmio) complexes.

Estertin chlorides, $(RO_2CCH_2CH_2)_2SnCl_2$ (**1**) and $RO_2CCH_2CH_2SnCl_3$, are readily available from reactions of $RO_2CCH{=}CH_2$ with Sn/HCl and $SnCl_2$/HCl, respectively [1]; $(RO_2CCH_2CH_2)_2SnX_2$ (X = Br or I) are similarly obtained using Sn/HX. Various estertin compounds have been produced from the chlorides. As the $RO_2CCH_2CH_2$ moieties have the potential to act as *C,O*-chelating groups, many studies of the estertin compounds have been concerned with the coordination chemistry and the strength of the Sn···O interactions, both in solution and in the solid state [2–15]. While the crystal structure has been determined for the chloride, **1** (R = Me) [2,3], no diffraction studies have been reported for other halide or pseudohalide derivatives, $(RO_2CCH_2CH_2)_2SnX_2$. In order to compare the effects of different halide and pseudohalides on the chelating abilities of the $MeO_2CCH_2CH_2$ group, the crystal structures of $(MeO_2CCH_2CH_2)_2SnI_2$ (**2**), $(MeO_2CCH_2CH_2)_2Sn(NCS)_2$ (**3**) and

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dmit **dmio**

Fig. 1. The dmio and dmit ligands.

$(MeO_2CCH_2CH_2)_2SnClBr$ (**4**) have been determined. In addition, $(MeO_2CCH_2CH_2)_2Sn(dmio)$ (**5**) and $[Q][MeO_2CCH_2CH_2Sn(dmio)_2]$ (**6**; Q = PPh_4, NEt_4 or 1,4-Me_2-pyridinium) (dmio = 1,3-dithiole-2-one-4,5-dithiolato) have been investigated and their properties compared with those recently reported [15] for $(MeO_2CCH_2CH_2)_2Sn(dmit)$ (**7**) and $[Q][MeO_2CCH_2CH_2Sn(dmit)_2]$, (**8**; Q = NEt_4 or 1,4-Me_2-pyridinium), (dmit = 1,3-dithiole-2-thione-4,5-dithiolato), Fig. 1.

EXPERIMENTAL

NMR spectra were obtained on a Bruker 250 MHz instrument; IR spectra were recorded on Philips Analytical PU9800 and Nicolet 205 Fourier-transform spectrometers. X-ray data for **3** and **4** were collected on a Nicolet P3 instrument, while data for **2** and **6** (Q = NEt_4) by the EPSRC data collection service, based at the University of Wales, Cardiff.

The compounds, $(MeO_2CCH_2CH_2)_2SnCl_2$ [1], $MeO_2CCH_2CH_2SnCl_3$ [1] and $[Q]_2$ $[Zn(dmio)_2]$, [Q = NEt_4, PPh_4 or 1,4-Me_2-pyridinium] [16] were prepared as previously reported.

Halide exchange reactions of (**1**; R = Me)

Solutions of **1** (R = Me) (0.005 mol) in Me_2CO (25 cm^3) and NaX (X = I or SCN, 0.025 mol; X = Br, 0.05 mol) in Me_2CO (25 cm^3) were mixed and gently heated for 30–45 min (X = I or SCN) or 90 min (X = Br), cooled and filtered. The filtrate was evaporated to leave a solid residue, which was taken up in $CHCl_3$, filtered and the filtrate evaporated to leave a solid residue, which was repeatedly recrystallised from ethanol to ethyl acetate. Details, including NMR spectral data, of the compounds are provided in Table 1. The elemental analyses of all compounds were in agreement with the expected values. Partial chloride–bromide exchanges resulted when reduced reaction times and reduced amounts of NaX were employed.

$(MeO_2CCH_2CH_2)_2Sn(dmio)$ **5**

Solutions of **1** (R = Me) (0.73 g, 2 mmol) in acetone (20 cm^3) and $[NEt_4]_2[Zn(dmio)_2]$ (0.685 g, 1 mmol) in acetone (20 cm^3) were mixed and maintained at room temperature. After 1 h, the reaction mixture was filtered and the filtrate evaporated to leave a solid residue, which, after washing with water, was crystallised from acetone to give **5** as an orange-red crystalline solid; yield 0.56 g, 58%; m.p. 108–110°C. Analysis. Found: C, 28.2; H, 3.0. Calc. for $C_{11}H_{14}O_5S_4Sn$: C, 27.9; H, 3.0%. ^1H NMR ($CDCl_3$, 250 MHz) δ: 1.86 [t, 4H, J(H—H) = 7.2 Hz, J (^{119}Sn—^1H) = 76.9 Hz, J(^{117}Sn—^1H) = 73.6 Hz, CH_2Sn], 2.94 [t, 4H, J(H—H) = 7.2 Hz, J(^{119}Sn—^1H) = 132.4 Hz, J(^{117}Sn—^1H) = 126.6 Hz, CH_2CO], 3.78 [s, 3H, OMe]. ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 18.9 [J(^{119}Sn—^{13}C) = 570 Hz, J(^{117}Sn—^{13}C) = 544 Hz), $SnCH_2$], 28.4 [J($^{119,117}Sn$—^{13}C) = 44.7 Hz, CH_2CO], 53.6 [OMe], 116.7 [C=C], 180.6 J($^{119,117}Sn$—^{13}C) = 39 Hz, CH_2CO], 192.3 [S_2C=O]. ^{119}Sn NMR ($CDCl_3$, 93.3 MHz) δ: 48.2. IR (KBr, cm^{-1}): 1692, 1668, 1631, 1621 [*C*=*O*].

$[NEt_4][MeO_2CCH_2CH_2Sn(dmio)_2]$ **6** (Q = NEt_4)

A mixture of $MeO_2CCH_2CH_2SnCl_3$ (0.312 g, 1.00 mmol) and $[NEt_4]_2[Zn(dmio)_2]$ (0.685 g, 1.00 mmol) in MeOH (20 cm^3) was agitated in an ultrasonic bath for 30 min. The reaction mixture was filtered to give an orange solid, which was recrystallised from MeOH to give orange needles of **6** (Q = NEt_4); yield, 0.28 g, 61%; m.p. 88–89°C. Analysis. Found: C, 31.0; H, 3.9; N, 2.0. Calc. for $C_{18}H_{27}NO_4S_8Sn$: C, 31.0; H, 3.9; N, 2.0%. ^1H NMR ($CDCl_3$, 250 MHz) δ: 1.37 [tt, 12H, J(H—H) = 7.4 Hz, J(H—N) = 1.8 Hz, Me of cation], 2.00 [t, 2H, J(H—H) = 7.4 Hz, J($^{119,117}Sn$—^1H) = 72 Hz, CH_2Sn], 2.87 [t, 2H, J(H—H) = 7.4 Hz, J(^{119}Sn—^1H) = 158 Hz, J(^{117}Sn—^1H) = 151 Hz, $COCH_2$], 3.28 [q, 8H, J(H—H) = 7.3 Hz, CH_2 of cation], 3.70 [s, 3H, OMe]. ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 7.66 [Me of cation], 29.6 [J($^{119,117}Sn$—^{13}C) = 41.0 Hz, CH_2CH_2Sn], 29.6 [[J(^{119}Sn—^{13}C) = 622 Hz, J(^{117}Sn—^{13}C) = 595 Hz, CH_2Sn], 52.1 [OMe], 52.7 [J(C—N) = 3.0 Hz, NCH_2], 117.5 [C=C], 175.1 [$J^{119,117}$Sn—^{13}C) = 83.0 Hz, CH_2CO], 190.5 [S_2C=O]. ^{119}Sn NMR ($CDCl_3$, 93.3 MHz) δ: −51.3. IR(KBr, cm^{-1}): 1713 (CH_2*C*=*O*), 1672 and 1616 (S_2*CO*). IR($CHCl_3$ solution, cm^{-1}): 1727 (v.br).

[1,4-Me_2-pyridinium]$[MeO_2CCH_2CH_2Sn(dmio)_2]$ **6** (Q = 1,4-Me_2-pyridinium)

This was obtained from $MeO_2CCH_2CH_2SnCl_3$ (0.312 g, 1 mmol) and [1,4-Me_2-pyridinium]$_2$ $[Zn(dmio)_2]$ (0.641 g, 1 mmol) by a similar method to that used for **6** (Q = NEt_4) as orange-yellow crystals, yield 0.216 g, 58%; m.p. 104–6°C. Analysis. Found: C, 30.1; H, 2.5; N, 2.6. Calc. for $C_{17}H_{17}NO_4S_8Sn$: C, 30.3; H, 2.5; N, 2.1%. ^1H NMR (CD_3SOCD_3, 250 MHz) δ: 1.67 [t, 2H, J(*H*—H) = 7.0 Hz, J(^{119}Sn—^1H) = 79.2 Hz, J(^{117}Sn—^1H) = 73.6 Hz, 2.58 [s, 3H, Me], 2.63 [t, 2H, J(H—H) = 7.2 Hz, J(^{119}Sn—^1H) = 132.1 Hz, J(^{117}Sn—^1H) = 126.6 Hz, 3.33 [s, 3H, Me of cation], 3.57 [s, 3H, Me of cation],

Table 1. Spectral data for estertin compounds, $(MeO_2C—C_\beta H_2—C_\alpha H_2)_2SnX_2$

Compound No.	X_2	m.p. (°C)	ν(CO) KBr cm^{-1}	δ(^{1}H) [$J(^{119}$Sn—^{1}H), $J(^{117}$Sn—^{1}H)]			δ(^{13}C) J[(Sn—)]				δ(^{119}Sn)	
				H_α[a]	H_β[a]	CO_2Me	C_α	C_β	C=O	OMe	Others	
3	$(NCS)_2$	124–6	1666	1.83 [109, 104]	2.82 [151, 147]	3.90	18.8 [865, 827][b]	28.0 [53][c]	182.7 [70, 67][b]	54.7	143.3 [14][d] (NCS)	−257.3 [113][e]
1 (R = Me)	Cl_2	130 lit[1] 132	1677	1.94 [102, 97]	2.93 [154, 147]	3.83	24.2 [786, 751][b]	28.6 [54][c]	181.3	53.8		−66±1.5
9	Br_2	135 lit[1] 137	1675	2.08 [97, 93]	2.92 [157, 150]	3.83	25.9 [743, 710][b]	29.1 [56][c]	181.0 [56][c]	53.8		−85.1
4	Cl,Br[f]	126–32	1676	1.95[g] [*ca.* 100] 2.01[h] [*ca.* 100] 2.08[i] [*ca.* 100]	2.93 [155, 148]	3.83	24.2[g] [787, 751][b] 25.4[h] [767, 732][b] 26.4[i] [744, 712][b]	28.6[g] 28.8[h] 29.1[i]	181.4[g] 181.2[h] 181.1[i]	53.9		−65.1 −75.5 −86.0
2	I_2		1677	2.23 [87, 83]	2.82 [158, 151]	3.81	27.5 [663, 633][b]	30.4 [55][c]	180.3 [50][c]	53.8		−164.6
6	dmio	108–10	1677	1.86 [77, 74]	2.93 [133, 127]	3.78	18.9 [570, 544][b]	28.4 [45][c]	180.6 [39][c]	53.6	116.7 (C=C) 192.3 (S_2C=O)	48.2
8	dmit[j]	102–4	1674	1.93 [79, 76]	2.98 [133, 127]	3.81	19.6[k] [574, 559][b]	28.8[k] [45][c]	180.9[k] [47][c]	53.8[k]	129.6[k] (C=C) 210.3[k] (C=S)	87.7[k]

[a] J(H—H) = *ca.* 7.2 Hz.

[b] [$J(^{119}$Sn—^{13}C), $J(^{117}$Sn—^{13}C] values.

[c] [$J(^{117,119}$Sn—^{13}C)] values.

[d] [$J(^{13}$C—N)].

[e] [[$J(^{119}$Sn–N)]].

[f] Mixed halide ([Br]·[Cl] = 1 : 1).

[g,h,i] Peak heights = 1 : 2 : 1.

[j] [15].

[k] In CD_3COCD_3.

7.94 [d, 2H, $J(H—H) = 6.5$ Hz] and 8.78 [d, 2H, $J(H—H) = 6.5$ Hz] (aryl-H). ^1H NMR ($CDCl_3$, 250 MHz) δ: 1.95 [t, 2H, $J(H—H) = 7.3$ Hz, $J(^{119}Sn—^1H) = 72$ Hz, $J(^{117}Sn—^1H) = 69$ Hz, CH_2Sn], 2.69 [s, 3H, Me], 2.83 [t, 2H, $J(H—H) = 7.3$ Hz, $J(^{119}Sn—^1H) = 166$ Hz, $J(^{117}Sn—^1H) = 158$ Hz, CH_2CO], 3.69 [s, 3H, Me], 4.40 [s, 3H, Me of cation], 7.79 [d, 2H, $J(H—H) = 6.5$ Hz] and 8.51 [d, 2H, $J(H—H) = 6.5$ Hz] (aryl-H). ^{13}C NMR (CD_3SOCD_3, 62.9 MHz) δ: 23.0 [Me], 32.2 [$J(^{119}Sn—^{13}C) = 569$ Hz, $J(^{117}Sn—^{13}C) = 544$ Hz), $SnCH_2$], 28.8 [$J(^{119,117}Sn—^{13}C) = 44.7$ Hz, CH_2CO], 53.6 [OMe], 119.7 [C=C], 129.6, 146.1, 159.9, 176.3 [CH_2CO], 191.7 [$S_2C=O$].

$[PPh_4][MeO_2CCH_2CH_2Sn(dmio)_2]$ **6** ($Q = PPh_4$)

This was obtained from $MeO_2CCH_2CH_2SnCl_3$ (0.312 g, 1 mmol) and $[PPh_4]_2$ $[Zn(dmio)_2]$ (1.10 g, 1 mmol) by a similar method to that used for **6** ($Q = NEt_4$) as orange-yellow crystals. ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 29.2 [CH_2CH_2Sn], 30.0 [CH_2Sn], 52.1 [OMe], 117.4 [$J(C—P) = 88.8$ Hz, C_i], 117.7 [C=C], 130.8 [$J(P—C)$ 12.7 Hz, C_o], 134.7 [$J(P—C)$ 17.5 Hz, C_m], 135.8 [$J(P—C)$ 2 Hz, C_p], 175.1 [$CH_2\mathit{C}O$], 190.5 [$S_2\mathit{C}=O$]. ^{119}Sn NMR ($CDCl_3$, 93.3 MHz) δ: -49.3. IR(KBr, cm^{-1}): 1728 ($CH_2\mathit{C}=\mathit{O}$), 1662 and 1608 ($S_2\mathit{CO}$).

Crystal structure determination of **3** *and* **4**

The samples used in the crystallographic determinations were recrystallised from ethyl acetate for **3** and ethanol for **4**. Data collection and cell refinement utilised Nicolet P3 software [17]. Data collection used ω scan rates of 5.33 ($I_p < 150$) to 58.6 ($I_p > 2500$)° min^{-1}, where I_p was the prescan intensity. Scan widths were 2.4 to 2.8° 2θ. Data reduction used the RDNIC program [18]. All computations were performed on the SUN SPARC server (UNIX operating system) of the Computing Centre of the University of Aberdeen. Structure solution and refinement software involved SHELXS86 [19] and SHELX76 [20]. Molecular graphics were prepared using PLOTAID [21] and ORTEX [22] software, while data for publication utilised XPUB software [23].

Crystal structure and refinement data are given in Table 2.

Compound **3**. The structure of **3** was solved by Patterson methods to yield the tin positions. The positions of the remaining non-H were determined from a sequence of electron density and difference map calculations. Refinement was by full matrix least squares. All non-H were refined anisotropically. H atoms were placed in calculated positions with C—H = 0.95 Å and refined riding upon the C atoms to which they were attached with separate group Uiso's for methylene and methyl H [refined values 0.15(2) and 0.16(3) Å^2 respectively].

Compound **4**. The positional parameters for the isostructural dichloride analogue, **1** (R = Me) [2,3], were extracted from the Cambridge Structural Database [24], available through the EPSRC's Chemical Database Service at Daresbury [25] and adopted for the refinement by full matrix least squares of the structure of **4**. A significant feature of the structure of **4** is the complete disorder over the halide sites. These sites, X(1) and X(2), were modelled as Br with the site occupancy factor fixed at 0.743 to provide the electron density corresponding to Br and Cl present in the same site in equal proportions but otherwise refined anisotropically in the normal manner. All other non-H atoms were also refined anisotropically. The H-atoms were placed in calculated positions with C—H = 0.95 Å and refined with a riding model with separate group Uiso's for methylene and methyl H [refined values 0.094(17) and 0.110(23) Å^2, respectively].

Crystal structure determinations of **2** *and* **6** ($Q = NEt_4$)

The colourless crystal of **2**, used in the analysis, was grown from ethyl acetate, while the orange needles of **6** ($Q = NEt_4$) were obtained from MeOH. Data were collected on a Delft Instruments Fast diffractometer with monochromated Mo-K_α radiation. Corrections were made for Lorentz and polarization effects. Corrections were made for absorptions effects for **2** using the empirical absorption correction program XABS2 [26]. The positions of the tin and iodine atoms were located from a Patterson vector map using SHELX86 [19]. The positions of the remaining non-hydrogen atoms were located on successive difference Fourier maps using SHELX93 [27]. The positions of the hydrogen atoms were calculated from geometrical calculations. During refinement hydrogens were allowed to ride on their attached carbon atoms. Full-matrix least-squares calculations with anisotropic temperature factors for non-hydrogen atoms and common isotropic temperature factors according to type (methyl, aromatic, etc.) for hydrogen atoms were calculated. Molecular diagrams were obtained by the ORTEX [22] and ZORTEP [28] programs.

RESULTS AND DISCUSSION

Synthesis and spectra of $(MeO_2CCH_2CH_2)_2SnX_2$

Exchange reactions of **1** (R = Me) with excess sodium halides and pseudohalides in acetone were used to produce $(MeO_2CCH_2CH_2)_2SnX_2$ [X = I (**2**); X = Br (**9**) X = NCS (**3**)]; analytically pure products, **2** and **3**, could be isolated after several recrystallisations. NMR data for the halides and pseudohalide are given in Table 1. To obtain pure **9**, larger excesses of the exchanging halide (Br^-) and longer reaction times were required, compared to the con-

Table 2. Crystal data and structure refinement

	2	**3**	**4**	**6** (Q = NEt_4)
Empirical formula	$C_8H_{14}I_2O_4Sn$	$C_{10}H_{14}N_2O_4S_2Sn$	$C_8H_{14}BrClO_4Sn$	$C_{18}H_{27}NO_4S_8Sn$
Formula weight	546.70	409.05	408.25	696.58
Temperature (K)	298	298	298	293
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P1$	$P2_1/n$	$I2/c$
Unit cell dimensions a (Å)	8.1775(12)	8.869(3)	8.082(3)	20.393(4)
b (Å)	17.0205(8)	11.983(5)	16.161(6)	10.668(3)
c (Å)	10.830(4)	16.174(9)	10.290(3)	26.0419(7)
α (°)	90	99.61(4)	90	90
β (°)	98.783(9)	90.78(4)	94.92(3)	92.28(5)
γ (°)	90	96.59(3)	90	90
Volume, (Å^3)	1489.8(6)	1682.6(13)	1339.0(8)	5661(2)
Z	4	4	4	8
Density (calculated) (Mg/m^3)	2.437	1.614	2.024	1.635
Absorption coefficient (mm^{-1})	5.853	1.770	5.065	1.518
$F(000)$	1000	808	784	2816
Crystal size (mm)	0.24 × 0.18 × 0.26	0.4 × 0.4 × 0.2	0.5 × 0.16 × 0.16	0.28 × 0.20 × 0.14
θ range for data collection (°)	2.25 to 25.02	max 30	max 30	2.00 to 25.14
Index ranges	$-9 \leqslant h \leqslant 9$ $0 \leqslant k \leqslant 19$ $0 \leqslant l \leqslant 12$	$-11 \leqslant h \leqslant 10$ $-15 \leqslant k \leqslant 15$ $0 \leqslant l \leqslant 22$	$-11 \leqslant h \leqslant 11$ $0 \leqslant k \leqslant 22$ $0 \leqslant l \leqslant 14$	$-22 <= h <= 22$ $-12 <= k <= 11$ $-21 <= l <= 28$
Reflections collected	2269	9873	4308	11409
Independent reflections	2269 [R(int) = 0.0000]	6980 [R(int) = 0.012]	3336 [R(int) = 0.026]	4233 [R(int) = 0.0879]
Observed reflections	[$I > 2s(I)$] 1723	[$F > 4\sigma(F)$] 3175	[$F > 4\sigma(F)$] 2092	[$I > 2s(I)$] 2787
Refinement method	Full-matrix l.s. on F^2	Full-matrix l.s. on F	Full-matrix l.s. on F	Full-matrix l.s. on F^2
Number of parameters	138	357	144	291
Goodness-of-fit	1.044	2.88	0.9232	0.889
Final R indices [$I > 2s(I)$]	$R1 = 0.0673$ $wR2 = 0.1435$	$R = 0.071$ $wR = 0.071$	$R = 0.069$ $wR = 0.070$	$R1 = 0.0452$ $wR2 = 0.1024$
R indices (all data)	$R1 = 0.0784$ $wR2 = 0.1484$			$R1 = 0.0675$ $wR2 = 0.1062$
Final weighting scheme (calc.)	$w = 1/[\sigma^2(F_o)^2+(0.0777P)^2]$ where $P = (F_o^2+2F_c^2)/3$	Unit weights	$w = 1.6636/(\sigma^2F+0.001993 \times F^2)$	$w = 1/[\sigma^2(F_o)^2+(0.0432P)^2]$ where $P = (F_o^2+2F_c^2)/2$
Residual diffraction max (min) (e/Å^3)	2.156^a (−1.391)	1.01^a (−0.74)	2.0^a (−1.82)	1.063^a (−0.543)

[a] Close to Sn.

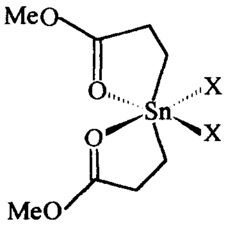
ditions used for **2** and **3**. Several products containing mixed chloride/bromide anions were produced from incomplete exchanges: a crystalline sample, (**4**), with a 1 : 1 chloride : bromide content was selected for X-ray crystallography, see later. The mixed halide species, $(MeO_2CCH_2CH_2)_2SnCl_xBr_{2-x}$, dissolved in organic solvents to give mixtures of all three halide species, $(MeO_2CCH_2CH_2)_2SnCl_2$ **1** (R = Me), $(MeO_2CCH_2CH_2)_2SnClBr$ (**4**) and $(MeO_2CCH_2CH_2)_2SnBr_2$ (**9**). The ^1H NMR spectrum of a $CDCl_3$ solution of crystalline **4** could be divided into three sets of signals in intensity ratios of 1 : 2 : 1. The two lowest intensity sets could be readily assigned to the dibromide **9** and dichloride **1** (R = Me), by comparison with the spectra of authentic compounds. The most intense set of signals, intermediate in δ^1H values, was assigned to the mixed halide. The ^{13}C NMR spectrum could similarly be resolved into three sets of signals. As the signals for each of the individual species are observed in the ^1H, ^{13}C and ^{119}Sn NMR spectra at 25°C, the equilibrium exchange process must be slow on the NMR time scale at that temperature.

Coordinated C═O units in $(MeO_2CCH_2CH_2)_2SnX_2$ [X = I, Br or NCS], see Fig. 2, are indicated by the ν(C═O) values [1670–1680 cm^{-1}], both in solution and in the solid state IR spectra]. Both the NCS units in **3** are bonded to tin *via* N in the solid state as shown by $\nu(NCS) = 2040\ cm^{-1}$ (and confirmed by the X-ray crystallography, see later): and in solution by the nitrogen-tin couplings $[J(^{119}Sn—N) = 113\ Hz]$ in the ^{119}Sn NMR spectrum in $CDCl_3$ solution: a 1 : 2 : 3 : 2 : 1 quintet is observed for the tin signal.

The NMR spectra of $(MeO_2CCH_2CH_2)_2SnX_2$ show the following trends: (i) both δ^1H_α and $\delta^{13}C_\alpha$, increase and (ii) both ^2J(Sn—H) and ^1J(Sn—C) decrease in the sequence $X_2 = (NCS)_2$, Cl_2, ClBr, Br_2, I_2: the sequence of decreasing electron withdrawing ability (electronegativity) of X_2 and also the sequence of the decreasing mean Sn—X bond energies.

Crystal structures of $(MeO_2CCH_2CH_2)_2SnX_2$

General. The compounds, **2** and **4** but not **3**, are isostructural with **1** (R = Me). The compounds exist as discrete molecules, with the tin atoms having distorted octahedral geometries. The $MeO_2CCH_2CH_2$ ligands are bidentate, with the carbonyl oxygen atoms *trans* to the *cis*-halides or pseudohalides (Fig. 2). The atom arrangements and numbering systems for **2** and **4** are shown in Fig. 3, those for **3** in Fig. 4. Selected bond angles and lengths are displayed in Table 3.



$X_2 = Cl_2$ (1)
$X_2 = I_2$ (2)
$X_2 = (NCS)_2$ (3)
$X_2 = Cl,Br$ (4)
$X_2 = Br_2$ (9)

Fig. 2. Chelated $(MeO_2CCH_2CH_2)_2SnX_2$ compounds.

Specific compounds: **2**. The Sn—I bond lengths in **2** are 2.7775(12) and 2.7801(11) Å [Sn—I(1) and Sn—I(2), respectively] and are, as expected, longer than the tin–iodide bond lengths, in tetrahedral, four-coordinate diorganotin diiodides, 2.6749–2.7190 Å [29]. However, these are considerably shorter than the Sn—I bond lengths [2.965(1) and 3.009(1) Å] found in octahedral $[(p\text{-}MeC_6H_4)\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\text{-}C,N,N'\}SnI_2]$, in which the iodide ligands are in a *trans* arrangement [30]. The axial Sn—I bond length, 2.778(2) Å, in the 5-coordinate trigonal bipyramidal (5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuran-5-yl-C,O^3)diiodophenylstannane, (**10**), is comparable to those in **2**; however the equatorial Sn—I bond length, 2.722(2) Å in (**10**) is shorter [31].

Crystal structure of **4**. A significant feature of the structure of **4** is the complete disorder over the halide sites. There is no preferential occupancy of either of the two halide sites. The quoted tin–halide bond lengths [2.501(2) and 2.521(2) Å] were calculated from a model with X = Br but with the occupancy factor set at 0.743 to provide the electron density corresponding to Br and Cl present in the same site in equal proportions. Although the halide sites are distinguishable in terms of the Sn–halide distances, 2.501(2) and 2.521(2) Å for Sn—X(1) and Sn—X(2), respectively, the similarity in the Ueq values [0.0742(7) and 0.0726(7) Å, respectively] suggests that there is no preferential occupancy of them. The Ueq values are noticeably large but this is attributed to the fact that X(1) and X(2) are both attempting to approximate the somewhat diffuse electron density arising from Br^-/Cl^- pairs where the atoms do not coincide exactly, i.e. the Sn—X distances are the mean of distinct Sn—Cl and Sn—Br distances. The distance difference, however, is not sufficiently great to permit refinement of the shared sites in terms of 2 pairs of distinct atoms each of half occupancy.

Crystal structure of **3**. The structure of the isothiocyanato complex **3** is unusual in that four molecules are present in the centrosymmetric triclinic unit cell: the asymmetric unit consists of two independent, octahedral molecules, designated A and B. In each molecule, one of the NCS groups is almost collinear with the N—Sn bond [C(9)—N(1)—Sn 176.9(19) and 171.8(23)° for A and B, respectively], while the other NCS ligand is at a much reduced angle [C(10)—N(2)—Sn 161.8(21) and 148.1(23)°, for the two molecules]. Similar differences between the NCS units were also reported in 7-coordinate $[Me_2Sn(NCS)_2terpyridyl]$ [32], while somewhat smaller differences arise in 6-coordinate $[Ph_2Sn(NCS)_2bipyridyl]$ [33].

This difference in the Sn—N—C angles represents the largest discrepancy in the geometries of molecules,

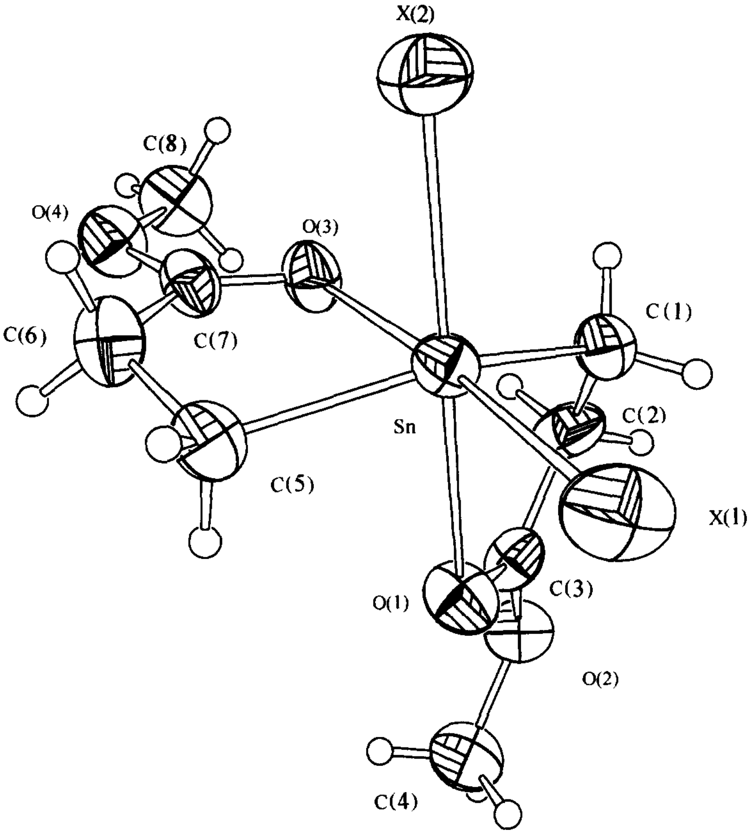


Fig. 3. Perspective view of the molecules of **2** [X(1) = I(1), X(2) = I(2)] and **4** [X(1)/X(2) = Cl/Br] showing the general atom numbering scheme. Non-H atoms are shown as 40% probability ellipsoids and H atoms as spheres of arbitrary radius.

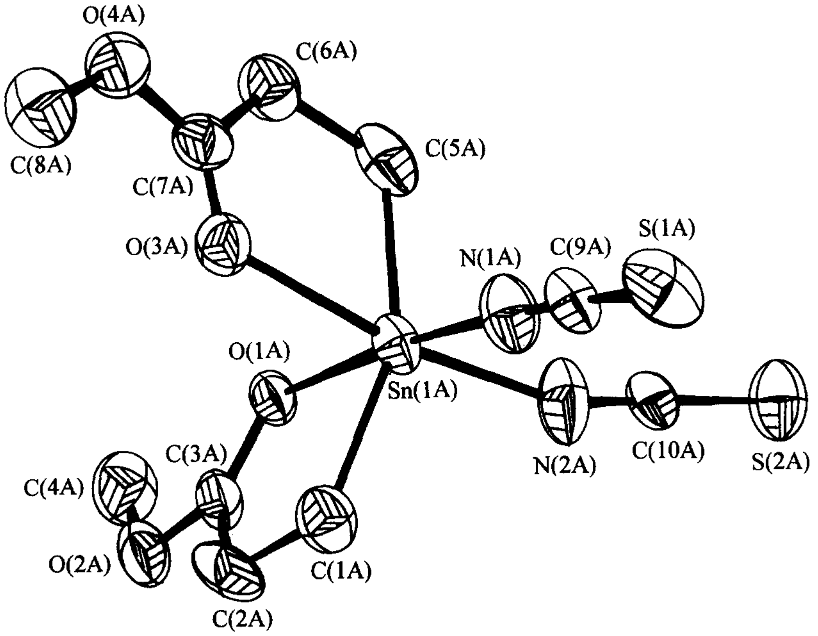


Fig. 4. Molecule A of **3** showing atom labels and 20% probability ellipsoids. Molecule B, although of the opposite land (see text), is virtually identical and uses the same numbering scheme. H have been omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for [(MeO$_2$CCH$_2$CH$_2$)$_2$SnX$_2$]

		3[b]		
	2[a]	mol A	mol B	4[c]
X(1)—Sn	2.7775(12)	2.162(18)	2.096(19)	2.501(2)
X(2)—Sn	2.7801(11)	2.124(16)	2.13(2)	2.521(2)
Sn—O(1)	2.522(8)	2.390(11)	2.443(13)	2.541(8)
Sn—O(3)	2.528(7)	2.498(12)	2.426(13)	2.531(8)
Sn—C(1)	2.123(10)	2.076(17)	2.11(2)	2.119(11)
Sn—C(5)	2.144(11)	2.065(19)	2.08(2)	2.137(12)
C(1)—C(2)	1.52(2)	1.52(2)	1.46(2)	1.504(16)
C(2)—C(3)	1.509(14)	1.48(2)	1.47(3)	1.498(16)
C(5)—C(6)	1.41(2)	1.50(2)	1.49(3)	1.496(18)
C(6)—C(7)	1.47(2)	1.53(3)	1.46(3)	1.485(17)
C(3)—O(1)	1.219(13)	1.223(18)	1.21(2)	1.203(12)
C(7)—O(3)	1.175(11)	1.19(2)	1.18(2)	1.210(13)
C(9)—N(1)		1.11(2)	1.14(2)	
C(9)—S(1)		1.58(2)	1.59(2)	
C(10)—N(2)		1.14(2)	1.15(3)	
C(10)—S(2)		1.568(19)	1.57(2)	
C(1)—Sn—C(5)	144.0(5)	155.6(7)	150.7(9)	144.6(5)
C(5)—Sn—O(1)	79.6(4)	86.0(5)	85.6(7)	82.1(4)
C(5)—Sn—O(3)	73.9(4)	75.3(6)	76.2(7)	73.4(4)
C(1)—Sn—X(1)	104.4(3)	96.2(7)	100.6(9)	100.2(4)
O(1)—Sn—X(1)	173.5(2)	174.1(6)	172.2(7)	87.5(2)
C(1)—Sn—X(2)	99.3(3)	100.0(8)	100.0(9)	104.2(3)
O(1)—Sn—X(2)	87.8(2)	90.6(6)	85.6(7)	175.0(2)
X(1)—Sn—X(2)	98.52(3)	88.9(7)	89.5(8)	97.0(1)
C(1)—Sn—O(1)	72.8(3)	78.2(6)	74.3(7)	72.9(4)
C(1)—Sn—O(3)	81.7(4)	88.0(6)	86.2(7)	81.0(4)
O(1)—Sn—O(3)	86.6(3)	96.3(4)	99.5(4)	88.1(3)
C(5)—Sn—X(1)	100.4(4)	99.9(7)	101.3(9)	103.4(4)
O(3)—Sn—X(1)	87.2(2)	84.9(6)	85.9(6)	174.9(2)
C(5)—Sn—X(2)	102.3(3)	98.6(8)	99.5(9)	98.8(4)
O(3)—Sn—X(2)	173.7(2)	170.4(6)	172.9(7)	87.4(2)
C(2)—C(1)—Sn	113.2(6)	113.2(12)	113.8(16)	111.9(8)
C(3)—O(1)—Sn	109.9(6)	109.1(12)	109.5(17)	106.9(7)
C(7)—O(3)—Sn	108.7(7)	108.7(13)	108.1(16)	108.5(7)
C(3)—C(2)—C(1)	112.6(10)	114.6(14)	114(2)	112.3(10)
C(2)—C(3)—O(1)	121.2(11)	124.2(17)	123(2)	123.6(11)
C(6)—C(5)—Sn	114.2(8)	116.0(12)	114.1(15)	113.1(8)
C(7)—C(6)—C(5)	120.1(9)	112.7(17)	114(2)	114.3(11)
C(6)—C(7)—O(3)	122.6(10)	124(2)	126(2)	123.0(11)
C(9)—N(1)—Sn		176.9(19)	172.(2)	
C(10)—N(2)—Sn		162(2)	148(2)	
N(2)—C(10)—S(2)		178(2)	175(2)	
N(1)—C(9)—S(1)		176(2)	179(2)	

[a] X(1) = I(1); X(2) = I(2).

[b] X(1) = N(1); X(2) = N(2).

[c] X(1)/X(2) = Cl/Br.

A and B, of **3**. The fact that the two NCS ligands are distinct within each molecule has the consequence that both molecules occur as pairs of stereoisomers. Whereas the molecules A and B of the asymmetric unit as shown in Fig. 5 are of opposite hand, the pairs A and B′ or A′ and B, where the prime represents the symmetry operation $1-x$, $1-y$, $-z$ are superimpossible. The molecules of the pair, A and B′, differ principally in their orientation with respect to the unit cell edges and since there is no evidence for intermolecular bonding it is concluded that the presence of the two molecules in the asymmetric unit is the result of the manner in which the molecules are packed in the unit cell constrained only by van der Waals forces.

The Sn—N bond lengths in **3** are in the range

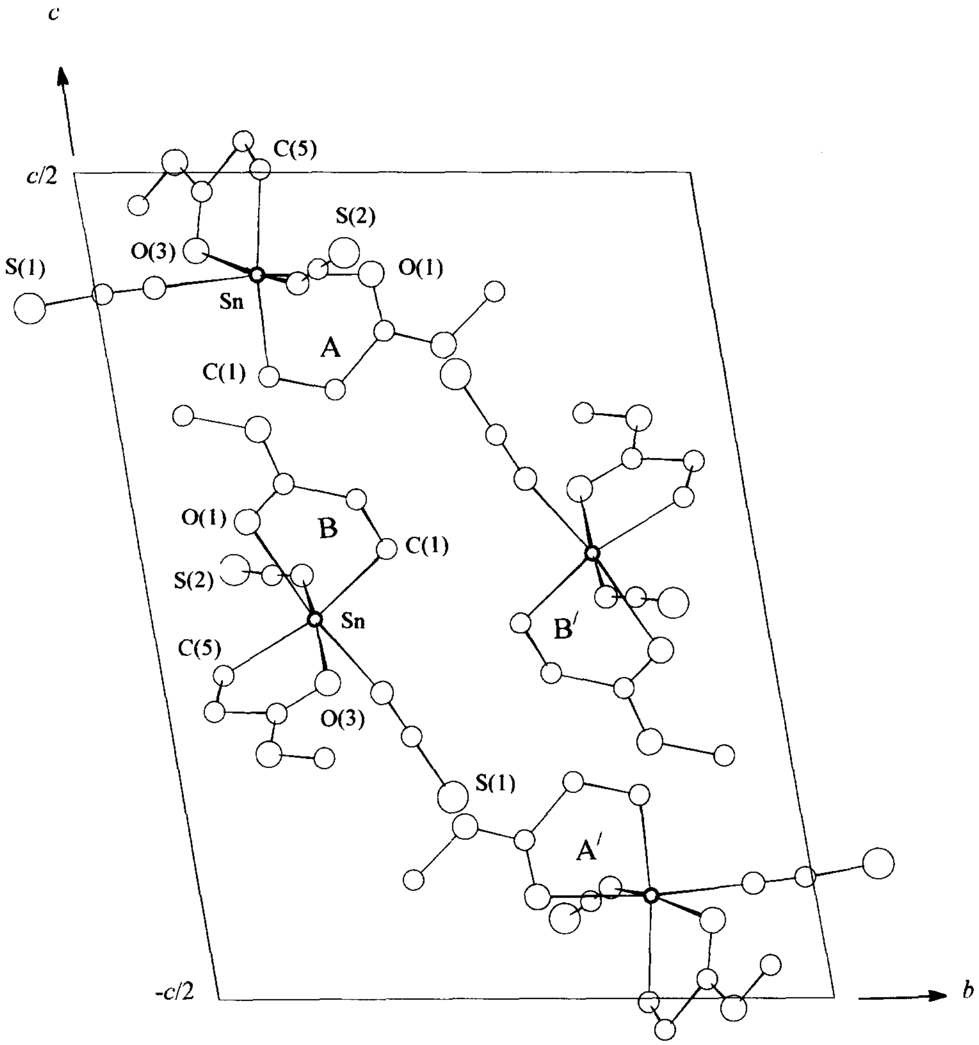


Fig. 5. The cell of **3** viewed down *a* with the cell edges *b* and *c* shown in projection. The cell outline has been translated relative to the molecules by *c*/2 and runs from 0 to 1 on *b* and −1/2 to 1/2 on *c*. The labels, A, A′, B and B′, identify the molecules discussed in the text.

2.096(19) to 2.162(18) Å and can be compared with those in other compounds found in the Cambridge Structural Database [24,25], for example, the values in **3** are similar to the quoted Sn–N(CS) bond lengths in the weakly Sn—S linked polymeric $Me_2Sn(NCS)_2$ [mean 2.139(13) Å] [34] 6-coordinate [$MeO_2CCH_2CH_2Sn(NCS)_2(BHPz_3)$] [2.143(5) and 2.117(4) Å] [35] and [$Ph_2Sn(NCS)_2(bipy)$] [2.196(5) and 2.140(6) Å] [33] but are shorter than those reported for 6-coordinate [$Ph_2Sn(NCS)_2(HMPA)_2$] [2.229(6) and 2.242(5) Å] [36] and 7-coordinate [$Me_2Sn(NCS)_2$terpyridyl] [2.282(4) Å] [32].

Comparison of $(MeO_2CCH_2CH_2)_2SnX_2$ *structures.* Comparison of selected geometric parameters, including the chelate bite angles, for $(MeO_2CCH_2CH_2)_2SnX_2$ are given in Table 4. Data are also included for **7** [15]. The average Sn—O bond lengths in **1** (R = Me), **2** or **4** are essentially the same but are appreciably longer than that in **3**. The shorter Sn—O bond lengths in **3**, compared to those in **1** (R = Me), **2** or **4**, arise from the greater Lewis acidity of the tin centre in **3**, as a consequence of the NCS groups being stronger electron withdrawing groups than the halides and the NCS ligands forming the stronger bonds to tin. Compounds, $R_2Sn(NCS)_2$, are generally recognized as being stronger acceptors than R_2SnCl_2, as illustrated by the values of formation constants of complexes in solution [37]. The data in Table 4 also clearly indicate differences in the O—Sn—O, C—Sn—C and X—Sn—X (X = halide or pseudohalide) values between **3**, on one hand, and **1**; (R = Me), **2** and **4**, on the other: the three halide complexes have very similar arrangements.

As reported earlier, there is a linear relationship between Sn—O bond lengths in chelated estertin compounds and the C—Sn—O bite angles [15]. The data

Table 4. Comparison of bond angles and lengths in $(MeO_2CCH_2CH_2)_2SnX_2$

Bond angle or length	X_2 $(NCS)_2$	Cl_2[a]	ClBr	I_2	dmit[e]
Compound	**3**	**1** (R = Me)	**4**	**2**	**8**
C—Sn—C (°)	155.6(7),[b] 150.7(6)[c]	144.5(2)	144.0(5)	144.6(5)	121.0(4)
O—Sn—O (°)	96.3(4),[b] 99.5(4)[c]	89.02(9)	86.6(3)	88.1(3)	123.8(2)
X—Sn—X (°)	88.9(7),[b] 89.5(8)[c]	96.87(4)	98.52(3)	97.0(1)	88.42(8)
C—Sn—O (°)[d]/Sn—O (Å)	78.2(6)/2.390(11)[b] 76.2(7)/2.426(13)[b] 75.3(6)/2.498(12)[c] 74.3(7)/2.443(13)[c]	73.9(1)/2.519(2) 72.9(1)/2.536(2)	73.9(4)/2.528(7) 72.8(3)/2.522(8)	73.4(4)/2.531(8) 72.9(4)/2.541(8)	72.7(3)/2.629(7)
Mean	76.0/2.439	73.4/2.528	73.4/2.525	73.3/2.536	72.7/2.629

[a] [3].
[b] Molecule A.
[c] Molecule B.
[d] Bite angle of chelate.
[e] [15].

Table 5. Torsion angles for the chelate rings in **2**, **3** and **6** (Q = NEt_4)

Torsion angle	Compound **2**	Compound **3**[a] (mol) A	B	Torsion angle[a]	**6** (Q = NEt_4)
Sn—C(5)—C(6)—C(7)	6.6(16)	21(2)	−13(3)	Sn—C(7)—C(8)—C(9)	62.2(7)
C(5)—C(6)—C(7)—O(3)	−0.1(19)	−15(3)	10(4)	C(7)—C(8)—C(9)—O(3)	−21.6(10)
C(6)—C(7)—O(3)—Sn	5.5(14)	2(2)	−2(3)	C(8)—C(9)—O(3)—Sn	−11.3(7)
C(7)—O(3)—Sn—C(5)	−6.7(8)	8(1)	−5(2)	C(9)—O(3)—Sn—C(7)	32.0(5)
O(3)—Sn—C(5)—C(6)	6.4(11)	−16(1)	9(2)	O(3)—Sn—C(7)—C(8)	−44.4(5)
Sn—C(1)—C(2)—C(3)	35.6(11)	9(2)	−27(3)		
C(1)—C(2)—C(3)—O(1)	−19.2(14)	−8(3)	18(3)		
C(2)—C(3)—O(1)—Sn	−3.8(12)	3(2)	−1(3)		
C(3)—O(1)—Sn—C(1)	17.9(8)	2.3(1)	−11(2)		
O(1)—Sn—C(1)—C(2)	−26.9(7)	−6(1)	21(2)		

[a] Although the numbering system is distinct for **6** (Q = NEt_4), values for corresponding torsional angles are listed across the rows.

from **2**, **3** and **4** clearly fit the correlation, see Fig. 6. The chelate rings, $\underline{Sn—CH_2—CH_2—C{=}O}$, exhibit different conformations, even in the same molecule, see Table 5. The rings vary from near envelope to near planar forms, with certain extents of twist forms also apparent. It appears that the relationship between the Sn—O bond lengths and the chelate bite angles holds no matter what the chelate ring conformations are.

$(MeO_2CCH_2CH_2)_2CH_2Sn(dmio)$ **5** *and* $[Q][MeO_2CCH_2Sn(dmio)_2]$ **6**

These compounds were prepared by similar routes as used for $(MeO_2CCH_2CH_2)_2Sn(dmit)$ **7** and $[Q][MeO_2CCH_2CH_2Sn(dmit)_2]$ **8** [15], equations (1) and (2).

Compound **5**. The dmio group in its complexes generally exhibits $\nu(C{=}O)$ bands at 1615 ± 8 and $1670 \pm 15\ cm^{-1}$. IR bands for the carbonyl groups in **5** in KBr disks are at 1692(sh), 1668, 1621; from the relative intensities of the carbonyl bands, the $\nu(C{=}O)$ value for the ester group in **5** appears to be at *ca.* 1668 cm^{-1}, indicating a coordinated ester group. The ester group in **5** remains coordinated in $CHCl_3$ solution. Apart from the $\delta^{13}C$ values for the $S_2C{=}O$ and $S_2C{=}S$ groups, the only significant differences in the NMR spectra of **5** and the dmit analogue, **7**, concern the $\delta^{13}C$ value for C═C [116.7 and 129.6, for **5** and **7**, respectively] and the $\delta^{119}Sn$ values [48.2 and 87.5, for **5** and **7**, respectively]. These differences reflect the differences in the electron delocalisation and electron effects of the dmio and dmit ligands. Compound **5** is predicted to have a similar structure to that of **7** [15].

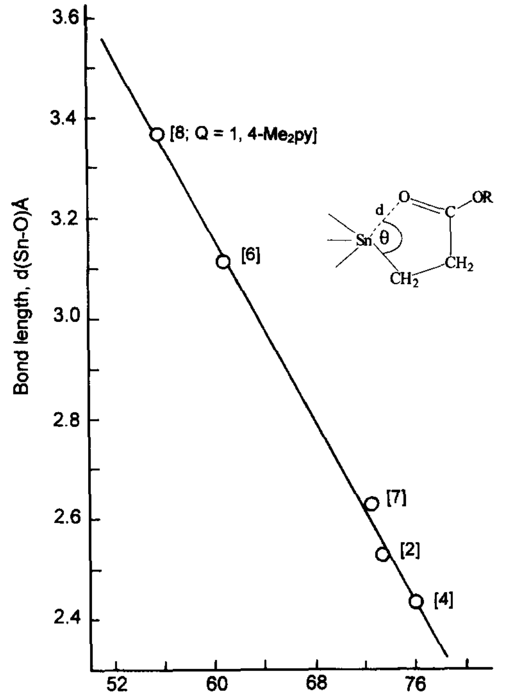
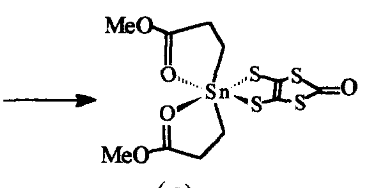


Fig. 6. Plot of Sn—O bond length (Å) against C—Sn—O (°) bite angle, for estertin complexes.

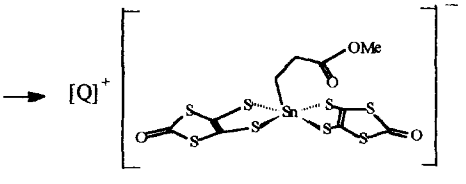
$2\,(MeO_2CCH_2CH_2)_2SnCl_2 + [NEt_4]_2[Zn(dmio)_2]$



(1)

(5)

$MeO_2CCH_2CH_2SnCl_3 + [Q]_2[Zn(dmio)_2]$



(2)

6 (Q = NEt₄, 1,4-Me₂-pyridinium or PPh₄)

Compound **6**. The ν(C=O) bands for solid **6** (Q = NEt$_4$) are at 1616, 1672 and 1713 cm^{-1}: the latter value is assigned to the ester C=O group. In CHCl$_3$ solution, there is a single very intense and broad band at 1727 cm^{-1}.

Significant differences in the NMR spectra of **6** in CDCl$_3$ solution and the dmit analogue **8** in CD$_3$COCD$_3$ solution involve δ^{13}C values for the C=C carbon atoms of 118 ± 1 and 130 ± 1 ppm in **6** and **8**, respectively and δ^{119}Sn values of -50 ± 1.5 and 6 ± 1 for **6** and **8**, respectively. These differences again reflect the differences in the electron delocalisation and electron effects of the dmio and dmit ligands.

Crystal structure determination **6** (Q = NEt$_4$). Bond lengths and angles are listed in Table 6. The atom arrangements are shown in Fig. 7. The molecule is ionic, with no interactions between the cation and the anion. The tin atom forms strong bonds to carbon [Sn—C(7) = 2.136(7) Å] and to the four thiolate atoms of the two dmio groups: the dmio units are bonded to tin in anisobidentate fashions [for dimo 1, Sn—S(1) and Sn—S(2) = 2.459(2) and 2.559(2) Å, respectively and for dmio 2, Sn—S(5) and Sn—S(6) = 2.583(2) Å and 2.472(2) Å, respectively]. The arrangement of these five bonds about tin is between trigonal bipyramidal and rectangular pyramidal, but closer to the former with the S(2) and S(5) atoms in the axial positions [S(2)—Sn—S(5) = 164.34(6) Å]. This is a similar arrangement to those found for [Q][RSn(dmit)$_2$] [Q = NBu$_4$, R = Bu or Ph] [38] and **8** (Q = NEt$_4$) [15].

In addition to the five strong bonds to tin in **6** (Q = NEt$_4$), the carbonyl-oxygen atom, O(3), is situated 3.111(5) Å from tin. This is just outside the limit normally taken for Sn—O bonding [*ca.* 3.0 Å], and while much longer than a single Sn—O bond [*ca.* 2.0 Å] is within the sum of the van der Waals radii of Sn and O [3.60 Å]. The ν(C=O) value in the solid state [1713 cm^{-1}] for **6** (Q = NEt$_4$) is between that for a coordinated and non-coordinated ester group [1670–80 and 1730–1740 cm^{-1}, respectively]. We suggest that there is weak bonding between Sn and the carbonyl oxygen in the solid state, which seems not to survive dissolution. With this weaker interaction, tin becomes six coordinate with a much distorted octahedral geometry—the "*trans*" angles {164.34(6)° [S(2)—Sn—S(5)], 158.4(1)° [O(3)—Sn—S(1)] and 131.7(2)° [C(7)—Sn—S(6)]} show variable deviations from the ideal 180°. The C(7)—Sn···O(3) angle, the "bite angle" of the MeO$_2$CCH$_2$CH$_2$ chelate, is 60.8(2)°; this angle and the corresponding Sn—O(3) bond length fit the bite angle/Sn—O bond length correlation, see Fig. 6. The situation for (**6**; Q = NEt$_4$) is different from that found for the dmit analogue, **8** (Q = NEt$_4$) [Sn···O separation = 4.84(1) Å], but similar to that found for **8** (Q = 1,4-Me$_2$-pyridinium) [Sn···O separation = 3.371(4) Å]. It can be argued that the crystal packing forces for complex **8** (Q = NEt$_4$), with the larger dmit ligand, must be greater than those for complex **6**, with the smaller dmio ligand: a consequence of this is that the Sn···O contact in the former complex is not necessary in the latter. In support of the crystal packing argument is the finding that Sn···O interactions also occur in the dmit complex, **8** (Q = 1,4-Me$_2$-pyridinium), with the smaller 1,4-Me$_2$-pyridinium cation.

The torsion angles for the "chelate ring", Sn—C(7)—C(8)—C(9)—O(3), in **6** (Q = NEt$_4$) are

Table 6. Selected bond lengths [Å] and angles [°] for **6** (Q = NEt$_4$)

Sn—C(7)	2.136(7)	S(1)—C(1)	1.736(6)
Sn—S(1)	2.459(2)	S(2)—C(2)	1.738(7)
Sn—S(6)	2.472(2)	S(3)—C(1)	1.758(6)
Sn—S(2)	2.559(2)	S(3)—C(3)	1.772(8)
Sn—S(5)	2.583(2)	S(4)—C(2)	1.740(6)
Sn—O(3)	3.111(5)	S(8)—C(5)	1.742(7)
S(4)—C(3)	1.753(8)	S(8)—C(6)	1.756(8)
S(5)—C(4)	1.725(7)	S(7)—C(6)	1.763(7)
S(6)—C(5)	1.747(7)	C(1)—C(2)	1.360(8)
S(7)—C(4)	1.758(6)	C(4)—C(5)	1.350(8)
C(6)—O(2)	1.212(8)	C(8)—C(9)	1.481(9)
C(7)—C(8)	1.526(8)	C(9)—O(3)	1.206(8)
C(11)—C(12)	1.68(2)	C(15)—C(16)	1.480(12)
C(13)—C(14)	1.63(2)	C(17)—C(18)	1.499(14)

C(7)—Sn—S(1)	110.8(2)	S(1)—Sn—S(2)	86.35(6)
C(7)—Sn—S(6)	131.7(2)	S(6)—Sn—S(2)	86.05(7)
S(1)—Sn—S(6)	117.10(7)	C(7)—Sn—S(5)	92.3(2)
C(7)—Sn—S(2)	103.3(2)	S(1)—Sn—S(5)	87.03(6)
S(2)—Sn—S(5)	164.34(6)	S(6)—Sn—S(5)	84.36(6)
O(3)—Sn—C(7)	60.8(2)	O(3)—Sn—S(1)	158.4(1)
O(3)—Sn—S(6)	76.0(1)	O(3)—Sn—S(2)	77.1(1)
O(3)—Sn—S(5)	112.3(1)	C(1)—S(3)—C(3)	96.6(3)
C(1)—S(1)—Sn	98.7(2)	C(2)—S(4)—C(3)	97.4(3)
C(2)—S(2)—Sn	96.8(2)	C(4)—S(7)—C(6)	97.2(3)
C(4)—S(5)—Sn	96.9(2)	C(5)—S(8)—C(6)	96.5(3)
C(5)—S(6)—Sn	100.0(2)	S(2)—C(2)—S(4)	116.7(4)
C(2)—C(1)—S(1)	127.1(5)	O(1)—C(3)—S(4)	124.9(7)
C(2)—C(1)—S(3)	116.5(5)	O(1)—C(3)—S(3)	122.5(6)
S(1)—C(1)—S(3)	116.4(4)	S(4)—C(3)—S(3)	112.6(4)
C(1)—C(2)—S(2)	126.3(5)	C(5)—C(4)—S(5)	127.0(5)
C(1)—C(2)—S(4)	117.0(5)	C(5)—C(4)—S(7)	115.2(5)
S(5)—C(4)—S(7)	117.8(3)	O(2)—C(6)—S(7)	123.3(6)
C(4)—C(5)—S(8)	118.3(5)	S(8)—C(6)—S(7)	112.5(5)
C(4)—C(5)—S(6)	125.1(5)	C(8)—C(7)—Sn	116.6(4)
S(8)—C(5)—S(6)	116.5(3)	C(9)—C(8)—C(7)	111.8(6)
O(2)—C(6)—S(8)	124.2(6)	O(3)—C(9)—C(8)	123.8(6)

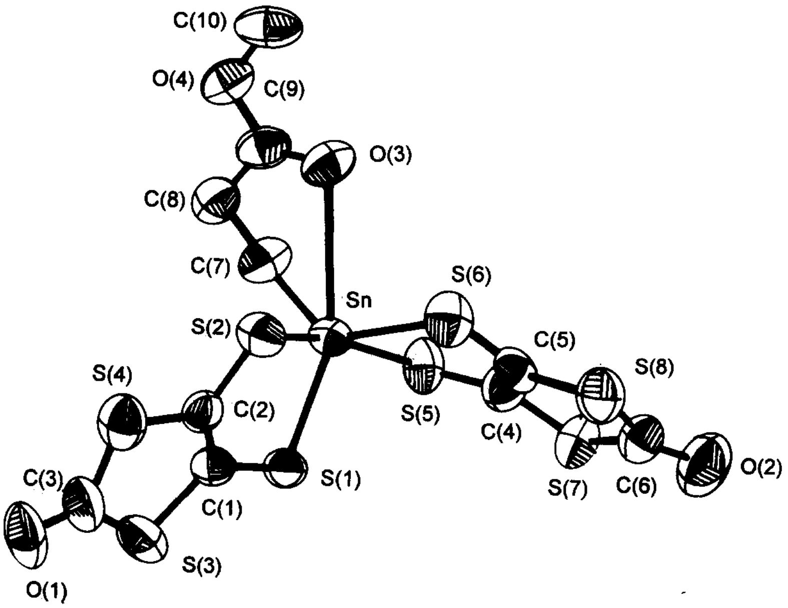


Fig. 7. The atom numbering system for the anion of **6** (Q = NEt$_4$); thermal vibration ellipsoids are drawn at the 40% probability level. H atoms have been omitted for clarity.

distinctly different from the corresponding angles in the $(MeO_2CCH_2CH_2)_2SnX_2$ molecules, see Table 5. The bite angles of the dmio groups in **6** (Q = NEt_4) are 84.36(6)° [S(5)—Sn—S(6)] and 86.35(6) [S(1)—Sn—S(2)] and are within the range of values found for the dmit ligands in **8** [83.4(1) to 87.9(1)°].

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