Diorgano(1,3-dithiole-2-one-4,5-dithiolato)tin compounds, $R_2Sn(dmio)$ and $[Q][R_2Sn(dmio)X]$ [Q = onium cation; R = alkyl or aryl; X = halide or pseudohalide]: crystal structures of $Me_2Sn(dmio)$ and $[NEt_4][Ph_2SnCl(dmio)]$

Zahid H. Chohan, R. Alan Howie, James L. Wardell *

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB24 3UE Scotland, UK

Abstract

Compounds, $[Q][R_2SnX(dmio)]$, [5: (**a**) Q = NEt$_4$, R = Et, X = Br: R = Ph, X = Cl, (**b**) Q = NEt$_4$, (**c**) Q = ferrocenyl–CH$_2$NMe$_3$], and $[R_2Sn(dmio)]_n$ [**6**: (**a**) R = Ph, (**b**) R = Me, (**c**) R = Et (**d**) R = Bu] (dmio = 1,3-dithiole-2-one-4,5-dithiolate), have been prepared from $[Q]_2[Zn(dmio)_2]$ and R_2SnX_2; compounds [**5**: Q = NEt$_4$; R = Ph; (**d**) X = Br, (**e**) X = I, (**f**) X = NCS] have been obtained by halide/pseudohalide exchange reactions from the chloride using NaX (X = Br, I or NCS). X-ray crystallography revealed that **6b** is six-coordinate in the solid state, as a result of intermolecular Sn–O interactions [Sn–O^i = 2.654(6) Å], which link the molecules into chains, and weak Sn–S interactions [Sn–S^{ii} = 3.649(3) Å], which link the chains into layers. The anion in ionic **5b**, as shown by X-ray crystallography, contains a distorted trigonal bipyramidal tin centre. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tin; 1,3-Dithiole-2-one-4,5-dithiolato-; Octahedral; Trigonal bipyramidal

1. Introduction

Organotin 1,2-dithiolate complexes have featured in many studies; the ligands used include aliphatic derivatives, e.g. $^-SCH_2CH_2S^-$ (edt) [1], $^-SCH_2CHMeS^-$ [2], alkenyl derivatives, e.g. $^-SCH=CHS^-$ [3], $^-SC(CN)=C(CN)S^-$ (mnt) [3,4], aryl derivatives, $^-SC_6H_4S^-$ (bdt) [5] and 3,4-($^-S)_2C_6H_3Me$ (tdt) [1b,c, 2b, 4a, 5b, 6], and heterocyclic derivatives (**1**: $C_3S_5^{2-}$) [7] and (**2**: $C_3OS_4^{2-}$) [8]. Much of the interest has centred on syntheses and structure determinations, although the uses of the chelates in heterocyclic synthesis have become of great interest [9,10]. During the last few years, complexes of the 1,3-dithiole-2-thione-4,5-dithiolato ligand, dmit, (**1**: $C_3S_5^{2-}$) have attracted particular attention [7]; less frequently studied have been com-

plexes of the related 1,3-dithiole-2-one-4,5-dithiolato ligand, dmio (**2**: $C_3OS_4^{2-}$)] [8].
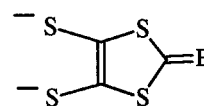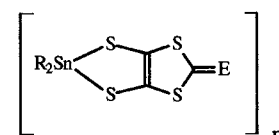

1: E = S

2: E = O
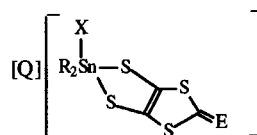
3: E = S

5: E = O

4: E = S

6: E = O

* Corresponding author. Fax: + 44-1224-272921; e-mail: j.wardell@abdn.ac.uk.

Table 1
Crystal data and structure refinement

Compound	Me$_2$Sn(dmio)	[NEt$_4$][Ph$_2$SnCl(dmio)]
Empirical formula	C$_5$H$_6$OS$_4$Sn	C$_{23}$H$_{30}$ClNOS$_4$Sn
Formula weight	329.05	604.89
Temperature (K)	298	298
Wavelength (Å)	0.71069	0.71069
Crystal system	Orthorhombic	Triclinic
Space group	*Pbcn*	*P*$\bar{1}$
a (Å)	17.642(9)	9.456(11)
b (Å)	7.683(4)	11.473(15)
c (Å)	15.031(9)	12.476(12)
α (°)	90	97.73(9)
β (°)	90	87.59(9)
γ (°)	90	95.90(10)
V (Å^3)	2037.4(19)	1333(3)
Z	8	2
D$_{calc.}$ (Mg m^{-3})	2.145	1.507
Absorption coefficient (mm^{-1})	3.25	1.38
Max/min transmission factors	0.1211/0.4265	None
F(000)	1264	628
Crystal size (mm)	0.65 × 0.6 × 0.1	0.6 × 0.36 × 0.16
Theta range for data collection (°)	Max. 30	Max. 25
Index ranges	0 ≤ *h* ≤ 24	−11 ≤ *h* ≤ 11
	0 ≤ *k* ≤ 10	−13 ≤ *k* ≤ 13
	0 ≤ *l* ≤ 21	0 ≤ *l* ≤ 14
Reflections collected	3404	4740
Independent reflections	2656	4477
Observed reflections [*F* > 4*σ*(*F*)]	2055	3828
R$_{int}$	0.0015	0.001
Refinement method	Full-matrix least-squares on *F*^{2}	Full-matrix least-squares on *F*^{2}
Number of parameters	120	258
Goodness-of-fit (*S*)	0.8964	1.31
Final *R* indices	*R* = 0.066 [*F* > 4*σ*(*F*)]	*R* = 0.051 [*F* > 4*σ*(*F*)]
	wR = 0.072	*wR* = 0.055
Final weighting scheme	*w* = 1/(*σ*^{2}*F* + 0.007046*F*^{2})	*w* = 1/(*σ*^{2}*F* + 0.001791*F*^{2})
Residual diffraction	2.56 (0.92[a] Å from Sn)	1.13 (0.96 Å from Sn)
Max/min (e A^{-3})	−2.62	−1.22

[a] One of four peaks of roughly equal intensity distant 0.77–0.92 Å from Sn.

While full reports of the synthesis and structures of the ionic mono-dmit complexes, (**3**: Q = cation; X = halide or pseudohalide) [7b,c] and polymeric species (**4**: R = simple alkyl or aryl) [7a] have been published, only preliminary reports, concentrating on structural aspects, have been made on two mono-dmio complexes (**5f**: Q = NEt$_4$, X = NCS, R = Ph) and (**5a**: Q = NEt$_4$, X = Br, R = Et) [8b,c]. We wish now to report on the neutral species [**6**: (a) R = Ph, (b) R = Me, (c) R = Et, (d) R = Bu] as well as further information on the ionic complexes (**5**: Q = NEt$_4$ or ferrocenylCH$_2$NMe$_3$; X = Cl, Br, I or NCS; R = Et or Ph). Comparisons of the structures of the related dmio and dmit complexes are also made.

2. Experimental

Melting points were measured using a Kofler hot-stage microscope and are uncorrected. NMR spectra were obtained on a Bruker 250 MHz instrument. Ten second pulse delays were utilised in the acquisition of the ^{13}C-NMR spectra of the dmio compounds. IR spectra were recorded on Phillips analytical PU900 and Nicolet 205 Fourier-transform instruments.

Zincate salts, [Q]$_2$[Zn(dmio)$_2$], [Q = NEt$_4$, or ferrocenylmethyl(trimethyl)ammonium] were obtained by published procedures [11,12]; Et$_2$SnBr$_2$, Me$_2$SnCl$_2$, Bu$_2$SnCl$_2$, and Ph$_2$SnCl$_2$ were obtained from appropriate tetraorganostannanes and stannic halides and had physical properties in agreement with published values [13].

2.1. [NEt$_4$][Et$_2$SnBr(dmio)] (5a)

A solution of Et$_2$SnBr$_2$ (0.67 g, 2.0 mmol) in MeOH (20 ml) was added to a stirred suspension of [NEt$_4$]$_2$[Zn(dmio)$_2$] (0.69 g, 1.0 mmol) in MeOH (20 ml). After 3 h, the orange precipitate was collected and recrystallised from MeOH as a red–brown crystalline
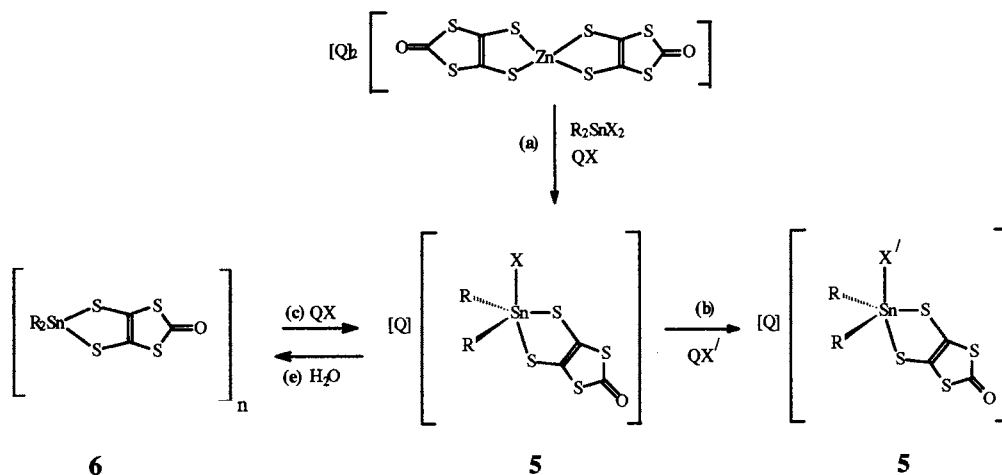
Scheme 1.

solid, m.p. 142–143°C; yield 0.75 g, 66%. Analysis: Found: C, 31.9; H, 5.1; N, 2.6. Calculated for $C_{15}H_{30}BrNOS_4Sn$: C, 31.8; H, 5.3; N, 2.5%.

IR (KBr, cm^{-1}) 1665, 1612, 1475, 1451. ^{1}H-NMR (Me_2SO-d_6, 250 MHz) δ: 1.20[t, 6H, J(H–H) 8.1 Hz, J(^{119,117}Sn–^{1}H) 128,122 Hz, (CH_3CH$_2$Sn)], 1.40[tt, 12 Hz, J(H–H) 7.2 Hz, J(H–N) 1.8 Hz, CH_3CH$_2$N], 1.56[q, 4H, J(H–H) 8.1 Hz, J(^{119,117}Sn–^{1}H) 59 Hz, CH$_2$Sn], 3.3[q, 8H, J(H–H) 7.2 Hz, CH$_2$N]. ^{13}C-NMR (Me_2SO-d_6, 62.9 MHz) δ: 7.5 [CH_3CH$_2$N], 11.8[J(^{119,117}Sn–^{13}C) 40.5 Hz, CH_3CH$_2$Sn], 23.5[J(^{119,117}Sn–^{13}C) 535, 510 Hz, CH$_2$Sn], 52.7[CH$_2$N], 119.4[C=C], 192.5[C=O]. ^{119}Sn (Me_2SO-d_6, 93.1 MHz) δ: −69.7.

2.2. [NEt$_4$][Ph$_2$SnCl(dmio)] (5b)

This compound was similarly prepared from Ph$_2$SnCl$_2$ (3.45 g, 10.1 mmol) in MeOH (30 ml) and [NEt$_4$]$_2$[Zn(dmio)$_2$] (3.45 g, 5.0 mmol) in MeOH (30 ml) and was recrystallised from MeOH; red–brown crystals, m.p. 133–135°C; yield 5.50 g, 88%. Analysis: Found: C, 44.1; H, 5.0; N, 2.4. Calculated for $C_{23}H_{30}ClNOS_4Sn$: C, 44.6; H, 4.9; N, 2.3%.

IR (KBr, cm^{-1}) 1664, 1614, 1458. ^{1}H-NMR (Me_2CO-d_6, 250 MHz) δ: 1.34[tt, 12 Hz, J(H–H) 7.2 Hz, J(H–N) 1.85 Hz, Me], 3.41[q, 8H, J(H–H) 7.2 Hz, CH$_2$N], 7.40[m, 6H, *m*-H + *p*-H], 8.11[m, 4H, J(^{119,117}Sn–^{1}H) ca. 80 Hz, *o*-H]. ^{13}C-NMR (Me_2CO-d_6, 62.9 MHz) δ: 7.6[Me], 52.9[J(C–N) 6.2 Hz, CH$_2$], 119.4[C=C], 128.7[J(^{119,117}Sn–^{13}C) 82.5, 79.1 Hz, *m*-C], 129.6[J(^{119,117}Sn–^{13}C) 16.9 Hz, *p*-C], 136.6[J(^{119,117}Sn–^{13}C) 611, 585 Hz, *o*-C], 148.3[J(^{119,117}Sn–^{13}C) 798, 767 Hz, *i*-C], 192.0[C=O]. ^{119}Sn (Me_2CO-d_6, 93.1 MHz) δ: −178.5.

2.3. [FcCH$_2$NMe$_3$][Ph$_2$SnCl(dmio)] (5c)

This compound was prepared similarly from Ph$_2$SnCl$_2$ (0.34 g, 1.00 mmol) in MeOH (20 ml) and

[FcCH$_2$NMe$_3$]$_2$[Zn(dmio)$_2$] (0.47g, 0.50 mmol) in MeOH (20 ml) and was recrystallised from MeOH; red–brown crystals, m.p. 134–136°C; yield 0.23 g, 62%. Analysis: Found: C, 46.3; H, 3.7; N, 1.8. Calculated for $C_{29}H_{30}ClFeNOS_4Sn$: C, 46.6; H, 4.0; N, 1.9%

IR (KBr, cm^{-1}) 1668, 1603, 1475. ^{1}H-NMR (Me_2SO-d_6, 250 MHz) δ: 2.89[s, 9H, Me], 4.23[s, 5H, unsubstituted cp-H], 4.36[s, 4H, substituted cp-H], 4.47[s, 2H, CH$_2$], 7.42[m, 6H, *m*-H + *p*-H], 7.92[m, 4H, J(^{119,117}Sn–^{1}H) ca. 80 Hz, *o*-H]. ^{13}C-NMR (Me_2SO-d_6, 62.9 MHz) δ: 53.0[J(C–N) 7.8 Hz, Me], 67.1[CH$_2$], 70.6[unsubstituted cp-C], 71.7, 73.6, 74.7[substituted cp-C], 119.4[C = C], 130.1[J(^{119,117}Sn–^{13}C) 82.2, 79.0 Hz, *m*-C], 130.9[J(^{119,117}Sn–^{13}C) 17.5 Hz, *p*-C], 136.9[J(^{119,117}Sn–^{13}C) 61.8, 59.0 Hz, *o*-C], 147.5[J(^{119,117}Sn–^{13}C) 843, 806 Hz, *i*-C], 191.3[C=O]. ^{119}Sn (Me_2SO-d_6, 93.1 MHz) δ: −168.3.

2.4. [NEt$_4$][Ph$_2$SnBr(dmio)] (5d)

A solution of [NEt$_4$][Ph$_2$SnCl(dmio)] (2.00 g, 3.23 mmol) and NaBr (1.50 g, 14.6 mmol) in MeOH (20 ml) was agitated in an ultrasonic bath for 1 h. The dark-orange precipitate was collected and recrystallised from MeOH; red-brown crystals, m.p. 118–120°C; yield 1.89 g, 86%. Analysis: Found: C, 41.3; H, 4.4; N, 2.1. Calculated for $C_{23}H_{30}BrNOS_4Sn$: C, 41.7; H, 4.5; N, 2.1%.

IR (KBr, cm^{-1}) 1663, 1613, 1465. ^{1}H-NMR (Me_2SO-d_6, 250 MHz) δ: 1.14[tt, 12 Hz, J(H–H) 7.2Hz, J(H–N) 1.8 Hz, Me], 3.16[q, 8H, J(H–H) 7.2 Hz, CH$_2$N], 7.43[m, 6H, *m*-H + *p*-H], 7.91[m, 4H, J(^{119,117}Sn–^{1}H) ca. 80 Hz, *o*-H]. ^{13}C-NMR (Me_2SO-d_6, 62.9 MHz) δ: 8.8 [Me], 53.0[J(C–N) 5.9 Hz, CH$_2$], 118.5[C=C], 130.1[J(^{119,117}Sn–^{13}C) 82.3,79.0 Hz, *m*-C], 131.0[J(^{119,117}Sn–^{13}C) 17.0 Hz, *p*-C], 136.9[J(^{119,117}Sn–^{13}C) 60.0, 58.5 Hz, *o*-C], 147.6 [J(^{119,117}Sn–^{13}C) 828,791 Hz, *i*-C], 191.2[C=O]. ^{119}Sn (Me_2SO-d_6, 93.1 MHz) δ: −172.2.
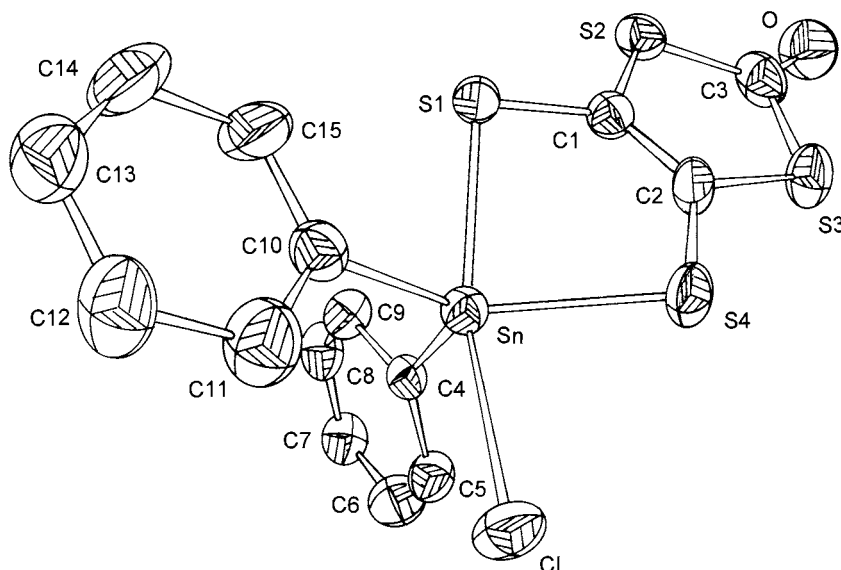
Fig. 1. Atom arrangement for the anion of **5b**. Probability ellipsoids drawn at 40%.

2.5. [NEt$_4$][Ph$_2$SnI(dmio)] (**5e**)

This compound was similarly prepared from [NEt$_4$][Ph$_2$SnCl(dmio)], (0.50 g, 0.81 mmol) and NaI (0.30 g, 2.0 mmol) in MeOH (35 ml) and was recrystallised from MeOH; red–brown crystals, m.p. 147–149°C; yield 0.46 g, 80%. Analysis: Found: C, 38.6; H, 4.2; N, 4.1. Calculated for C$_{23}$H$_{30}$INOS$_4$Sn: C, 38.9; H, 4.3; N, 2.0%.

IR (KBr, cm^{-1}) 1661, 1614, 1470. ^{1}H-NMR (Me$_2$SO-d$_6$, 250 MHz) δ: 1.15[tt, 12 Hz, J(H–H) 7.2 Hz, J(H–N) 1.7 Hz, Me], 3.20[q, 8H, J(H–H) 7.2 Hz,

CH$_2$N], 7.47[m, 6H, m-H + p-H], 7.82[m, 4H, J(^{119,117}Sn–^{1}H) ca. 80 Hz, o-H]. ^{13}C-NMR (Me$_2$SO-d$_6$, 62.9 MHz) δ: 8.9[Me], 53.0[J(C–N) 5.9 Hz, CH$_2$], 118.5[C=C], 130.1[J(^{119,117}Sn–^{13}C) 82.3,79.0 Hz, m-C], 131.0[J(^{119,117}Sn–^{13}C) 17.0 Hz, p-C], 136.9[J(^{119,117}Sn–^{13}C) 60.6, 58.9 Hz, o-C], 145.9 [J(^{119,117}Sn–^{13}C) 844, 806 Hz, i-C], 191.4[C=O]. ^{119}Sn (Me$_2$SO-d$_6$, 93.1 MHz) δ: −159.4.

2.6. [NEt$_4$][Ph$_2$Sn(NCS)dmio] (**5f**)

This compound was similarly prepared from [NEt$_4$][Ph$_2$SnCl(dmio)], (2.00 g, 3.23 mmol) and

Table 2
Bond lengths (Å) and angles (°) for **5b**

Bond lengths (Å)			
Sn–S1	2.626(2)	Sn–S4	2.463(2)
Sn–Cl	2.524(2)	Sn–C4	2.142(7)
Sn–C10	2.150(7)	C1–S1	1.734(7)
C1–S2	1.751(7)	C3–S2	1.745(9)
C2–S3	1.750(7)	C3–S3	1.780(9)
C2–S4	1.740(8)	C3–O	1.204(9)
C2–C1	1.357(10)		
Bond angles (°)			
S4–Sn–S1	84.2(1)	C1–Sn–S1	165.4(1)
Cl–Sn–S4	82.1(1)	C4–Sn–S1	95.8(2)
C4–Sn–S4	114.2(2)	C4–Sn–C1	94.4(2)
C10–Sn–S1	91.5(2)	C10–Sn–S4	127.9(2)
C10–Sn–C1	92.9(2)	C10–Sn–C4	117.9(3)
C1–S1–Sn	96.1(2)	C3–S2–C1	97.8(4)
C3–S3–C2	97.3(4)	C2–S4–Sn	100.0(2)
C2–C1–S2	116.7(5)	S4–C2–S3	117.496
C1–C2–S3	116.3(6)	C1–C2–S4	126.4(6)
S3–C3–S2	111.9(4)	O–C3–S2	124.6(8)
O–C3–S3	123.5(7)	C2–C1–S1	126.4(6)
S2–C1–S1	116.9(4)		

Table 3
Selected structural details of [Q][R$_2$SnX(dmio)] compound **5**

R	Ph[a]	Et [8b]	Ph[a] [8c]
X	Cl	Br	NCS
Sn–X	2.524(2)	2.876(2)	2.240(6)
Sn–C(A)	2.142(7)	2.093(8)	2.133(7)
Sn–C(B)	2.150(7)	2.093(8)	2.162(7)
Sn–S(eq)	2.463(2)	2.465(3)	2.433(2)
Sn–S(ax)	2.626(2)	2.567(3)	2.583(2)
X–Sn–S(ax)	165.4(1)	166.65(9)	166.4(2)
X–Sn–C(A)	94.4(2)	87.6(3)	90.7(2)
X–Sn–C(B)	92.9(2)	87.6(3)	91.7(2)
X–Sn–S(eq)	82.1(1)	79.86(8)	80.0(2)
C(A)–Sn–C(B)	117.9(3)	138.0(6)	116.1(2)
C(A)–Sn–S(eq)	114.2(2)	110.1(3)	119.8(2)
C(B)–Sn–S(eq)	127.9(2)	110.1(3)	123.5(2)
C(A)–Sn–S(ax)	95.8(2)	97.1(2)	95.7(2)
C(B)–Sn–S(ax)	91.5(2)	97.1(3)	96.1(2)
S(eq)–Sn–S(ax)	86.2(1)	86.78(9)	86.47(6)

[a] For **5b**: Q = NEt$_4$; R = Ph; X = Cl: C(A) = C4; C(B) = C10: S(eq) = S4; S(ax) = S1, in Fig. 1 and Table 2.

Table 4
Comparison of δ^{119}Sn values of **3** and **5** [Q][Ph$_2$SnX(C$_3$S$_4$E)]

X	δ^{119}Sn E = O (Me$_2$SO-d_6)	δ^{119}Sn E = S (Me$_2$CO-d_6) [8f]	$\Delta\delta^{119}$Sn[a]
(a) Q = NEt$_4$			
Cl	−178.5	−143.2	−35.3
Br	−172.2	−149.6	−23.3
I	−179.4	−158.2	−21.2
NCS	−182.4	−162.9	−19.5
(b) Q = FcCH$_2$Nme$_3$			
Cl	−163.3	−145.8	−17.5
		−146.3(CDCl$_3$)	

[a] $\Delta\delta^{119}$Sn = δ^{119}Sn(E = O) − δ^{119}Sn(E = S).

NaSCN · 2H$_2$O (0.59 g, 5.0 mmol) in MeOH (35 ml) and was recrystallised from MeOH/Me$_2$CO; red–brown crystals, m.p. 103–105°C; yield 1.78 g, 86%. Analysis: Found: C, 45.3; H, 4.8; N, 4.1. Calculated for C$_{24}$H$_{30}$N$_2$OS$_5$Sn: C, 44.9 H, 4.7; N, 4.4%

IR (KBr, cm^{-1}) 2057, 1667, 1620, 1475, 1458. ^{1}H-NMR (Me$_2$SO-d$_6$, 250 MHz) δ: 1.14[tt, 12 Hz, J(H–H) 7.5 Hz, J(H–N) 1.7 Hz, Me], 3.17[q, 8H, J(H–H) 7.5 Hz, CH$_2$N], 7.46[m, 6H, *m*-H + *p*-H], 7.83[m, 4H, J(^{119,117}Sn–^{1}H) ca. 80 Hz, *o*-H]. ^{13}C-NMR (Me$_2$SO-d$_6$, 62.9M Hz) δ: 8.8[Me], 53.1[J(C–N) 6.0 Hz, CH$_2$], 118.1[C=C], 130.4[J(^{119,117}Sn–^{13}C) 82.5, 79.2 Hz, *m*-C], 133.6[NCS], 131.0[J(^{119,117}Sn–^{13}C) 17.0 Hz, *p*-C], 136.8[J(^{119,117}Sn–^{13}C) 60.6, 58.9 Hz, *o*-C], 145.9 [J(^{119,117}Sn–^{13}C) 869, 818 Hz, *i*-C], 191.4[C=O]. ^{119}Sn (Me$_2$SO–d_6, 93.1 M Hz) δ: −182.4.

3. R$_2$Sn(dmio) compounds

A solution of R$_2$SnCl$_2$ (2.00 mmol) and [NEt$_4$]$_2$[Zn(dmio)$_2$] (0.68 g, 1.0 mmol) in Me$_2$CO (30 ml) was stirred for 10–15 min. Water (60 ml) was added with vigorous stirring. Addition of petroleum ether (b.p. 40–60°C, 15 ml), with scraping the walls of the reaction vessel, resulted in the deposition of a brown to red coloured solid, which was collected and refluxed for 1 h in H$_2$O/MeOH (2:1 v:v, 50 ml), filtered and dried under vacuum at 100°C.

3.1. Ph$_2$Sn(dmio) (**6a**)

This compound was sparingly soluble in organic solvents and was isolated as an orange–red powder. The product was purified by repeated washings with water and small quantities of Me$_2$CO; m.p. 197–200°C; yield 0.81 g, 75%. Analysis: Found: C, 39.9; H, 2.1. Calculated for C$_{12}$H$_{10}$NOS$_4$Sn: C, 39.7; H 2.2%.

IR (KBr, cm^{-1}) 1662, 1606, 1475. ^{13}C-NMR (Me$_2$SO-d$_6$, 62.9MHz) δ: 118.7[C=C], 130.8[J(^{119,117}Sn–

^{13}C) 80.7, 77.6 Hz, *m*-C], 131.9[J(^{119,117}Sn–^{13}C) 17.0 Hz, *p*-C], 137.6[J(^{119,117}Sn–^{13}C) 61.2, 58.8 Hz, *o*-C], 147.6 [J(^{119,117}Sn–^{13}C) 798, 767 Hz, *i*-C], 191.3[C=O]. ^{119}Sn (Me$_2$SO-d_6, 93.1 MHz) δ: −236.9.

3.2. Me$_2$Sn(dmio) (**6b**)

This compound was obtained after recrystallisation from MeOH as an orange microcrystalline solid, m.p. 187–189°C; yield 0.26 g, 40%. Analysis: Found: C, 18.7; H, 1.7. Calculated for C$_5$H$_6$OS$_4$Sn: C, 18.2; H, 1.8%.

IR (KBr, cm^{-1}) 1662, 1610, 1475, 1467, 1452. ^{1}H-NMR (Me$_2$SO-d_6, 250 MHz) δ: 1.00[s, J(^{119,117}Sn–^{1}H) 82.3, 78.8 Hz, Me]. ^{13}C-NMR (Me$_2$SO-d$_6$, 62.9 MHz) δ: 13.8[J(^{119,117}Sn–^{13}C) 617, 598 Hz, Me], 118.6[C=C], 192.5[C=O]. ^{119}Sn (Me$_2$SO-d_6, 93.1 MHz) δ: −37.5.

3.3. Et$_2$Sn(dmio) (**6c**)

This compound was obtained after recrystallisation from MeOH as an orange–red crystalline solid, m.p. 196–198°C; yield 0.55 g, 75%. Analysis: Found: C, 23.9, H, 2.9. Calculated for C$_7$H$_{10}$OS$_4$Sn: C, 23.5; H, 2.8%.

IR (KBr, cm^{-1}) 1666, 1612, 1477. ^{1}H-NMR (Me$_2$SO-d_6, 250 MHz) δ: 1.32[t, J(H–H) 7.8 Hz, J(^{119,117}Sn–^{1}H) 128, 122 MHz, Me], 1.54[q, J(H–H) 7.8 Hz, J(^{119,117}Sn–^{1}H) 59 Hz, CH$_2$]. ^{13}C-NMR (Me$_2$SO-d_6, 62.9 MHz) δ: 12.1[J(^{119,117}Sn–^{13}C) 43.4 Hz, Me], 23.6[J(^{119,117}Sn–^{13}C) 585, 559 Hz, CH$_2$ 118.8[C=C], 192.9 [C=O]. ^{119}Sn (Me$_2$SO-d_6, 93.1 MHz) δ: −18.2.

3.4. Bu$_2$Sn(dmio) (**6d**)

This compound was obtained after recrystallisation from MeOH as an orange microcrystalline solid, m.p. 178–180°C; yield 0.51 g, 62%. Analysis: Found: C, 31.9; H, 4.4. Calculated for C$_{11}$H$_{18}$OS$_4$Sn: C, 32.0; H, 4.4%.

IR (KBr, cm^{-1}) 1673br, 1481. ^{1}H-NMR (Me$_2$SO-d$_6$, 250 MHz) δ: 0.95[t, 6H, J(H–H) 7.3 Hz, Me], 1.38[m, 4H, CH$_2$], 1.78[m. 8H, CH$_2$CH$_2$]. ^{13}C-NMR (Me$_2$SO-d$_6$, 62.9 MHz) δ: 13.4[Me], 23.9, 26.4, 27.6, 116.6[C=C], 192.6 [C=O]. ^{119}Sn (Me$_2$SO-d_6, 93.1 MHz) δ: −22.0.

4. Crystal structure determinations

4.1. General

The crystals of Me$_2$Sn(dmio)] and [NEt$_4$][Ph$_2$SnCl-(dmio)], used in the X-ray structure determinations, were grown from MeOH solutions. Data collection and cell refinement employed Nicolet P3 software [14]. Data collection used 2θ scan rates of 5.33 (I_p < 150) to 58.6
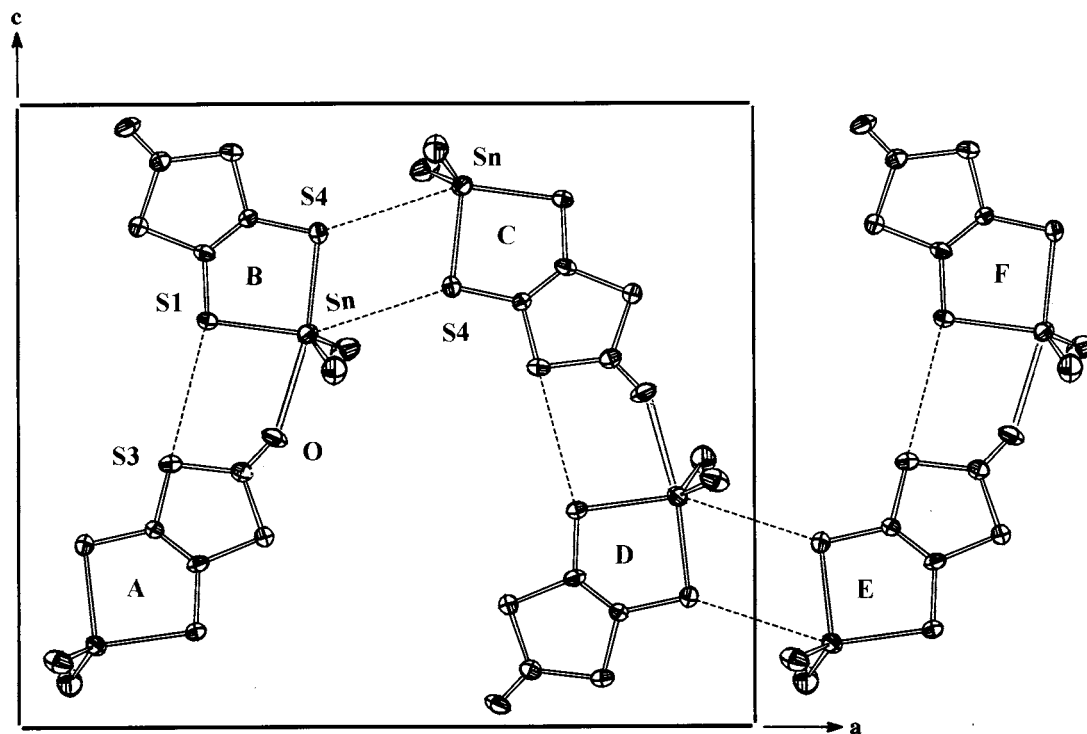
Fig. 2. Interactions within a layer of **6b** molecules with centroids at $0 < y < 1/2$. Probability ellipsoids drawn at 40%. Symmetry operations; A: x, y, z; B: $1/2 - x$, $1/2 - y$, $1/2 + z$; C: $1/2 + x$, $1/2 - y$, $1 - z$; D: $1 - x$, y, $1/2 - z$; E: $1 + x$; y, z; F: $3/2 - x$, $1/2 - y$, $1/2 + z$.

$(I_\text{p} > 2500)°$ min^{-1}, where I_p is the prescan intensity. Scan widths were 2.4–2.8° 2θ. Data reduction used the program, RDNIC [15]. Refinement was by least squares. All computations were performed on the SUN SPARC-server (unix operating system) at the University of Aberdeen. Structure solution and refinement software: SHELX86 [16] and SHELX76 [17]. Molecular graphics: ORTEX [18]. Software used to prepare the data for publication: XPUB [19].

4.2. Me₂Sn(dmio)

Absorption correction involved an empirical method based on psi scans [20]. All non-hydrogens were refined anisotropically. H-atoms were initially placed in calculated positions with C–H = 0.95 Å then refined subject to distance constraints such that C–H and H···H (within each methyl group) distances were constrained to be equal and in the ratio 1:1.633 (18 in all) to control the shape of the Me groups and Sn···H were fixed at 2.6395 Å to control the orientation of the methyl groups relative to the Sn–C bond. The C–H bond distance and a common group U_iso for H were included in the refinement to yield values of 1.102(5) Å and 0.076(16) Å^2, respectively.

4.3. [NEt₄][Ph₂SnCl(dmio)]

All non-H-atoms, except C of the disordered cation, were refined anisotropically. The nature of the disorder is such that the methylene C of the cation occupy two sets of sites C(16, 18, 20, 22) and C(16A, C18A, C20A, C22A) with occupancies of 0.687(12) and 0.313(12), respectively. As a consequence no attempt was made to determine the positions of the alkyl H atoms of the cation. Phenyl H of the anion, however, were placed in calculated positions with C–H = 0.95 Å and refined riding upon the C atom to which they were attached with a common U_iso (final value of 0.091(9)).

Crystal data and structure refinement details are listed in Table 1.

5. Results and discussion

5.1. Synthesis

The syntheses of [Q][R₂Sn(dmio)X] (**5**) and [R₂Sn(dmio)] **6** are shown in Scheme 1. Two routes to **5** were used: (a) from reaction between R₂SnX₂ and [Q]₂[Zn(dmio)₂] and (b) from halide/pseudohalide exchange reaction between [Q][R₂Sn(dmio)Cl] and NaX.

Table 5
Bond lengths (Å) and angles (°) for **6b**[a]

Bond lengths (Å)

S1–Sn	2.440(2)	S4–Sn	2.487(2)
C4–Sn	2.124(7)	C5–Sn	2.123(7)
C1–S1	1.750(8)	C1–S2	1.746(9)
C3–S2	1.757(9)	C2–S3	1.747(8)
C3–S3	1.729(10)	C2–S4	1.729(9)
C3–O	1.226(10)	C2–C1	1.367(11)
Sn–O^i	2.654(6)	Sn–S4^{ii}	3.649(3)

Bond angles (°)

S4–Sn–S1	89.47(8)	C4–Sn–S1	110.6(3)
C4–Sn–S4	107.1(3)	C5–Sn–S1	115.6(3)
C5–Sn–S4	102.8(3)	C5–Sn–C4	124.2(4)
S1–Sn–O^i	79.43(16)	S4–Sn–O^i	168.21(16)
C4–Sn–O^i	81.1(3)	C5–Sn–O^i	78.6(3)
S4^{ii}–Sn–O^i	126.46(16)	S4^{ii}–Sn–C4	76.6(3)
S4^{ii}–Sn–C5	75.2(3)	S4^{ii}–Sn–S1	154.10(7)
S4^{ii}–Sn–S2	96.96(15)	S4^{ii}–Sn–S4	64.78(8)
C1–S1–Sn	97.3(4)	C2–S4–Sn	97.1(3)
S2–C1–S1	116.4(5)	C2–C1–S1	127.5(7)
C2–C1–S2	116.1(6)	S4–C2–S3	116.7(5)
C1–C2–S3	116.4(6)	C1–C2–S4	126.8(6)
S3–C3–S2	113.3(5)	C3–S2–C1	96.9(4)
O–C3–S3	124.6(7)	O–C3–S2	122.0(7)
C3–S3–C2	97.3(4)		

[a] Symmetry operators: (i) $1/2-x$, $1/2-y$, $z-1/2$; (ii) $-x$, y, $1/2-z$.

Compounds (**6**) could also be obtained from R$_2$SnCl$_2$ and [Q]$_2$[Zn(dmio)$_2$] if aqueous extractions were carried out to remove QX. As found for the analogous dmit complexes, **3** and **4** [7a,f], **5** could also be formed from **6** on reaction with QX. Conversely, **5** could be converted to **6** on aqueous solution extractions. Hence, in the preparations of **5**, aqueous extractions to remove inorganic salts, were kept to a minimum.

5.2. [Q][R$_2$SnX(dmio)] **5**

Compounds **5** were orange to red–brown in colour. They were considerably more soluble in coordinating solvents (e.g. Me$_2$CO or Me$_2$SO) than in non-coordinating solvents. (e.g. CH$_2$Cl$_2$ or CHCl$_3$).

5.3. Solid state structure of (**5b**)

As indicated in Section 1, the structures of two compounds, **5f** [8b and **5a** [8c], have been reported in preliminary accounts. The atom arrangements of a third complex, **5b** are shown in Fig. 1. This complex, like **5f** and **5a**, exists as an ionic species, with the geometry at tin in the anion being trigonal bipyramidal. The axial sites in **5b** are occupied by Cl [Sn–Cl = 2.524(2) Å] and a dithiolate S atom, S1 [Sn–S1 = 2.626(2) Å] with S1–Sn–C1 = 165.4(1)°, see Table 2 for selected geometric parameters. The equatorial sites are occupied by the other dithiolate atom S2 [Sn–S2 = 2.463(2) Å] and the two carbon atoms, Sn–C4 = 2.141(7) and Sn–C10 = 2.150(7) Å. The Sn–Cl bond length in **5b** is comparable to the axial Sn–Cl bond length in trigonal bipyramidal [NEt$_4$][Ph$_2$SnCl(tdt)] [2.588(2) Å] [6b]. There are no interactions between cations and anions, however, there are weak S···S interactions between anions, within twice the van der Waals radius of S (1.85 Å) [21].

Comparison of the geometric parameters about tin in the three compounds, **5a,b** and **f**: is available in Table 3. All three anions have distorted trigonal bipyramidal geometries with the SnSCCS metallocycles having envelope conformations with the flap at tin. There are relatively small ranges for the Sn–S$_{ax}$ and Sn–S$_{eq}$ bond lengths and the bite angles of the dmio ligands, all, in addition, being similar to the equivalent parameters in the dmit analogues **3** [7f]. However, other bond angles about tin do show some differences between the three structures of **5**, most noticeably for the equatorial–Sn–equatorial angles. While the sum of the three equatorial–Sn–equatorial angles in each anion do sum up to ca. 360°, the C–Sn–C angle for **5a** [8b] is at 138.0(6)°,
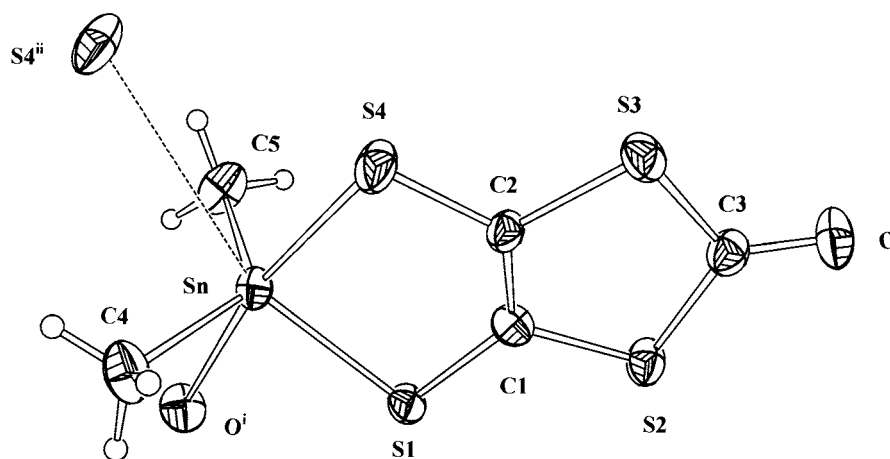

Fig. 3. Atom arrangement for **6b**. Probability ellipsoids drawn at 40%. Symmetry operations: (i) $1/2-x$; $1/2-y$, $z-1/2$; (ii) $-x$, y, $1/2-z$.

Table 6
δ^{119}Sn values for **4** and **6**

R	R$_2$Sn(dmio) [Me$_2$CO-d_6] δ^{119}Sn	R$_2$Sn(dmit) [Me$_2$SO-d_6] δ^{119}Sn [7a]	$\Delta\delta^{119}$Sn^a
Me	−37.5	135.2	−172.7
Et	−18.2	166.5	−184.7
Bu	−22.0	161.5	−183.5
Ph	−235.9	−24.8	−211.1

^{a} $\Delta\delta^{119}$Sn = R$_2$Sn(dmio) − R$_2$Sn(dmit).

more than 20° larger than those in the other two compounds [8c].

5.4. Spectra of 5

In the IR spectra in KBr, the range of ν(C=C) values were 1451–1475 and those for ν(C=O) were 1660–1667 and 1609–1614 cm^{-1}. In the NMR spectra in Me$_2$SO$_2$-d_6 solution, δ^{13}C(C=C) and δ^{13}C(C=O) were between 118–120 and 191–193 ppm, respectively: the δ^{13}C(C=C) values for **3** in Me$_2$CO-d_6 solution are at a somewhat lower field (in the range 129.7 and 131.7 ppm) [7f]. Comparison of the δ^{119}Sn values of **3** and **5**, listed in Table 4, indicates that the tin atoms in the dmio complexes are more shielded than in the dmit analogues. Both sets of δ^{119}Sn values indicate five-coordinate tin species.

5.5. [R$_2$Sn(dmio)] compounds 6

Neutral compounds **6** are orange in colour. They are also considerably more soluble in coordinating solvents than in non-coordinating solvents. This, plus the high m.p.s (between 178 and 200°C), suggest that the R$_2$Sn(dmio) compounds are aggregated in the solid state; this was confirmed by the X-ray diffraction study for Me$_2$Sn(dmio).

5.6. Solid state structure of 6b

The structure consists of aggregated molecules, see Fig. 2. The major intermolecular interaction is an Sn–O interaction, [Sn–O^i = 2.654(6) Å], which links the molecules into chains parallel to c, with weaker interactions, [Sn–S4^{ii} = 3.649(3) and S4–S4^{ii} = 3.430(3) Å], linking the chains into layers: symmetry operators, i: 1/2 − x, 1/2 − y, z − 1/2; ii: − x, y 1/2 − z. In addition, there are S1–S3^i [3.595(3) Å] interactions within the chains. There are no interactions between the layers at distances less than the sum of appropriate the van der Waals radii [Sn = 2.20, S = 1.85 and O = 1.50 Å] [21]. The intermolecular Sn–O and Sn–S separations are considerably longer than single covalent bonds, e.g. 1.940(1) Å in (Me$_3$Sn)$_2$O [22], and 2.39–2.44 Å for four-coordinate R$_3$SnSR compounds [23], but are within the sum of the van der Waals radii [21] of 3.70 and 4.05 Å for Sn/O and Sn/S, respectively. The Sn–S4^{ii} interactions involve thiolate S atoms. Similar weak Sn–S interactions (Sn–S = 3.69 Å) have been determined in Bu$_2$Sn(edt) [1e]: two such interactions link each molecule of Bu$_2$Sn(edt) to neighbouring molecules [1e]. In both Bu$_2$Sn(edt) and Me$_2$Sn(dmio), Sn$_2$S$_2$ rings arise as central features of the structures. In Me$_2$Sn(edt), a single but stronger Sn–S interaction [Sn–S^i = 3.18 Å] [1a] links molecules into chains.

Table 5 lists bond lengths and angles for **6b**. With the intermolecular Sn–O and Sn–S interactions, the tin centre becomes six-coordinate, see Fig. 3. The arrangement of the six groups about tin is far from regular, a description as a highly distorted octahedral complex is barely acceptable since the *trans*-angles are 124.2(4), 154.10(7) and 168.21(16)°. Ignoring the weaker Sn–S interaction, the geometry at tin would be slightly distorted trigonal bipyramidal, with the quasi axial sites occupied by O and a dithiolate S atom, (S4), (Sn–S4 = 2.687(2) Å and o-Sn–S(4) = 168.21(16)°). The other dithiolato S atom (S1) in Me$_2$Sn(dmio) forms a slightly stronger bond to tin (Sn–S1 = 2.440(2) Å). The difference in the intramolecular Sn–S bond lengths is noticeably less than that found in **5**. The bite angle of the dithiolate chelate group in Me$_2$Sn(dmio) is, at 89.47(8)°, slightly greater than those found in **5** (between 86.2(1) and 86.47(6)°), this is matched by the Sn–S bond lengths in Me$_2$Sn(dmio) being on average shorter than in **5**.

The compounds, Et$_2$Sn(dmit) [7g] and PhMeSn(dmit) [7a] contain five-coordinate tin atoms with trigonal bipyramidal geometries in the solid state, as a consequence of intermolecular interactions between the tin centres and thione sulfur atoms (Sn–S(=C) = 3.042(5) and 3.139(1) Å, respectively); neither molecule exhibits intermolecular tin–thiolate bonding.

A tin centre in a four-coordinate diorganotin dithiolate is clearly coordinatively unsaturated and will coordinate, at least in the solid state, with available donor groups, unless other factors, e.g. steric hindrance, intervene. Complexes of R$_2$Sn(dithiolate) with halide ions and with nitrogen donors, D, to give [R$_2$SnX(dithiolate)]$^-$ [4a, 6b, 7a,b,f] and [R$_2$Sn(dithiolate)·D] [1c, 3, 7a], respectively, have been isolated for various dithio-

lates. In the estertin compounds, $(RO_2CCH_2CH_2)_2Sn(dmio)$ (**7**) [8a] and $(RO_2CCH_2CH_2)_2Sn(dmit)$ (**8**) [7d], the additional coordination, in both solution and in the solid state, is with the two intramolecular carbonyl groups, while in the simpler dithiolates, $R_2Sn(edt)$ (R = Me or Bu), additional coordination in the solid state, as mentioned earlier, concerns dithiolate S atoms of neighbouring molecules. On dissolution, however, the intermolecular associations in $R_2Sn(edt)$ are broken with the formation of four-cordinate compounds [1e, 2a]. The bulkier $^tBu_2Sn(edt)$ is monomeric in both the solid state and in solution [1f].

7: E = O

8: E = S
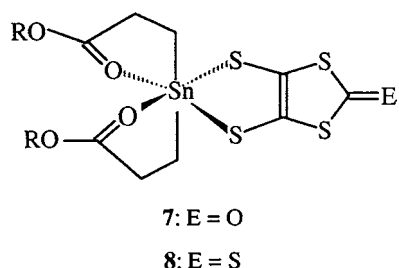
Despite the differing intermolecular interactions in **4** and **6**, the two sets of monomers have similar structures, with the chelate bite angles, the intramolecular Sn–S bond lengths, and geometric parameters of the metallocyclic [SnSCCS] units in **4** and **6** being very similar.

5.7. Spectra

In the IR spectra of **6** in KBr, ν(C=C) occurs at 1452–1461 cm^{-1} and ν(C=O) at 1662–1673 and 1610–1615 cm^{-1}; in the NMR spectra in Me$_2$SO-d$_6$, δ(C=C) and δ(C=O) are in the ranges 116.7–118.8 and 191.3–192.6 ppm, respectively. Values for the C=C unit in the analogous dmit compounds, **4**, were ν(C=C) = 1433–1456 cm^{-1} and δ(C=C) 129.5–130.3 ppm in Me$_2$CO solution [7a]. Again, δ(C=C) values for the dmio compounds appear at higher field.

The solution δ^{119}Sn values of **6** in Me$_2$SO solution are shown in Table 6. The values suggest five-coordinate tin centres, i.e. the Sn–O interactions still persist in solution. The weaker intermolecular interactions are probably absent as found with $R_2Sn(edt)$ in solution. Comparison of the solution δ^{119}Sn values of **6** and **4** in Table 6 indicate that the dmio componds exhibit the higher field values (by between 170 and 211 ppm). The differences in the δ^{119}Sn values, $(\Delta\delta^{119}Sn = \delta^{119}Sn[R_2Sn(dmio)]-\delta^{119}Sn[R_2Sn(dmit)])$ reflect both the differences in the dithiolate units and the intermolecular associations. The δ^{119}Sn values for the six coordinate species, **7** [8a] and **8** [7d], are 48.2 and 89.7 ppm, respectively, in CDCl$_3$ solution. From these values and δ^{119}Sn values for **3** and **5**, it can be estimated

that ca. 20–40 ppm of the differences in δ^{119}Sn values of **6** and **4** is attributable to the differences between the dithiolate ligands, the remainder being due to the differences in the intermolecular donor groups.

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