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Preparation and crystal structures of the crowded triorganotin isothiocyanate $(PhMe_2Si)_3CSnMe_2NCS$ and nitrate $(PhMe_2Si)_3CSnMe_2ONO_2$ *

Salih S. Al-Juaid, Mustafa Al-Rawi, Colin Eaborn, Peter B. Hitchcock and J. David Smith
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (UK)

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Abstract

The crowded organotin compound $(PhMe_2Si)_3CSnMe_2NCS$ is monomeric in the solid state and contains tetracoordinate tin, the first tin isothiocyanate to be shown to do so. The related nitrate $(PhMe_2Si)_3CSnMe_2ONO_2$ is also monomeric, but there is a weak intramolecular interaction between the tin atom and one of the oxygen atoms of the NO_2 group, making the tin quasi-pentacoordinate. The weak coordination appears, however, to have no significant effect on the disposition of the four full bonds around the tin, the geometry being markedly distorted from tetrahedral by steric interactions to a similar extent in both the nitrate and the isothiocyanate.

1. Introduction

In the great majority of organotin(IV) compounds bearing one or more groups capable of acting as donor ligands, *e.g.* halogens, pseudohalogens, OH, OR, O_2CR, etc., the coordination at tin is greater than four as a result of inter- or intra-molecular interaction between the tin and the lone-pairs of these ligands [1]. In order to obtain information about the physical properties of four-coordinate species containing such ligands it is usually necessary sterically to inhibit the extra-coordination. For example, in contrast to organotin fluorides bearing less bulky alkyl or aryl groups, the compounds $(C_6H_{11})_3SnF$ (C_6H_{11} = cyclohexyl) [2], $(Me_3Si)_3CSnMe_2F$, $(Me_3Si)_3CSnPh_2F$, and $(PhMe_2Si)_3CSnMe_2F$ [3] show no F $\cdots$ Sn interactions in the solid state.

The simple organotin isothiocyanates that have been studied by X-ray diffraction, *viz.* Me_3SnNCS [4], Ph_3SnNCS [5], and $Me_2Sn(NCS)_2$ [6], are all polymeric in the solid state as a result of SnNCS $\cdots$ Sn interactions *. Likewise, all the nitrates of tin so studied, *viz.* compounds **1–4**, contain bidentate nitrato ligands, the ON–O $\cdots$ Sn interactions being either intra- or intermolecular.

$Sn(NO_3)_4$	$MeSn(No_3)_3$	$Me_2Sn(NO_3)_2$	Me_3SnNO_3
(1)	**(2)**	**(3)**	**(4)**

In **1** all four nitrato ligands are bidentate (perhaps, symmetrically so, any apparent asymmetry being within the limits of experimental uncertainty) and the tin is thus eight-coordinate, see I [7]. In **2** the tin atom is seven-coordinate, and has a pentagonal bipyramidal geometry, see II, with three slightly asymmetrically bidentate nitrato ligands (*i.e.* each such ligand provides one longer and one shorter O–Sn bond) [8]. In **3** the

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Correspondence to: Professor C. Eaborn or Dr. J. D. Smith.

* Dedicated to Professor M. G. Voronkov in recognition of his extensive pioneering contributions to organosilicon chemistry.

* We use the description 'simple' to distinguish species of the type $R_xSn(NCS)_{4-x}$ from their complexes with donor ligands, several of which have been structurally characterized [1].

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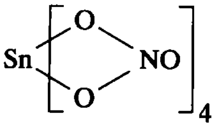
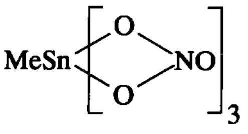
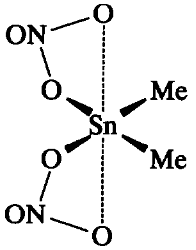
tin atom is six-coordinate, in a distorted octahedral environment, with two asymmetrically bidentate nitrato ligands [9], as shown in exaggerated fashion in III by use of a broken line for the longer Sn–O bonds.



(I)



(II)



(III)

For **4** largely unpublished data [10] point to a polymeric structure with near-planar Me_3Sn groups asymmetrically linked by nitrate groups to give a trigonal bipyramidal geometry at tin. In the case of the trialkyltin nitrate $(PhMe_2CCH_2)_3SnNO_3$, IR and Mössbauer spectroscopic data indicate that the tin is pentaccoordinate, as a result either of intermolecular bridging or intramolecular coordination within the monomeric species, with molecular weight studies favouring the latter alternative in dilute solution [11].

In the expectation of observing the first clearly four-coordinate organotin isothiocyanate and nitrate we have determined the crystal structures of compounds **5** and **6** containing the very bulky ligand $(PhMe_2Si)_3C$. In the event the expectation was realized in the case of the isothiocyanate **5**, but the nitrate **6** was found to show a weak intramolecular O ··· Sn interaction.

$(PhMe_2Si)_3CSnMe_2NCS$ (**5**)

$(PhMe_2Si)_3CSnMe_2ONO_2$ (**6**)

2. Results and discussion

Compound **5** was made by treatment of the bromide $(PhMe_2Si)_3CSnMe_2Br$ [12] with AgSCN and **6** by treatment of $(PhMe_2Si)_3CSnMe_2Cl$ [12] with $AgNO_3$.

TABLE 1. Intramolecular bond lengths (Å) and bond angles (°) in **5**, with estimated standard deviations in parentheses

Sn–N	2.12(3)	Sn–C(1)	2.23(3)
Sn–C(26)	2.16(3)	Sn–C(27)	2.22(4)
S–C(28)	1.65(4)	Si(1)–C(1)	1.89(3)
Si(1)–C(2)	1.87(3)	Si(1)–C(3)	1.91(4)
Si(1)–C(4)	1.90(3)	Si(2)–C(1)	1.92(3)
Si(2)–C(10)	1.87(4)	Si(2)–C(11)	1.89(4)
Si(2)–C(12)	1.90(4)	Si(3)–C(1)	1.93(3)
Si(3)–C(18)	1.87(4)	Si(3)–C(19)	1.88(4)
Si(3)–C(20)	1.90(4)	N–C(28)	1.05(4)
C(4)–C(5)	1.36(5)	C(4)–C(9)	1.38(5)
C(5)–C(6)	1.32(5)	C(6)–C(7)	1.30(6)
C(7)–C(8)	1.30(6)	C(8)–C(9)	1.30(5)
C(12)–C(13)	1.35(5)	C(12)–C(17)	1.42(5)
C(13)–C(14)	1.42(6)	C(14)–C(15)	1.48(6)
C(15)–C(16)	1.31(5)	C(16)–C(17)	1.38(5)
C(20)–C(21)	1.30(5)	C(20)–C(25)	1.42(4)
C(21)–C(22)	1.47(5)	C(22)–C(23)	1.34(5)
C(23)–C(24)	1.40(5)	C(24)–C(25)	1.44(5)
N–Sn–C(1)	106(1)	N–Sn–C(26)	96(1)
N–Sn–C(27)	101(1)	C(1)–Sn–C(26)	118(1)
C(1)–Sn–C(27)	120(1)	C(26)–Sn–C(27)	111(1)
C(1)–Si(1)–C(2)	110(1)	C(1)–Si(1)–C(3)	112(2)
C(1)–Si(1)–C(4)	114(1)	C(2)–Si(1)–C(3)	105(2)
C(2)–Si(1)–C(4)	107(1)	C(3)–Si(1)–C(4)	107(2)
C(1)–Si(2)–C(10)	112(1)	C(1)–Si(2)–C(11)	115(2)
C(1)–Si(2)–C(12)	115(1)	C(10)–Si(2)–C(11)	102(2)
C(10)–Si(2)–C(12)	104(2)	C(11)–Si(2)–C(12)	107(2)
C(1)–Si(3)–C(18)	112(2)	C(1)–Si(3)–C(19)	117(1)
C(1)–Si(3)–C(20)	114(1)	C(18)–Si(3)–C(19)	106(2)
C(18)–Si(3)–C(20)	105(2)	C(19)–Si(3)–C(20)	102(2)
Sn–N–C(28)	171(4)	Sn–C(1)–Si(1)	101(1)
Sn–C(1)–Si(2)	105(1)	Sn–C(1)–Si(3)	106(1)
Si(1)–C(1)–Si(2)	116(1)	Si(1)–C(1)–Si(3)	116(1)
Si(2)–C(1)–Si(3)	112(1)	Si(1)–C(4)–C(5)	124(3)
Si(1)–C(4)–C(9)	125(3)	C(5)–C(4)–C(9)	111(3)
C(4)–C(5)–C(6)	124(3)	C(5)–C(6)–C(7)	120(4)
C(6)–C(7)–C(8)	122(4)	C(7)–C(8)–C(9)	118(4)
C(4)–C(9)–C(8)	126(4)	Si(2)–C(12)–C(13)	120(3)
Si(2)–C(12)–C(17)	119(3)	C(13)–C(12)–C(17)	120(3)
C(12)–C(13)–C(14)	119(3)	C(13)–C(14)–C(15)	114(4)
C(14)–C(15)–C(16)	127(4)	C(15)–C(16)–C(17)	114(3)
C(12)–C(17)–C(16)	124(3)	Si(3)–C(20)–C(21)	124(3)
Si(3)–C(20)–C(25)	120(2)	C(21)–C(20)–C(25)	116(3)
C(20)–C(21)–C(22)	128(3)	C(21)–C(22)–C(23)	112(3)
C(22)–C(23)–C(24)	126(4)	C(23)–C(24)–C(25)	116(3)
C(20)–C(25)–C(24)	120(3)	S–C(28)–N	172(4)

In spite of several attempts to obtain better ones, the crystals of **5** that had to be used were of rather poor quality and thus the estimated standard deviations in the bond lengths and angles rather high (Table 1); however, this does not affect the conclusions drawn below. The crystals are made up of discrete molecules, the nearest intermolecular S ··· Sn contacts being 4.66 Å. The molecular structure is shown in Fig. 1. The geometry around tin is markedly distorted from tetrahedral as a result of the movement of the Me groups away from the $PhMe_2Si$ groups towards the small NCS ligand in order to relieve the steric strain; the C(1)–Sn–Me angles are 118(1) and 120(1)°, the C(1)–Sn–N angle 106(1)°, and the Me–Sn–NCS angles 96(1) and 101(1)°. (In view of the crowding around tin implied by these angles it is not surprising that there is no additional coordination to the metal atom.) The Sn–N=C=S system is not far from linear, the Sn–N–C and N–C–S

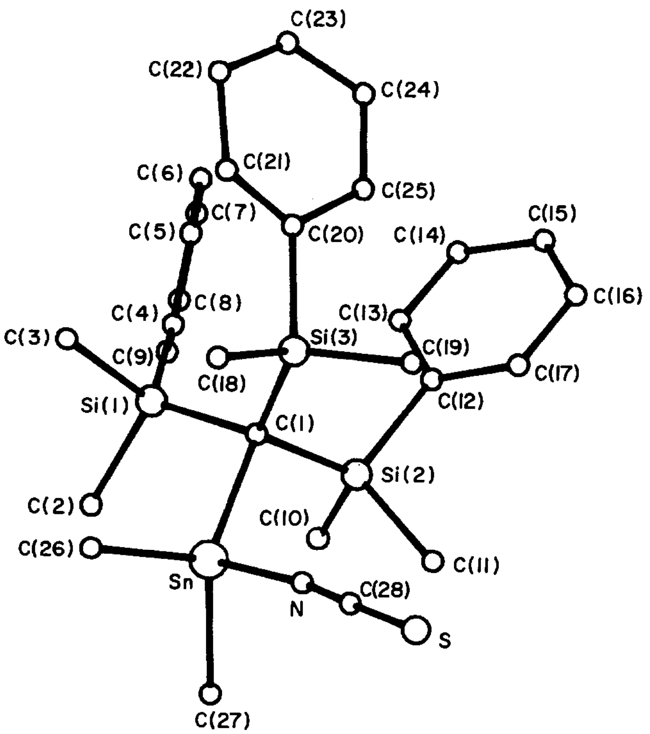


Fig. 1. Molecular structure of $(PhMe_2Si)_3CSiMe_2NCS$, 5.

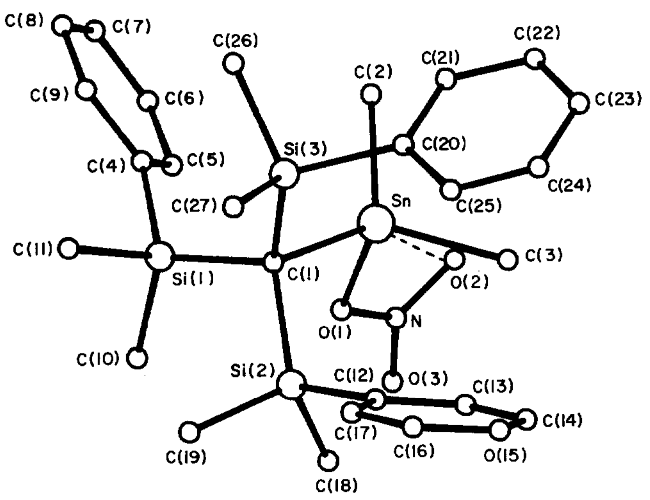


Fig. 2. Molecular structure of $(PhMe_2Si)_3CSiMe_2ONO_2$, 6.

angles being 171(4) and 172(4)°, respectively. These angles compare with 161(4) and 172(4)°, respectively, in Ph_3SnNCS [5] and 173(5) and 175(6)°, respectively, in Me_3SnNCS [4]. The Sn–N, N–C, and C–S bond lengths in **5**, *viz.* 2.12(3), 1.05(4), and 1.65(4) Å are not significantly different from those in Me_3SnNCS (2.15(6), 1.15(7), and 1.64(7) Å) or Ph_3SnNCS (2.22(5), 1.17(8), and 1.58(7) Å) even though there is substantial intermolecular S ··· Sn interaction in these species. It is possible, of course, that small differences would be observed if more precise data were available for all three compounds.

Crystals of the nitrate **6** were also found to consist of discrete molecules, the shortest intermolecular Sn ··· O distance being 5.3 Å. The molecular structure is depicted in Fig. 2, and the bond lengths and angles are listed in Table 2. There is again considerable distortion from the tetrahedral geometry, the C(1)–Sn–Me angles being 118.9(3) and 120.7(3)°, the C(1)–Sn–O(1) angle 98.0(2)°, and the Me–Sn–O(1) angles 102.8(3) and 102.2(3)°. These values are closely similar to those of the corresponding angles in **5**, indicating that the distortion is wholly or almost wholly attributable to the bulk of the $(PhMe_2Si)_3C$ ligand, the fairly close approach of the O(2) atoms to tin having no discernible effect. Nevertheless this approach, involving an O(2) ··· Sn distance of 2.929(8) Å, *i.e.* 0.8 Å less than the sum of the relevant van der Waals radii, probably does represent a real, though fairly weak, bonding interaction. Thus in **3** (see III) the two stronger Sn–O bonds have lengths of 2.17(2) and 2.15(1) Å, comparable with that of 2.095(5) Å for the Sn–O(1) bond in **5**, and the two weaker Sn–O bonds have lengths of 2.42(1) and 2.70(2) Å, the latter only 0.23 Å shorter than that of the Sn ··· O(2) distance in **6**. The N–O(2) ··· Sn angle in **6**, *viz.* 76.0(5)°, is fairly close to the corresponding angle, 80.7(9)°, involving the longest O ··· Sn bond in **3**. The geometry at the nitrogen atom in **6** is planar, the sum of the O–N–O angles being 360.1°. It is likely that upon further increase in the steric hindrance around tin, *e.g.* on going to compounds $(PhMe_2Si)_3CSnR_2ONO_2$ with R bulkier than Me, *e.g.* ^iPr or possibly even Ph, the O ··· Sn interaction would be completely inhibited and the tin clearly four-coordinate.

In both **5** and **6** the geometry within the $(PhMe_2Si)_3C$ group is mostly as usual; in particular the C(1)–Si–C angles (ranging from 111.3(3) to 116.7(3)° in **6**) are larger and the Me–Si–Me angles (ranging from 102.3(3) to 108.4(4)° in **6**) smaller than the tetrahedral angle, and the C(1)–Si bonds (mean 1.928(6) Å in **6**) markedly longer than the Me–Si bonds (1.881(8) Å in **6**). However the dispositions of the Ph groups in **6** are somewhat different from those most commonly observed in that the dihedral angles between the planes of the C(4)–C(9), C(12)–C(17) and C(20)–C(25) rings and the Si_3 plane are 61.4, 81.75, and 58.2°, respectively, whereas all three such angles are often in the range 80–85° [13]. In the isothiocyanate **5** the arrangement of the Ph groups is closer to the common pattern, the torsion angles between the planes of the C(4)–C(9), C(12)–C(17), and C(20)–C(25) rings and the Si_3 plane being 95.9, 88.2 and 85.4° respectively.

3. Experimental details

The compounds $(PhMe_2Si)_3CSnMe_2X$ (X = Cl or Br) were prepared as previously described [12]. The AgSCN and $AgNO_3$ were dried for some hours at 60°C under 0.1 mmHg.

The NMR spectra were recorded with a Brüker AC 250 spectrometer; for ^1H at 250.13 MHz (reference internal Me_4Si); ^{13}C at 62.9 MHz (external $CDCl_3$); ^{29}Si at 49 MHz (external Me_4Si); ^{119}Sn at 93 MHz (external $SnMe_4$). The IR spectra (KBr discs) were recorded with a Perkin-Elmer 1720 FTIR spectrometer. Mass spectra were obtained by positive ion FAB (Xe) for samples in toluene/3-nitrobenzyl alcohol. Melting points were determined with samples in sealed capillaries.

TABLE 2. Intramolecular bond lengths (Å) and bond angles (°) in **6**, with estimated standard deviations in parentheses

Sn–O(1)	2.095(5)	Sn–C(1)	2.178(6)
Sn–C(2)	2.138(8)	Sn–C(3)	2.112(7)
Si(1)–C(1)	1.929(6)	Si(1)–C(4)	1.877(7)
Si(1)–C(10)	1.878(8)	Si(1)–C(11)	1.888(8)
Si(2)–C(1)	1.933(6)	Si(2)–C(12)	1.885(7)
Si(2)–C(18)	1.869(9)	Si(2)–C(19)	1.872(8)
Si(3)–C(1)	1.921(7)	Si(3)–C(20)	1.896(6)
Si(3)–C(26)	1.886(8)	Si(3)–C(27)	1.875(9)
O(1)–N	1.265(9)	O(2)–N	1.243(11)
O(3)–N	1.211(12)	C(4)–C(5)	1.393(11)
C(4)–C(9)	1.403(10)	C(5)–C(6)	1.401(11)
C(6)–C(7)	1.366(12)	C(7)–C(8)	1.372(13)
C(8)–C(9)	1.384(11)	C(12)–C(13)	1.404(9)
C(12)–C(17)	1.392(12)	C(13)–C(14)	1.395(11)
C(14)–C(15)	1.395(14)	C(15)–C(16)	1.351(11)
C(16)–C(17)	1.375(11)	C(20)–C(21)	1.370(10)
C(20)–C(25)	1.398(10)	C(21)–C(22)	1.407(9)
C(22)–C(23)	1.349(13)	C(23)–C(24)	1.354(14)
C(24)–C(25)	1.397(10)	Sn···O(2)	2.929(8)
O(1)–Sn–C(1)	98.0(2)	O(1)–Sn–C(2)	102.8(3)
O(1)–Sn–C(3)	102.2(3)	C(1)–Sn–C(2)	118.9(3)
C(1)–Sn–C(3)	120.7(3)	C(2)–Sn–C(3)	109.8(3)
C(1)–Si(1)–C(4)	116.7(3)	C(1)–Si(1)–C(10)	112.4(3)
C(1)–Si(1)–C(11)	111.7(3)	C(4)–Si(1)–C(10)	102.3(3)
C(4)–Si(1)–C(11)	105.6(3)	C(10)–Si(1)–C(11)	107.3(3)
C(1)–Si(2)–C(12)	115.9(3)	C(1)–Si(2)–C(18)	112.2(3)
C(1)–Si(2)–C(19)	111.3(3)	C(12)–Si(2)–C(18)	105.0(3)
C(12)–Si(2)–C(19)	103.4(3)	C(18)–Si(2)–C(19)	108.4(4)
C(1)–Si(3)–C(20)	111.9(3)	C(1)–Si(3)–C(26)	112.0(3)
C(1)–Si(3)–C(27)	114.4(3)	C(20)–Si(3)–C(26)	104.2(3)
C(20)–Si(3)–C(27)	107.4(3)	C(26)–Si(3)–C(27)	106.3(4)
Sn–O(1)–N	116.6(4)	O(1)–N–O(2)	118.2(8)
O(1)–N–O(3)	120.4(7)	O(2)–N–O(3)	121.5(8)
Sn–C(1)–Si(1)	110.6(3)	Sn–C(1)–Si(2)	110.2(3)
Sn–C(1)–Si(3)	102.9(3)	Si(1)–C(1)–Si(2)	108.1(3)
Si(1)–C(1)–Si(3)	111.5(3)	Si(2)–C(1)–Si(3)	113.5(3)
Si(1)–C(4)–C(5)	121.4(5)	Si(1)–C(4)–C(9)	122.1(6)
C(5)–C(4)–C(9)	115.9(6)	C(4)–C(5)–C(6)	121.7(7)
C(5)–C(6)–C(7)	120.3(8)	C(6)–C(7)–C(8)	119.8(7)
C(7)–C(8)–C(9)	119.9(7)	C(4)–C(9)–C(8)	122.5(8)
Si(2)–C(12)–C(13)	121.2(6)	Si(2)–C(12)–C(17)	121.6(5)
C(13)–C(12)–C(17)	116.9(6)	C(12)–C(13)–C(14)	120.3(8)
C(13)–C(14)–C(15)	120.8(7)	C(14)–C(15)–C(16)	118.5(7)
C(15)–C(16)–C(17)	121.7(9)	C(12)–C(17)–C(16)	121.8(7)
Si(3)–C(20)–C(21)	121.4(5)	Si(3)–C(20)–C(25)	121.0(5)
C(21)–C(20)–C(25)	117.6(6)	C(20)–C(21)–C(22)	121.4(7)
C(21)–C(22)–C(23)	120.0(8)	C(22)–C(23)–C(24)	120.0(7)
C(23)–C(24)–C(25)	121.1(8)	C(20)–C(25)–C(24)	119.9(7)
O(1)–Sn–O(2)	47.2(2)	C(3)–Sn–O(2)	73.4(3)
C(2)–Sn–O(2)	78.4(3)	N–O(2)–Sn	76.0(5)

3.1. Preparation of $(PhMe_2Si)_3CSnMe_2NCS$, 5

A solution of $(PhMe_2Si)_3CSnMe_2Br$ (2.0 g, 3.2 mmol) in acetone (20 cm^3) was heated with AgSCN (0.55 g, 3.3 mmol) for 1 h. The solvent was evaporated and the residue extracted with CH_2Cl_2 (30 cm^3). The extract was filtered and the solvent removed to leave colourless crystals of **5**. Anal. Found: C, 53.9; H, 6.3; N, 2.3. Calc. for $C_{28}H_{39}NSSi_3Sn$: C, 53.8; H, 6.2; N, 2.2%. M.p. 146°C. IR: ν(NCS) 2066 cm^{-1}. ^1H NMR: δ 0.54 (6H, s, Me_2Sn), 0.68 (18H, s, Me_2Si), 6.8–7.39 (15H, m, Ph). ^{13}C NMR: δ 4.3 (Me_2Si), 5.0 (Me_2Sn, $^1J(^{13}C-^{119}Sn)$ 400 Hz), 127.6 (C_3 of Ph), 129.2 (C_4), 135.4 (C_2), 138.8 (C_1, $^1J(^{13}C-^{29}Si)$ 5.2 Hz). ^{29}Si NMR: δ – 5.4 (s). ^{119}Sn NMR: 42.4 (t, $^1J(^{119}Sn-^{14}N)$ 123 Hz). ^{14}N NMR: δ –250.7 ($^1J(^{14}N-^{119}Sn)$ 123 Hz. MS: m/z 567 (6%, $[M-NCS]^+$), 551 (3), 489 (4), 325 (10), 309 (20), 197 (25), 175 (20), 170 (40), 135 (100, $[PhMe_2Si]^+$), 90 (55), 77 (90), 58 (100). Suitable crystals for the X-ray diffraction study were obtained by recrystallization from MeOH.

TABLE 3. Fractional atomic coordinates ($\times 10^3$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for **5**

Atom	x	y	z	U_{eq} [a]
Sn	969.3(23)	414.6(27)	1912.3(9)	48(1)
S	1973(16)	2095(13)	3468(5)	129(10)
Si(1)	1127(8)	1089(10)	850(3)	37(5)
Si(2)	3736(8)	966(11)	1565(3)	47(6)
Si(3)	1841(8)	3351(10)	1614(3)	39(5)
N	1430(29)	1260(37)	2581(8)	81(21)
C(1)	2014(24)	1567(27)	1437(9)	21(7)
C(2)	668(27)	–661(31)	848(10)	39(9)
C(3)	–435(38)	2019(42)	710(14)	79(13)
C(4)	2048(27)	1351(31)	341(10)	37(9)
C(5)	2222(30)	2524(34)	147(12)	48(10)
C(6)	2804(35)	2692(40)	–223(14)	71(12)
C(7)	3292(40)	1701(43)	–410(15)	88(14)
C(8)	3178(34)	528(41)	–257(12)	70(11)
C(9)	2570(30)	371(38)	101(11)	57(10)
C(10)	3960(33)	–650(37)	1296(12)	64(11)
C(11)	4326(40)	647(44)	2201(15)	91(14)
C(12)	4958(32)	2050(36)	1333(12)	56(11)
C(13)	4963(33)	2175(36)	869(12)	59(11)
C(14)	5909(37)	2949(42)	704(14)	79(13)
C(15)	6635(38)	3776(44)	1068(14)	83(14)
C(16)	6624(30)	3712(35)	1519(12)	51(10)
C(17)	5767(30)	2833(34)	1652(12)	49(10)
C(18)	229(34)	3689(39)	1781(13)	65(12)
C(19)	3014(33)	3982(38)	2108(13)	65(12)
C(20)	2027(29)	4563(37)	1135(11)	50(9)
C(21)	1078(34)	5093(38)	872(13)	71(12)
C(22)	1115(30)	6060(34)	502(11)	47(10)
C(23)	2304(37)	6287(42)	415(14)	80(13)
C(24)	3418(32)	5816(34)	675(12)	60(11)
C(25)	3261(28)	4877(31)	1032(11)	43(9)
C(26)	–1064(28)	706(31)	1866(10)	42(9)
C(27)	1476(30)	–1649(34)	2061(12)	50(10)
C(28)	1714(32)	1541(35)	2929(12)	56(11)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 4. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for **6**

Sn	3340.0(3)	–3.5(6)	2367.9(2)	52.2(1)
Si(1)	1325.8(12)	–594.8(22)	1288.0(9)	47(1)
Si(2)	2221.7(13)	–3025.0(22)	2295.6(10)	52(1)
Si(3)	1700.7(11)	–136.7(22)	2891.4(9)	46(1)
O(1)	3571(3)	–762(6)	1487(2)	64(3)
O(2)	4798(4)	288(9)	1852(4)	159(6)
O(3)	4574(4)	–1294(11)	1070(4)	180(6)
N	4323(5)	–592(10)	1460(3)	107(5)
C(1)	2092(4)	–998(7)	2200(3)	40(3)
C(2)	3398(5)	2238(8)	2259(4)	75(5)
C(3)	4440(5)	–708(10)	3161(4)	76(5)
C(4)	1387(4)	1227(7)	946(3)	45(3)
C(5)	2023(5)	1589(8)	662(3)	59(4)
C(6)	2001(5)	2872(9)	318(4)	76(4)
C(7)	1355(5)	3821(8)	262(4)	77(4)
C(8)	710(5)	3496(8)	526(4)	72(4)
C(9)	730(5)	2226(8)	864(3)	61(4)
C(10)	1539(5)	–1749(8)	618(3)	62(4)
C(11)	161(5)	–855(9)	1222(4)	69(4)
C(12)	2600(4)	–3719(8)	3203(3)	56(4)
C(13)	3478(5)	–3738(9)	3594(4)	75(4)
C(14)	3747(5)	–4313(10)	4254(4)	91(5)
C(15)	3154(6)	–4893(9)	4534(4)	91(5)
C(16)	2313(6)	–4903(9)	4148(4)	83(4)
C(17)	2034(5)	–4342(8)	3496(4)	69(4)
C(18)	3012(5)	–3729(8)	1896(4)	72(4)
C(19)	1168(5)	–3947(8)	1897(4)	78(5)
C(20)	2614(4)	143(7)	3726(3)	54(3)
C(21)	3106(5)	1345(9)	3841(4)	70(4)
C(22)	3799(5)	1533(10)	4453(4)	90(5)
C(23)	3971(6)	541(11)	4950(4)	103(6)
C(24)	3484(6)	–644(10)	4857(4)	96(5)
C(25)	2810(5)	–876(9)	4246(4)	73(4)
C(26)	1258(4)	1693(8)	2635(4)	63(4)
C(27)	836(5)	–1149(9)	3101(4)	70(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

3.2. Preparation of $(PhMe_2Si)_3CSnMe_2ONO_2$, 6

A solution of $(PhMe_2Si)_3CSnMe_2Cl$ (2.0 g, 3.4 mmol) in CH_2Cl_2 (40 cm^3) was stirred with $AgNO_3$ (0.68 g, 4.0 mmol) for 3 h with protection from light. The solution was then filtered, the solvent removed under reduced pressure, and the solid residue recrystallized from methanol to give colourless crystals of **6** (1.8 g, 87%). Anal. Found: C, 51.7; H, 6.4. Calc. for $C_{27}H_{39}NO_3Si_3Sn$: C, 51.6; H, 6.2%. M.p. 177°C. IR: (NO_3) 1536 cm^{-1}. ^1H NMR: δ 0.49 (6H, s, Me_2Sn), 0.69 (18H, s, Me_2Si, $^2J(^1H-^{29}Si)$ 6.3 Hz), 7.2–7.39 (15H, m, Ph). ^{13}C NMR: δ 4.7, 6.1 (Me_2Sn), $^1J(^{13}C-^{119}Sn)$ 401 Hz, 127.7 (C_3 of Ph), 129.4 (C_4), 135.5 (C_2), 139.1 (C_1). ^{29}Si NMR: δ – 0.59. ^{119}Sn NMR: δ 135.6. MS: m/z 567 (25%, $[M-NO_3]^+$), 551 (10, $[M-NO_3-MeH]^+$), 489 (25, $[M-NO_3-Ph]^+$), 309 (40), 247

(20), 197 (45), 175 (35), 135 (100, $[PhMe_2Si]^+$), 105 (40), 73 (65). Crystals for the crystallographic study were obtained by recrystallization from MeOH.

3.3. Crystallographic studies

3.3.1. Compound 5

Crystal data: $C_{28}H_{39}NSSi_3Sn$, M 624.7; monoclinic, $P2_1/c$, $a = 10.616(4)$, $b = 10.312(3)$, $c = 28.942(9)$ Å, $\beta = 97.95(3)°$, $U = 3137.7$ Å^3, $Z = 4$, $D_c = 1.32$ g cm^{-3}, $F(000) = 1288$. Monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 10.1$ cm^{-1}.

A crystal of *ca.* 0.15 × 0.20 × 0.13 mm was mounted on a glass fibre in a random orientation. A total of 6158 reflections with $+h + k \pm l$ and $2° < \theta < 25°$ were measured with an Enraf–Nonius CAD4 diffractometer by a $\theta/2\theta$ scan with a scan width θ of $(0.8 + 0.35 \tan \theta)°$ and a maximum scan time of 1 min. After corrections for Lorentz and polarization effects, and for absorption by use of DIFABS (max 1.25, min 0.34), and averaging of equivalent reflections, there were 5853 unique reflections, but of these only 1805 with $I > 3\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$.

The tin atom was found from the Patterson map, and the remaining non-hydrogen atoms were located in successive difference maps. Hydrogen atoms were placed at calculated positions, with $U_{iso} = 1.3U_{eq}$ for the atoms to which they are bonded, and included in the structure factor calculations but not refined. The structure was refined by full-matrix-least-squares with temperature factors anisotropic for Si, Sn, N, and S atoms but isotropic for C atoms. Refinement converged at $R = 0.107$, $R' = 0.149$, with weighting scheme $w = 1/\sigma^2(F)$. Non-hydrogen atom coordinates are listed in Table 3. A table of anisotropic thermal parameters and a list of observed and calculated structure factors are available from PBH.

Compound 6

Crystal data: $C_{27}H_{39}NO_3Si_3Sn$, M 628.6, monoclinic, $P2_1/c$, $a = 16.417(3)$, $b = 9.463(5)$, $c = 20.570(4)$ Å, $\beta = 108.92(2)°$, $U = 3022.8$ Å^3, $Z = 4$, $D_c = 1.4$ g cm^{-3}, $F(000) = 1296$. Monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 9.9$ cm^{-1}.

A crystal of *ca.* 0.15 × 0.4 × 0.1 mm was used. Data collection, for 5863 unique reflections with $hk \pm l$, was as described for 5. After corrections as for 5, 2527 reflections with $|F^2| > 3\sigma(F^2)$ were used. Non-hydrogen atoms were located by use of the heavy atom routines of SHELXS-86 and refined by full matrix least squares with anisotropic temperature factors by use of the program in the Enraf–Nonius SDP package. Hydrogen atoms were treated as for 5. Refinement converged at $R = 0.040$, $R' = 0.047$ with the weighting scheme as for 5. Non-hydrogen atom coordinates are listed in Table 4. A table of anisotropic thermal parameters and a list of observed and calculated structure factors are available from PBH.

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