

Journal of Organometallic Chemistry, 436 (1992) 23–33
 Elsevier Sequoia S.A., Lausanne
 JOM 22697

Main group metal 1,3-dithiole-2-thione-4,5-dithiolate (DMIT) compounds

II *. Synthesis and structures of tetrabutylammonium butyl- and phenyl-bis(1,3-dithiole-2-thione-4,5-dithiolato)stannates, $[\text{Bu}_4\text{N}][\text{RSn}(\text{DMIT})_2]$ (R = Bu or Ph)

Solange M.S.V. Doidge-Harrison, R. Alan Howie, John T.S. Irvine,
 Gavin M. Spencer and James L. Wardell

Chemistry Department, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE (UK)

(Received February 11, 1992)

Abstract

Structures have been determined for $[\text{Bu}_4\text{N}][\text{RSn}(\text{DMIT})_2]$ (III; R = Bu and IV; R = Ph), obtained from $[\text{Bu}_4\text{N}]_2[\text{Zn}(\text{DMIT})_2]$ and RSnCl_3 . These complexes are isostructural. In the spirocyclic anions, the tin atoms are pentacoordinate and have geometries between trigonal bipyramidal (TBP) and rectangular pyramidal: the distortions away from TBP geometry are calculated to be *ca.* 48 and 70% for II and IV respectively. The S atoms in the chelate ligands form the quasi-basal planes with the R groups in axial sites. The DMIT ligands, while individually planar, are not coplanar: the angles between the DMIT mean planes are 19.2 and 10.8° for III and IV respectively.

The anions are packed side by side in the *c* direction with $\text{S} \cdots \text{S}$ separations close to the sum of the van der Waals radii. In the *a* and *b* directions, there are arrays of alternating cation and anion units.

Introduction

Complexes of the DMIT ligand (I; $\text{H}_2\text{DMIT} = 4,5\text{-dimercapto-1,3-dithiole-2-thione}$) have attracted interest, particularly since the discovery of superconductivity in salts of nickel and palladium DMITs. By far the majority of DMIT complexes studied have involved transition metals [1–8]. DMIT complexes of main group metals have attracted only scattered and limited attention: some inorganic complexes of zinc, cadmium and mercury $[\text{R}_4\text{N}]_2[\text{M}(\text{DMIT})_2]$ [9] and of In and Tl [10] have however been studied. We earlier reported [11] on $[\text{Bu}_4\text{N}][\text{Me}_2\text{ClSn}(\text{DMIT})]$ (II) and as part of our investigation of DMIT complexes, we now report the

Correspondence to: Dr. J.L. Wardell, Chemistry Department, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, UK.

* For Part I, see ref. 11.

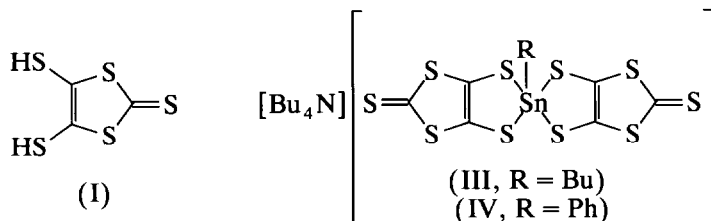
Table 1

Anionic pentacoordinate tin complexes, containing mono- and bis-(dithiolato) groups

	θ_{15}^a	θ_{24}^a	δ_{24}^b	% Distortion from trig. bipy to rect. py	Sn-S bond lengths (Å)	$\Delta(\text{Sn-S})$	Ref.
<i>Mono(dithiolato) complex</i>							
[Me ₄ N][Ph ₃ SnS ₂ C ₂ (CN) ₂]	161.6	127.7	34.0	35.1	2.864(2), 2.496(2)	0.368	14
[Bu ₄ N][Me ₂ ClSn(DMIT)]	167.3	120.8	40.4	5.9	2.620(3), 2.452(3)	0.168	11
[Et ₄ N][Ph ₂ ClSn(S ₂ C ₇ H ₆) ₂]	165.9	121.2	44.1	14.1	2.544(2), 2.436(2)	0.108	13
[Et ₄ N][MeClSn(SCH ₂ CH ₂ S)-[SCH ₂ CH ₂ S]	167.3	124.0	39.9	23.5	2.506(2), 2.420(2)	0.086	12
<i>Bis(dithiolato) complexes</i>							
[Et ₃ NH] ₂ [Sn(SCH ₂ CH ₂ S) ₂]-[SCH ₂ CH ₂ S] (V; R ₄ M=Et ₃ NH, Y = SCH ₂ CH ₂ S)	169.0	130.9	35.5	33.6	2.540(2), 2.454(2)	0.086	12
[Me ₄ N][ClSn(S ₂ C ₇ H ₆) ₂] (VII; R ₄ M=Me ₄ N, Y = Cl)	161.3	147.6	13.6	76.9	2.463(3), 2.437(4)	0.026	13
[MePh ₃ P][BrSn(S ₂ C ₇ H ₆) ₂] (VII; R ₄ M=MePh ₃ P, Y = Br)	155.7	152.0	3.7	94.2	2.461(2), 2.449(2)	0.012	15
[Et ₄ N][MeSn(S ₂ C ₂ (CN) ₂) ₂] (VI; R ₄ M=Et ₄ N, Y = Me)	150.2	140.7	9.5	80.4	2.517(2), 2.478(2)	0.039	14
[Et ₄ N][BuSn(SCH ₂ CH ₂ S) ₂] (V; R ₄ M=Et ₄ N, Y = Bu)	153.5	142.3	10.9	78.7	2.521(3), 2.467(3)	0.054	12
[Et ₄ N][BuSn(S ₂ C ₂ (CN) ₂) ₂] (VI; R ₄ M=Et ₄ N, Y = Bu)	144.8	144.8	0	96.7	2.523(3), 2.480(3)	0.043	14
[Bu ₄ N][BuSn(DMIT) ₂] (III)	157.5	127.7	26.4	47.8	2.549(4), 2.461(5)	0.088	This study
[Et ₄ N][PhSn(SCH ₂ CH ₂ S) ₂] (V; R ₄ M=Et ₄ N; Y = Bu)	159.2	137.6	20.9	60.2	2.530(4), 2.472(4)	0.058	12
[Bu ₄ N][PhSn(DMIT) ₂] (IV)	152.3	136.8	14.5	69.5	2.523(4), 2.483(4)	0.040	This study

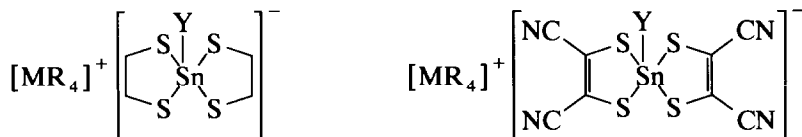
^a θ_{15} and θ_{24} are the *trans*-basal angles of rectangular pyramids, which correspond to axial and equatorial angles of the corresponding trigonal bipyramids. ^b δ_{24} dihedral angle between trigonal bipyramid faces, 124 and 245, that have the common equatorial edge 24.

synthesis and structures of two anionic organotin spirocyclic bis(DMIT) complexes, III and IV.



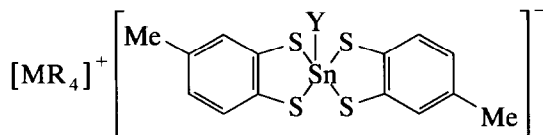
Other anionic spirocyclic pentaco-ordinate tin species, having Sn-S bonds, *e.g.* V-VII have been previously studied by Holmes *et al.* [12-15] (see also Table 1). These, and other pentacoordinate tin complexes listed in Table 1, have structures which are between trigonal bipyramidal and rectangular pyramidal in geometry. The extents of the distortions of V-VII away from trigonal bipyramidal geometry

have been quantified by Holmes and co-workers [12–15]. A similar approach was also used in this study for II–IV.



V [Y = Bu, Ph or $\frac{1}{2}(\text{SCH}_2\text{CH}_2\text{S})$]

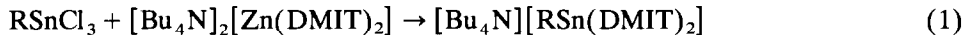
VI [Y = Me or Bu]



VII [Y = Cl or Br]

Results and discussion

Compounds III and IV, were obtained by direct reactions of RSnCl_3 (R = Bu or Ph) with equimolar $[\text{Bu}_4\text{N}]_2[\text{Zn}(\text{DMIT})_2]$ in CDCl_3 solution (eq. 1). The same products could also be obtained using a 2:1 mole ratio of $\text{RSnCl}_3 : [\text{Bu}_4\text{N}]_2[\text{Zn}(\text{DMIT})_2]$. The $\delta^{119}\text{Sn}$ values in the ^{119}Sn NMR spectra of III and IV in CDCl_3 solution are 27.0 and -21.9 ppm respectively.



Solid state $\delta^{119}\text{Sn}$ values for III and IV are only slightly shifted to 37.6 and -9.4 ppm respectively [16]. Thus, there are no major changes in the molecular structures on passing from the solid state to solution in CDCl_3 .

Comparison of $\delta^{119}\text{Sn}$ values for IV in CDCl_3 and for V ($\text{R}_4\text{N} = \text{Et}_4\text{N}$; Y = Ph) in MeCN [12] (-21.9 and -82.4 ppm respectively) indicates that the DMIT ligand causes a greater shift to lower field than does the $\text{SCH}_2\text{CH}_2\text{S}$ ligand.

In the Mössbauer spectrum of III, the value of the quadrupole splitting is 1.33 mm s^{-1} . The QS value for VII ($\text{R}_4\text{N} = \text{Me}_4\text{N}$; Y = Cl) is 1.44 mm s^{-1} [13], while those for VII ($\text{R}_4\text{N} = \text{Et}_4\text{N}$; Y = Cl, Br and I) are 1.35, 1.08 and 1.11 mm s^{-1} respectively [17]. All these values are indicative of rectangular pyramidal geometries (see below).

Molecular structure

Atomic coordinates for III and IV are listed in Tables 2 and 3; bond lengths and angles are in Table 4. Figures 1 and 2 show the molecular structures and numbering systems of III and IV respectively. In both III and IV, Sn and N atoms lie on a crystallographic 2-fold axis. For III, C(31) of the rotationally disordered butyl group also lies on the 2-fold axis; for IV, C(31) and C(34) of the phenyl ring do similarly.

Compounds III and IV, exist as ionic compounds and are isostructural. The tin atoms in the anions are pentacoordinate and have distorted rectangular pyramidal geometries. The organic groups, R, are in the apical positions and the bases are formed by the S atoms of the symmetry related bidentate DMIT ligands. Thus the complexes III and IV are spirocyclic pentacoordinate species.

Table 2

Atomic coordinates $\times 10^4$ and $U_{\text{eq}} \times 10^3$ (\AA^2) for III with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}^a
Sn	0	927(1)	2500	108(1)
S(1)	1066(3)	248(3)	3839(3)	117(2)
S(2)	650(3)	615(3)	1164(4)	126(2)
S(3)	2614(3)	306(3)	3913(5)	132(2)
S(4)	2268(3)	588(3)	1661(5)	135(2)
S(5)	3837(4)	340(4)	3036(7)	192(4)
C(1)	1706(11)	399(9)	3169(16)	111(8)
C(2)	1504(10)	532(8)	2075(15)	98(7)
C(3)	2924(11)	434(9)	2839(18)	124(8)
N	0	7628(9)	2500	77(4)
C(11)	-447(8)	7028(9)	1613(12)	92(4)
C(12)	-941(9)	7457(11)	656(13)	115(5)
C(13)	-1335(12)	6740(15)	-179(19)	168(8)
C(14)	-1802(17)	7066(21)	-1138(27)	240(13)
C(21)	-491(7)	8200(8)	2875(10)	79(4)
C(22)	-1045(8)	7731(9)	3288(11)	94(4)
C(23)	-1502(8)	8360(10)	3617(12)	106(5)
C(24)	-2069(9)	7902(11)	4033(14)	120(5)
C(31)	0	2363(39)	2500	295(28)
C(32)	334(25)	2552(27)	3149(38)	128(12)
C(33)	197(21)	3673(24)	2946(26)	137(13)
C(34)	646(28)	4042(31)	3944(40)	189(19)

^a $U_{\text{eq}} = (1/3)\Sigma_i \Sigma_j a_i^* a_j^* a_i \cdot a_j$ for Sn to C(3) and is U_{iso} otherwise. C(32) is badly affected by disorder.

The Sn-S bond lengths in III are 2.461(5) and 2.549(4) \AA [$\Delta(\text{Sn-S}) = 0.088 \text{\AA}$] and in IV are 2.483(4) and 2.523(4) \AA [$\Delta(\text{Sn-S}) = 0.040 \text{\AA}$]. All the Sn-S bond lengths are within the usual ranges for such bonds (*e.g.*, see Table 1). The Sn-C carbon lengths are 2.28(6) and 2.17(2) \AA in III and IV respectively and are also normal.

The DMIT ligands in III and IV, while individually planar, are not co-planar. The angles between the DMIT mean planes are 19.2 and 10.8° for III and IV respectively. The displacements of the Sn atoms from the basal planes, in a direction towards the apical R groups, are 0.732 \AA and 0.773 \AA in III and IV respectively.

As with the other bis-5-membered chelated complexes listed in Table 1, III and IV show distortions away from rectangular pyramidal towards trigonal bipyramidal structures. The extents of these distortions can be calculated using the dihedral angle method, initially outlined by Muetterties and Guggenberg [18], and further developed by Holmes and *et al.* [14]. Percentage distortions from trigonal bipyramidal structures for III and IV, as well as for II, were thereby calculated to be 47.8, 69.5 and 5.9% respectively. A very convenient view of the extents of the structural distortion for pentacoordinated species can be obtained from plots of δ_{24} (the dihedral angle *) against the *trans*-basal angles, δ_{15} and δ_{24} , *i.e.* 1-Sn-5 and 2-Sn-4 bond angles of the rectangular pyramids, which become the axial and

* δ_{24} is the dihedral angle formed between the planes of the trigonal bipyramid faces 124 and 245 that have the common equatorial edge 24.

Table 3

Atomic coordinates $\times 10^4$ and $U_{\text{eq}} \times 10^3$ (Å) for IV with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}^a
Sn	0	891(1)	2500	64(1)
S(1)	-1127(2)	341(3)	1061(3)	86(1)
S(2)	-654(2)	529(3)	3827(3)	86(1)
S(3)	-2696(3)	469(3)	1029(4)	100(1)
S(4)	-2306(3)	619(3)	3350(4)	100(2)
S(5)	-3914(3)	528(3)	1952(6)	148(3)
C(1)	-1756(8)	473(8)	1756(11)	77(6)
C(2)	-1553(8)	538(8)	2875(11)	72(5)
C(3)	-3017(9)	532(8)	2116(15)	95(7)
N	0	7742(10)	2500	87(5)
C(11)	-412(8)	7154(9)	1565(12)	92(5)
C(12)	-901(11)	7654(12)	542(15)	134(7)
C(13)	-1151(22)	6789(23)	-571(30)	267(18)
C(14)	-1611(21)	6868(24)	-345(30)	267(17)
C(21)	537(9)	8313(10)	2182(12)	96(5)
C(22)	1128(9)	7814(11)	1835(13)	110(6)
C(23)	1668(11)	8432(12)	1641(14)	128(6)
C(24)	2273(10)	7975(11)	1293(15)	130(6)
C(31)	0	2195(13)	2500	92(7)
C(32)	576(11)	2570(13)	3363(16)	138(7)
C(33)	525(13)	3471(16)	3361(18)	169(8)
C(34)	0	3827(19)	2500	152(11)

^a $U_{\text{eq}} = (1/3)\sum_i \sum_j a_i^* a_j^* a_i \cdot a_j$ for Sn to C(3) and is U_{iso} otherwise. C(13) and C(14) are artefacts of disorder.

equatorial angles of the corresponding trigonal bipyramids (see Fig. 3) [14]. Table 1 lists values of δ_{24} , δ_{15} and δ_{24} obtained for II–IV and for similar complexes, which are used in the plot of δ_{15} and δ_{24} against δ_{24} , shown in Fig. 4. The bold lines drawn in Fig. 3 link data for an ideal trigonal bipyramid (for which $\delta_{24} = 120^\circ$, $\delta_{15} = 180^\circ$ and $\delta_{24} = 53.1^\circ$) and for a limiting rectangular pyramid (for which $\delta_{24} = \delta_{15} = 150^\circ$ and $\delta_{24} = 0^\circ$).

The differences in the Sn–S bond lengths [$\Delta(\text{Sn–S})$], for complexes such as III–VII, can also be used as reflections of the distortions from regular rectangular pyramidal arrays: generally the smaller the $\Delta(\text{Sn–S})$, the closer is the structure to that of a rectangular pyramid (see Table 1).

Crystal structure

Projected views down the *b* axis of III and IV are shown in Fig. 5. The anions are packed side by side in the cell forming chains in the *c* direction. Within these chains the Sn \cdots S separations are close to the sum of the van der Waals radii (3.70 Å) for both III and IV, although those separations are slightly less than 3.70 Å for IV, possibly indicating an interligand interaction.

The structure is developed in the *a* direction by more or less linear chains of alternating cations and anions. The cation N and anion S(5) separations are 4.471(13) and 4.399(6) Å for III and IV respectively.

An alternating arrangement also occurs in the *b* direction. However here each cation is not equidistant from its neighbouring anions, due to the apical groups R. The cation is able to approach more closely to an anion on the side *trans* to the R

Table 4

Bond lengths (Å) and angles (deg) for III and IV with e.s.d.s in parenthesis

Bond lengths		III		IV	
Sn–S(1)	2.461(5)	2.483(4)	Sn–S(2)	2.549(4)	2.523(4)
Sn–C(31)	2.29(6)	2.17(2)	C(31)–C(32)	0.93(5) ^a	1.41(2)
C(32)–C(33)	1.82(6) ^a	1.50(3)	C(33)–C(34)	1.44(5)	1.35(3)
S(1)–C(1)	1.77(1)	1.74(2)	S(2)–C(2)	1.68(2)	1.73(2)
S(3)–C(1)	1.70(2)	1.71(2)	S(3)–C(3)	1.74(2)	1.73(2)
S(4)–C(2)	1.74(1)	1.75(1)	S(4)–C(3)	1.66(2)	1.71(2)
S(5)–C(3)	1.70(2)	1.65(2)	C(1)–C(2)	1.39(3)	1.38(2)
N–C(11)	1.53(2)	1.55(2)	N–C(21)	1.52(1)	1.55(2)
C(11)–C(12)	1.47(2)	1.57(2)	C(21)–C(22)	1.55(2)	1.58(3)
C(12)–C(13)	1.59(3)	1.98(4) ^b	C(22)–C(23)	1.50(2)	1.53(3)
C(13)–C(14)	1.38(3)	1.02(6) ^b	C(23)–C(24)	1.57(3)	1.57(2)
C(12)–C(14)	–	1.95(4) ^b			
Bond angles					
S(1)–Sn–S(2)	85.7(2)	85.8(1)	S(1)–Sn–S(1')	127.7(2)	136.8(1)
S(1')–Sn–S(2')	84.4(2)	84.1(1)	Sn(1)–Sn–C(31)	116.1(1)	111.6(1)
S(2)–Sn–S(2')	157.5(2)	152.3(1)	S(2)–Sn–C(31)	101.3(1)	103.8(1)
C(32)–C(31)–Sn	109(6)	116(1)	C(32)–C(31)–C(32')	–	128(2)
C(33)–C(32)–C(31)	99(6) ^a	114(2)	C(34)–C(33)–C(32)	105(3)	118(2)
C(33')–C(34)–C(33)	–	128(2)	Sn–S(2)–C(2)	96.5(5)	96.2(4)
Sn–S(1)–C(1)	97.7(7)	97.6(5)	S(1)–C(1)–S(3)	117(1)	119.1(8)
S(1)–C(1)–C(2)	124(1)	124(1)	S(2)–C(2)–S(4)	120(1)	118.4(8)
S(2)–C(2)–C(1)	128(1)	127(1)	C(1)–C(2)–S(4)	112(1)	115(1)
C(2)–C(1)–S(3)	119(1)	116(1)	C(1)–S(3)–C(3)	95(1)	98.3(7)
C(2)–S(4)–C(3)	99(1)	98.1(7)	S(3)–C(3)–S(4)	115(1)	113(1)
S(5)–C(3)–S(3)	120(1)	123(1)	S(5)–C(3)–S(4)	125(1)	125(1)
C(11)–N–C(21)	112.2(7)	112(1)	C(11)–N–C(11')	102.6(9)	102(1)
C(11)–N–C(21')	112.0(9)	113(1)	N–C(11)–C(12)	114(1)	109(1)
C(11)–C(12)–C(13)	106(2)	99(2) ^b	C(11)–C(12)–C(14)	–	103(2) ^b
C(12)–C(13)–C(14)	112(2)	73(3) ^b	C(13)–C(12)–C(14)	–	30(2) ^b
C(13)–C(14)–C(12)	–	77(3) ^b	C(21)–N–C(21')	106.0(8)	104(1)
N–C(21)–C(22)	114(1)	111(1)	C(21)–C(22)–C(23)	109(1)	106(1)
C(22)–C(23)–C(24)	110(1)	109(2)			

Symmetry operation: $-x, y, \frac{1}{2} - z$. ^a These values are associated with disordered atoms C(32) and are therefore unreliable. ^b These values are associated with disordered atoms C(13) and C(14) and are therefore unreliable.

groups which leads to Sn \cdots N distances along the *b* axis of 5.267 and 10.697 Å for III and of 5.237 and 11.392 Å for IV.

Experimental

Melting points were uncorrected and were measured on a Kofler hotstage. NMR spectra were obtained on a Bruker 250 MHz instrument and IR spectra on a Philips Analytical PU9800 FTIR spectrometer.

Compound $[\text{Bu}_4\text{N}]_2[\text{Zn}(\text{DMIT})_2]$ was obtained by a published procedure [9].

Synthesis

$[\text{Bu}_4\text{N}][\text{BuSn}(\text{DMIT})_2]$ (III). A solution of BuSnCl_3 (0.282 g mmol^{-1}) in CHCl_3 (10 ml) was added to one of $[\text{Bu}_4\text{N}]_2[\text{Zn}(\text{DMIT})_2]$ (0.941 g, 1 mmol) in

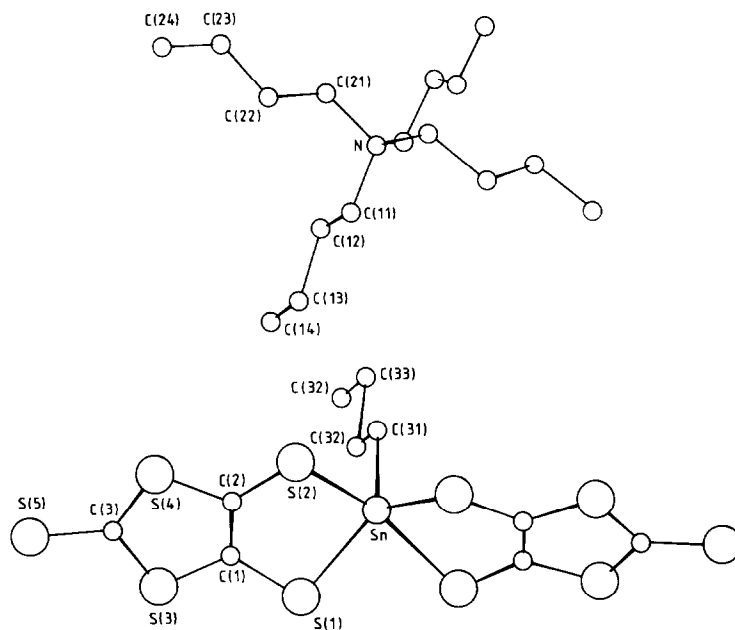


Fig. 1. Atomic arrangements of III.

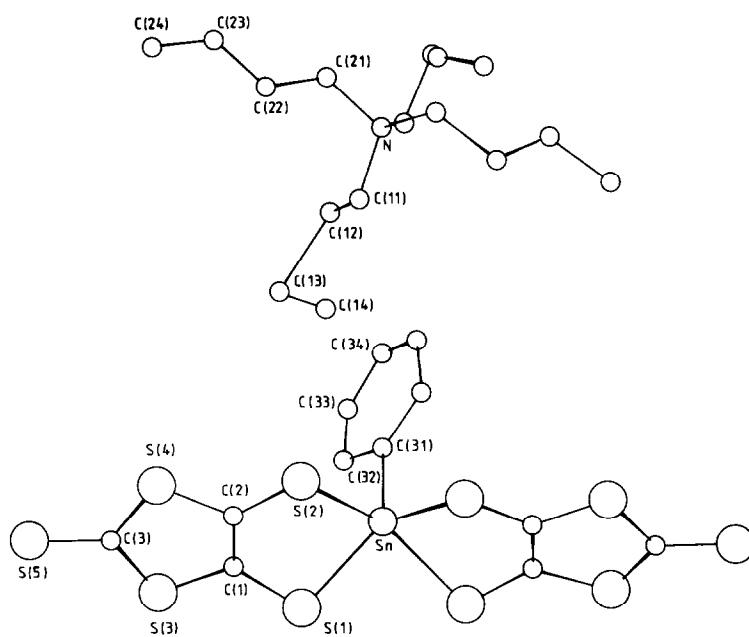


Fig. 2. Atomic arrangements of IV.

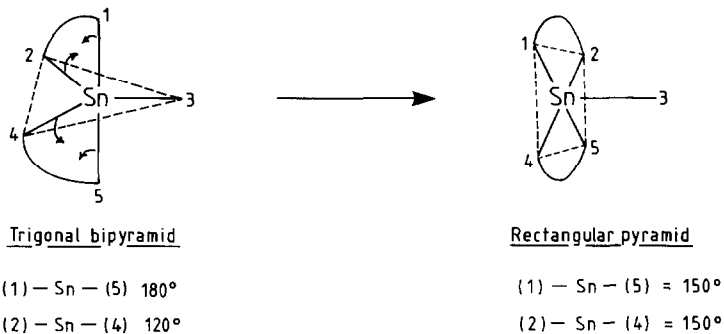


Fig. 3. Relationship between trigonal bipyramid and rectangular pyramid.

CHCl_3 (10 ml); the colour of the solution changed to red. The solution was left overnight and the solvent was removed under reduced pressure, leaving a red oil. Addition of CHCl_3 / $^1\text{PrOH}$ (1/1) to the oil gave green-brown crystals, m.p. $97-98^\circ$. Anal. Found: C, 38.54; H, 5.71; S, 41.71. $\text{C}_{26}\text{H}_{45}\text{NS}_{10}\text{Sn}$ calc.: C, 38.51; H, 5.59; S, 39.54%. ^1H NMR (250 MHz, CDCl_3): δ 0.91 (t, 3H, J 7.2, Me of anion), 1.02 (t, 12H, J 7.0, Me of cation), 1.45 (m, 10H, CH_2 of anion and CH_2 of cation), 1.61 (m, 8H) (CH_2 of cation), 1.74 (m, 2H), and 1.90 (m, 2H) ($\text{CH}_2\text{CH}_2\text{CH}_3$ of

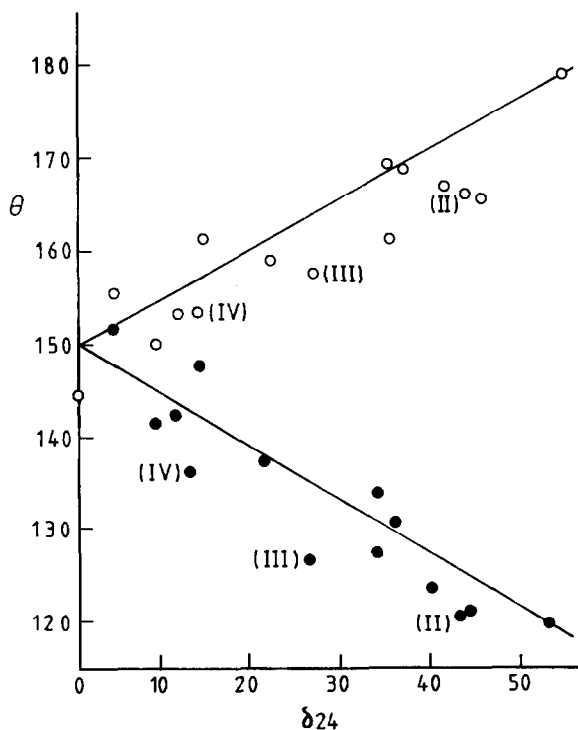


Fig. 4. Plot of δ_{15} (deg) and δ_{24} (deg) against δ_{24} ; $\delta_{15} = [(1)-\text{Sn}-(5)]$; $\delta_{24} = [(2)-\text{Sn}-(4)]$. δ_{24} = dihedral angle between the planes of the trigonal bipyramid faces 124 and 245.

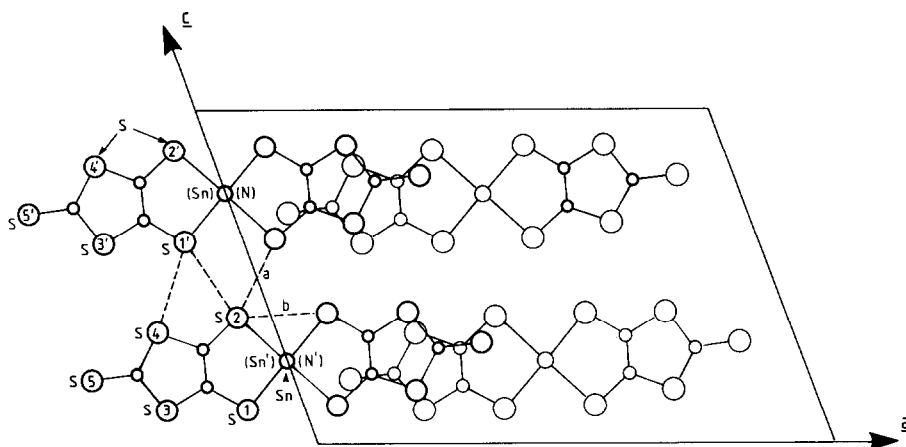


Fig. 5. Projected views onto the *ac* plane of anions of III and IV.

Sulphur separations	III (Å)	IV (Å)
S(4)–S(1')	3.901(8)	3.815(6)
S(2)–S(1')	3.712(7)	3.625(6)
a	3.791(7)	3.654(6)
b	3.366(8)	3.354(7)

Relative heights of anions [(Sn) and (Sn')] and cations [(N) and (N')], in terms of $10^2/b = [41$ and $59]$ and $[73$ and $27]$ for III and $[-9$ and $9]$ and $[23$ and $-23]$ for IV.

Bu–Sn), 3.16 (m, 8H, CH_2N). ^{13}C NMR (62.9 MHz, CDCl_3): δ 13.60, 19.69 and 23.83 ($-\text{CH}_2\text{CH}_2\text{CH}_3$ of cation), 24.76 (Me of BuSn), 25.62 [$J(^{119}\text{Sn}-^{13}\text{C})$ 113 Hz], 27.37 [$J(^{119}\text{Sn}-^{13}\text{C})$ 43.1 Hz] and 36.51 [$J(^{119}\text{Sn}-^{13}\text{C})$ 510.0 Hz, $J(^{117}\text{Sn}-^{13}\text{C})$ 484.5 Hz] ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Sn}$ of Bu), 58.86 (CH_2N), 130.22 (C=C), 207.32 (C=S). ^{119}Sn NMR (93.3 MHz, CDCl_3): δ 27.0 ppm (rel. to Me_4Sn). Mössbauer spectrum: I.S. 1.30 mm s^{-1} ; Q.S. 1.33 mm s^{-1} ; Γ 0.81. IR (KBr disc): 2953–2868, 1439, 1059, 1033, 999, 893, 883, 862, 669 cm^{-1} .

$[\text{Bu}_4\text{N}][\text{PhSn}(\text{DMIT})_2]$ (IV). This was prepared analogously to III, from PhSnCl_3 (0.604 g, 2 mmol) and $[\text{Bu}_4\text{N}]_2[\text{Zn}(\text{DMIT})_2]$ (0.941 g, 1 mmol). Orange crystals, yield 73%, m.p. 128–130°C. Anal. Found: C, 40.71; H, 5.10; S, 38.21. $\text{C}_{28}\text{H}_{41}\text{NS}_{10}\text{Sn}$ Calc.: C, 40.47; H, 4.97; S, 38.58%. ^1H NMR (250 MHz, CDCl_3): δ 1.03 (t, 12H, J 7.2 Hz, Me); 1.43 (m, 8H) and 1.62 (m, 8H) ($\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.12 (t, 8H, CH_2N), 7.42 (m, 3H, $m + p$ -H of Ph), 7.84 (m, 2H, o -H of Ph). ^{13}C NMR (62.9 MHz, CDCl_3): δ 13.69 (Me), 19.76 and 23.91 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 128.83 [$J(^{119}\text{Sn}-^{13}\text{C})$ 91.6 Hz, m -C of Ph–Sn], 130.01 (p -C of Ph–Sn), 134.30 [$J(^{119}\text{Sn}-^{13}\text{C})$ 69.7 Hz, o -C of Ph–Sn], 136.00 (i -C of Ph–Sn), 140.01 (C=C), 207.06 (C=S). ^{119}Sn NMR (93.3 MHz, CDCl_3): δ -21.92 ppm (rel. to Me_4Sn). IR (KBr disc): 3059, 2955–2868, 1439, 1059, 1034, 893, 740, 700 cm^{-1} .

Crystal structure determination

Crystal data, data collection and processing details are presented in Tables 5 and 6.

Table 5

Crystal data

	III	IV
Formula	C ₂₆ H ₄₅ NS ₁₀ Sn	C ₂₈ H ₄₁ NS ₁₀ Sn
<i>M</i>	810.984	830.974
Crystal system	monoclinic	monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	19.326(16)	19.025(11)
<i>b</i> (Å)	15.964(10)	16.629(14)
<i>c</i> (Å)	13.270(9)	13.001(7)
β (deg)	110.12(5)	110.16(4)
<i>V</i> (Å ³)	3844(2)	3861(5)
<i>Z</i>	4	4
<i>D_c</i> (g cm ⁻³)	1.401	1.429
<i>F</i> (000)	1672	1704
μ (mm ⁻¹)	1.21	1.20

Data were obtained for compounds III and IV with a Nicolet P3 four-circle diffractometer with graphite monochromator and Mo- K_{α} radiation. The cell dimensions were obtained from setting angles of 17 independent reflections with $2\theta \approx 20^{\circ}$. Data were collected for Lorentz polarisation effects but absorption was ignored. Two reference reflections, monitored periodically, showed no significant variation in intensity.

The position of the tin atoms in III and IV were located from the three-dimensional Patterson function, while the remaining non-hydrogen atoms were located from successive difference Fourier maps using SHELX-76 [19]. Full-matrix least-squares calculations on *F* with anisotropic thermal parameters for Sn and DMIT ligand atoms and isotropic thermal parameters for all other non-H atoms converged at *R* 0.071, *R_w* 0.078 for III and *R* 0.053, *R_w* 0.055 for IV. H atoms were not included in the refinements. Final $w = 1.0/[\sigma^2(F) + 2.677(F^2)]$ for III and $w = 1.0/[\sigma^2(F) + 1.217(F^2)]$ for IV. Final $\Delta_{\rho\max} = 0.53$, $\Delta_{\rho\min} = -0.36 \text{ e } \text{Å}^{-3}$ for III. Corresponding values for IV are 0.63 and $-0.32 \text{ e } \text{Å}^{-3}$.

Table 6

Data collection and processing

	III	IV
Crystal colour	green-brown	orange
Crystal dimensions (mm)	0.1 × 0.4 × 0.3	0.5 × 0.7 × 0.16
Scan technique	$\omega - 2\theta$	$\omega - 2\theta$
2θ range (deg)	0–50	0–50
<i>hkl</i> range	$0 \leq h \leq 25, 0 \leq k \leq 20,$ $-17 \leq l \leq 17$	$0 \leq h \leq 24, 0 \leq k \leq 21,$ $-17 \leq l \leq 17$
No. of reflexions measured	3713	3627
No. of unique observed reflexions	1332	1174
<i>I</i> > <i>mσ</i> (<i>I</i>)	<i>m</i> = 3	<i>m</i> = 4

Acknowledgment

The authors thank Dr. K. Molloy of Bath University for obtaining the Mössbauer spectra.

References

- 1 C. Tejel, B. Pomarede, J.-P. Legros, L. Valade, P. Cassoux and J.P. Ulmet, *Chem. Mater.*, 1 (1989) 578; P. Cassoux, L. Valade, J.-P. Legros, L. Interrante and C. Roucau, *Physica B*, 143 (1986) 313; P. Cassoux, L. Valade, M. Bousseau, J.-P. Legros, M. Garbaskas and L. Interrante, *Mol. Cryst. Liq. Cryst.*, 120 (1985) 377; J.P. Ulmet, M. Mazzaschi, C. Tejel, P. Cassoux and L. Brossard, *Solid State Commun.*, 74 (1990) 91 and refs. therein; L. Brossard, M. Ribault, L. Valade and P. Cassoux, *Physica*, 143B (1986) 378; L. Valade, J.-P. Legros and P. Cassoux, *Mol. Cryst. Liq. Cryst.*, 140 (1986) 335; M. Bosseau, L. Valade, J.-P. Legros, P. Cassoux, M. Garbaskas and L.V. Interrante, *J. Am. Chem. Soc.*, 108 (1986) 1908.
- 2 A. Clark, A.E. Underhill, I.D. Parker and R.H. Friend, *J. Chem. Soc., Chem. Commun.*, (1989) 228.
- 3 A. Kobayashi, Y. Sasaki, R. Kato and H. Kobayashi, *Chem. Lett.*, (1986) 387; H. Kobayashi, R. Kato, A. Kobayashi and Y. Sasaki, *Chem. Lett.*, (1985) 191; A. Kobayashi, R. Kato, H. Kobayashi, T. Mori and H. Inokuchi, *Physica*, 143B (1986) 562; R. Kato, H. Kobayashi, A. Kobayashi, T. Naito, M. Tamura, H. Tajima and H. Kuroda, *Chem. Lett.*, (1989), 1839; A. Kobayashi, H. Kim, Y. Sasaki, K. Murata, R. Kato and H. Kobayashi, *J. Chem. Soc., Faraday Trans.*, 86 (1990) 361; R. Kato, H. Kobayashi, A. Kobayashi and Y. Sasaki, *Chem. Lett.*, (1985) 131; H. Kobayashi, R. Kato, A. Kobayashi and Y. Sasaki, *Chem. Lett.*, (1985) 535; H. Kim, A. Kobayashi, Y. Sasaki, R. Kato and H. Kobayashi, *Chem. Lett.*, (1987) 1799.
- 4 L. Johannsen, K. Bechgaard, G. Rindorf, N. Thorup, C.S. Jacobsen and K. Mortensen, *Synth. Met.*, 15 (1986) 333.
- 5 K. Akiba, G.E. Matsubayashi and T. Tanaki, *Chim. Acta*, 165 (1989) 245.
- 6 G.J. Kramar, L.R. Groeneveld, J.L. Joppe, H.B. Brom, L.J. de Jough and J. Reedijk, *Synth. Met.*, 19 (1987) 745.
- 7 W.E. Broderick, E.M. McGhee, M.R. Godfrey, B.M. Hoffmann and J.A. Ibers, *Inorg. Chem.*, 28 (1989) 2902.
- 8 A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, (1987) 1819.
- 9 See for example W. Dietzsch, S. Rauer, R.-M. Olk, R. Kirmse, K. Kohler, L. Golic and B. Olk, *Inorg. Chim. Acta*, 169 (1990) 55; R.-M. Olk, W. Dietzsch, K. Kohler, R. Kirmse, J. Reinhold, E. Hoyer, L. Golic and B. Olk, *Z. Anorg. Allgem. Chem.*, 567 (1988) 131.
- 10 R.-M. Olk, W. Dietzsch, R. Kirmse, J. Stach, E. Hoyer and L. Golic, *Inorg. Chim. Acta*, 128 (1987) 251.
- 11 S.M.S.V. Doidge-Harrison, R.A. Howie, J.T.S. Irvine, G.M. Spencer and J.L. Wardell, *J. Organomet. Chem.*, 414 (1991) C5.
- 12 R.R. Holmes, S. Shafieezad, J.M. Holmes and R.O. Day, *Inorg. Chem.*, 27 (1988) 1232.
- 13 A.C. Sau, R.O. Day and R.R. Holmes, *Inorg. Chem.*, 20 (1981) 3076.
- 14 R.O. Day, J.M. Holmes, S. Shafieezad, V. Chandrasekhar and R.R. Holmes, *J. Am. Chem. Soc.*, 110 (1988) 5377 and refs. therein.
- 15 R.R. Holmes, S. Shafieezad, V. Chandrasekhar, A.C. Sau, J.M. Holmes and R.O. Day, *J. Am. Chem. Soc.*, 110 (1988) 1168.
- 16 D.M. Tunstall, personal communication.
- 17 A.C. Sau, R.R. Holmes, K.C. Molloy and J.J. Zuckermann, *Inorg. Chem.*, 21 (1982) 1421.
- 18 E.L. Muettterties and L.J. Guggenberger, *J. Am. Chem. Soc.*, 96 (1974) 1748.
- 19 G.M. Sheldrick, *SHELX-76*, Program for Crystal Structure Determination, University of Cambridge, UK, 1976.