

# Synthesis and spectral characterisation of organotin(IV) 1,3,5-triazine-2,4,6-trithiolato complexes, including the crystal structures of 1,3,5-(R<sub>3</sub>Sn)<sub>3</sub>C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> (R = Me, Ph)

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## Abstract

Novel organotin(IV) 1,3,5-triazine-2,4,6-trithiolato complexes: (R<sub>3</sub>Sn)<sub>3</sub>C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>, (R = Ph, Bz, Me, Bu) and (R<sub>2</sub>Sn)<sub>3</sub>(C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)<sub>2</sub>, (R = Ph, Me) have been prepared and characterised by elemental analysis, FT-IR, Mössbauer and multinuclear NMR spectroscopy. The crystal and molecular structures of 1,3,5-(R<sub>3</sub>Sn)<sub>3</sub>C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> (R = Me, Ph) have been determined and contain tetrahedral organotin units in a ‘manxane’ arrangement about the central triazine. There are no close intermolecular interactions. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Tin; 1,3,5-Triazine-2,4,6-trithiolato; Mössbauer; ‘Manxane’

## 1. Introduction

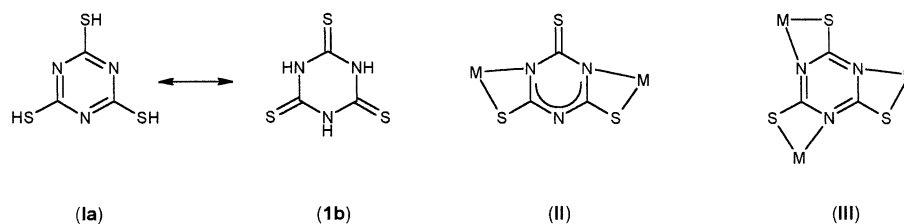
While the co-ordination chemistry of heterocyclic thiol/thione donors has, for many years, been of great interest both from a biological and pharmaceutical perspective [1], it is the supramolecular chemistry of this class of compound which is currently exciting interest [2]. The self-assembly of metal centers with heterocyclic thiol/thione ligands containing different binding sites results in the formation of novel supramolecules which have intriguing novel structures and/or magnetic properties. For example, organotin-substituted tetrazole thiolates are known to adopt monomer [3,4] trimer [5], polymer [6] and sheet [7] structures all containing σ-Sn–ligand bonds. In addition, one intriguing example of a lead compound, Ph<sub>3</sub>PbSCN<sub>4</sub>Ph-1, has a polymeric arrangement similar to that of Bz<sub>3</sub>SnSCN<sub>4</sub>Ph-1 [6] though the intermolecular interaction between lead and the tetrazole–thiol is

suggestive of the onset of π-bonding between the metal and the 6e tetrazole ring [8].

In this paper we wish to report of studies of organotin derivatives of 1,3,5-triazine-2,4,6-trithiol (**I**) (also referred to as 2,4,6-trimercaptotriazine or trithiocyanuric acid). Compound **I**, which can exist in either thiol (**1a**) or thione (**1b**) forms, is an analytical reagent currently used to remove heavy metals (Ag<sup>+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Pd<sup>2+</sup>, Cu<sup>2+</sup>) from waste waters [9]. Interest in the coordination chemistry of the 1,3,5-triazine-2,4,6-trithiolato anion [C<sub>3</sub>N<sub>3</sub>S<sub>3</sub><sup>3-</sup>] is more limited and is mainly confined to derivatives of s- (Li<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>) [9,10] and d-block elements [11–17] where it can behave as either a chelating [13] or bridging [15–17] ligand. However, very few structural studies have been reported, largely due to the lack of solubility of these compounds [11,12]. Of the available structures, the cobalt(III) complex [14] [ $\{\text{Co(en)}_2\}_2(\mu\text{-C}_3\text{N}_3\text{S}_3)\text{]}\cdot[\text{ClO}_4]_3\cdot 2\text{H}_2\text{O}$ ] incorporates only the bis-chelating co-ordination pattern (**II**) of C<sub>3</sub>N<sub>3</sub>S<sub>3</sub><sup>3-</sup> in the solid state, while both bis- and tris-chelating (**III**) forms are present in solution. No intermolecular interactions are mentioned for this complex.

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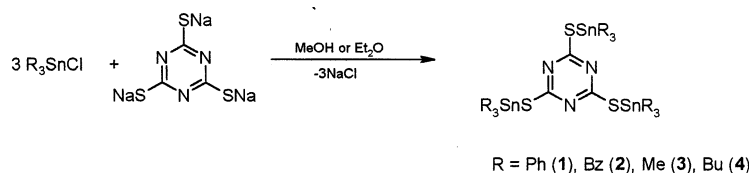


More recently, the gold(I) complex  $[(\text{Ph}_3\text{P})\text{Au}]_3[\text{C}_3\text{N}_3\text{S}_3]$  has been prepared [16] and characterised structurally [17] and shown to contain Au–S (rather than Au–N) bonds in a  $C_{3h}$  ‘manxane’ arrangement derived from **I**. Gold complexes of this type decompose in solution to yield  $[(\text{AuC}_3\text{N}_3\text{S}_3)(\text{AuL})_2]_2$  ( $\text{L} = \text{Me}_2\text{PhP}$  [16], ‘BuNC [17]) which adopt two-dimensional supramolecular structures via intermolecular Au(I)⋯Au(I) interactions and in which the  $\text{C}_3\text{N}_3\text{S}_3^{3-}$  anions involve three different binding modes (*S*-, *N*- and *S,S*-). In contrast, the copper(I) complex  $[(\text{CuPPh}_3)_3(\text{C}_3\text{N}_3\text{S}_3)]_2$  provides the single example of a hexadentate triazine-2,4,6-trithiolato ligand with all the available *N*, *S* binding sites involved in co-ordination. The molecule shows a self-assembled, dimeric, hexanuclear structure which consists of two parallel triazine rings held in close proximity (3.07 Å) by six N–Cu–S bridges.

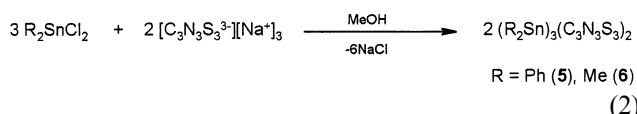
To our knowledge, no organometallic derivatives of **I** have been studied. Organotin compounds suggested themselves for investigation, both from their potential for supramolecular assembly and as potential reagents for the synthesis of other complexes of 1,3,5-triazine-2,4,6-trithiol, particularly where non-aqueous chemistry is required. The corresponding organotin derivatives of cyanuric acid,  $(\text{R}_3\text{Sn})_3\text{C}_3\text{N}_3\text{O}_3$  have, however, been known since 1965. No structural studies have been carried out on these species which have been assumed to contain *N*-bonded tin [18].

## 2. Synthesis

Reaction of the tri-sodium salt of **I** ( $\text{C}_3\text{N}_3\text{S}_3\text{Na}_3 \cdot 9\text{H}_2\text{O}$ ) with triorganotin(IV) chlorides (1:3 ratio) in ether or methanol yields the triorganotin(IV) 1,3,5-triazine-2,4,6-trithiolato complexes  $(\text{R}_3\text{Sn})_3\text{C}_3\text{N}_3\text{S}_3$  as crystalline solids [ $\text{R} = \text{Ph}$  (**1**), *Bz* (**2**), *Me* (**3**) or oils [ $\text{R} = \text{Bu}$  (**4**)] (Eq. (1)). All the complexes **1–4** are air stable in their natural state and are soluble in most common organic solvents with the exception of **1** and **2** which are insoluble in methanol and *n*-hexane.



Similarly, reaction of same sodium salt with diorganotin(IV) dichlorides (2:3 ratio) in methanol yields the diorganotin(IV) 1,3,5-triazine-2,4,6-trithiolato complexes  $(\text{R}_2\text{Sn})_3(\text{C}_3\text{N}_3\text{S}_3)_2$ , [ $\text{R} = \text{Ph}$  (**5**), *Me* (**6**)] as white powder solids (Eq. (2)). The complexes **5** and **6** are air stable and insoluble in common organic solvents, rendering them difficult to purify.



Compounds **1–6** can also be prepared by reaction of the corresponding organotin oxide and trithiocyanuric acid; in a typical example, **4** was prepared in 62% from  $(\text{Bu}_3\text{Sn})_2\text{O}$  and  $\text{C}_3\text{N}_3\text{S}_3\text{H}_3$ . However, this offers little advantage over the methodology of Eqns 1, 2 as the free acid needs to be purchased commercially at far greater cost than its sodium salt, or prepared from the salt by reaction with HCl.

$(\text{Me}_3\text{Sn})_3\text{C}_3\text{N}_3$  (**3**) was heated over its melting point (118°C) for 30 min after which time it recrystallised unchanged as a colourless solid. Alternatively, **3** was stirred in *n*-decane at ca. 140°C under  $\text{N}_2$  for 1 h and the solvent was removed to low volume. In both cases the product was isolated as a microcrystalline solid whose IR data are consistent with unchanged starting material. We have no evidence that these compounds dissociate into  $\text{R}_3\text{SnSCN}$  on heating.

## 3. Spectroscopy

The IR spectra of  $\text{C}_3\text{N}_3\text{S}_3\text{Na}_3 \cdot 9\text{H}_2\text{O}$  and the corresponding organotin(IV) complexes (**1–6**) were recorded in the 4500–500  $\text{cm}^{-1}$  spectral range. The assignments of  $\nu(\text{N}_2\text{CS})$  and  $\delta(\text{C}_3\text{N}_3)$  (out of plane ring bending by ‘sextants’) modes in the spectrum of  $\text{C}_3\text{N}_3\text{S}_3\text{Na}_3 \cdot 9\text{H}_2\text{O}$  at 1216 and 850  $\text{cm}^{-1}$  respectively, are in good agreement with the corresponding vibrational data published for the neutral ligand [11]. In comparison with the data

for  $\text{C}_3\text{N}_3\text{S}_3\text{Na}_3 \cdot 9\text{H}_2\text{O}$ , the IR spectra of **1–6** reveal a significant shift of  $\nu(\text{N}_2\text{CS})$  from  $1216\text{ cm}^{-1}$  to higher frequencies ( $1234\text{--}1242\text{ cm}^{-1}$ ), which we ascribe to the co-ordination of sulphur to the metal centre.

The quadrupole splittings (q.s.) for **1–3** are in the range  $1.84\text{--}2.21\text{ mm s}^{-1}$  which is consistent with a tetrahedral geometry about tin [7,19]. The q.s. of **6** ( $2.96\text{ mm s}^{-1}$ ) is comparable with the value  $2.98\text{ mm s}^{-1}$  for  $\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)\text{Cl}$  which is essentially *cis*-trigonal bipyramidal at tin [19] and it is in good agreement with the q.s. calculated for diorganotin(IV) complexes exhibiting *cis*- $\text{R}_2\text{SnX}_3$  coordination environment based upon a point charge model (ca.  $3.07\text{ mm s}^{-1}$ ) [20]. In the case of **5** the q.s. ( $2.68\text{ mm s}^{-1}$ ) is intermediate between those corresponding to tetrahedral and trigonal bipyramidal geometries, thus suggesting a weak contribution by the ring nitrogen to the metal coordination. Considering the low solubility of **5**, **6** it would appear that this latter interaction is intermolecular in nature and that the two species are polymeric materials.

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data show no unusual features, suggesting in all cases the equivalence of the  $\text{R}_3\text{Sn}$  groups as well as the ring carbon atoms. The resonance at ca.  $\delta\ 180\text{ ppm}$  due to  $\text{C}=\text{S}$  in the  $^{13}\text{C}$  spectra confirms the presence of the triazine ring. The  $^{119}\text{Sn}$ -NMR data of **1**, **3**, and **4** indicate that the co-ordination number of four suggested by the Mössbauer

data is maintained in solution. The  $^1J(\text{SnC})$  couplings observed in the  $^{13}\text{C}$ -NMR spectra of **3**, **4** ( $329\text{--}376\text{ Hz}$ ) are also indicative of a tetrahedral geometry at tin [19,21].

#### 4. The structures of $(\text{Ph}_3\text{SnS})_3\text{C}_3\text{N}_3$ (**1**) and $(\text{Me}_3\text{SnS})_3\text{C}_3\text{N}_3$ (**3**)

The asymmetric unit of **1** is shown in Fig. 1. As implied by the collective spectroscopic data tin is bonded to the thiocyanuric acid via sulphur (i.e. the thiol form of the ligand) and the geometry about tin is tetrahedral. The structure is similar to that of  $(\text{Ph}_3\text{PAu})_3\text{C}_3\text{N}_3\text{S}_3$  [17] which has been described as incorporating a ‘manxane’ core, and  $[\text{Os}_3\text{H}(\text{CO})_{10}]_3\text{C}_3\text{N}_3\text{S}_3$  [13]. The Sn–S bonds are similar, though  $\text{Sn}(1)\text{--S}(1)$  [ $2.435(3)\text{ \AA}$ ] is marginally shorter than distances involving the other two metal centres [ $2.457(3)$ ,  $2.453(3)\text{ \AA}$ ] and are short with respect to Sn–S bonds in a range of organotin tetrazole-thioates [ $2.477(4)\text{--}2.607(2)\text{ \AA}$ ]. The Sn–S bond in  $\text{Ph}_3\text{SnSPh}$  [ $2.421(1)\text{ \AA}$ ] [22] is, however, directly comparable. There is no discrimination in the lengths of the C–S bonds [ $1.726(9)\text{--}1.744(8)\text{ \AA}$ ], while the C–N bonds are consistent with a delocalised system [ $1.325(11)\text{--}1.352(11)\text{ \AA}$ ]. The bond angles at each tin show a consistent trend and in each case a wide range of angles is observed

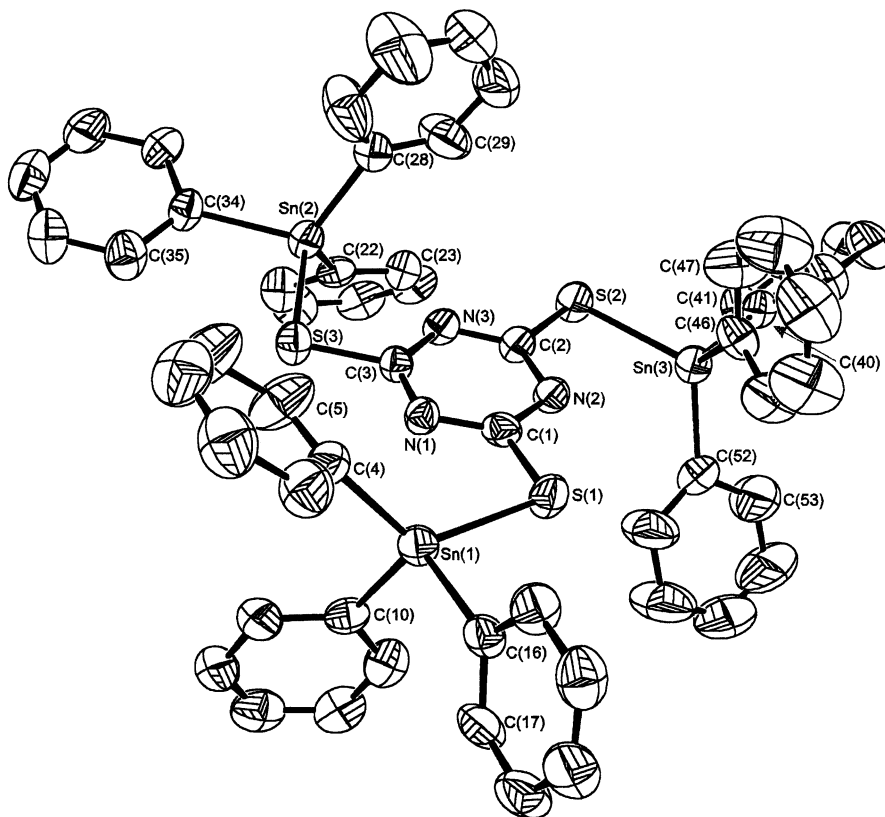


Fig. 1. The asymmetric unit of **1** showing the labelling scheme used in the text and tables. Thermal ellipsoids are at the 30% probability level.

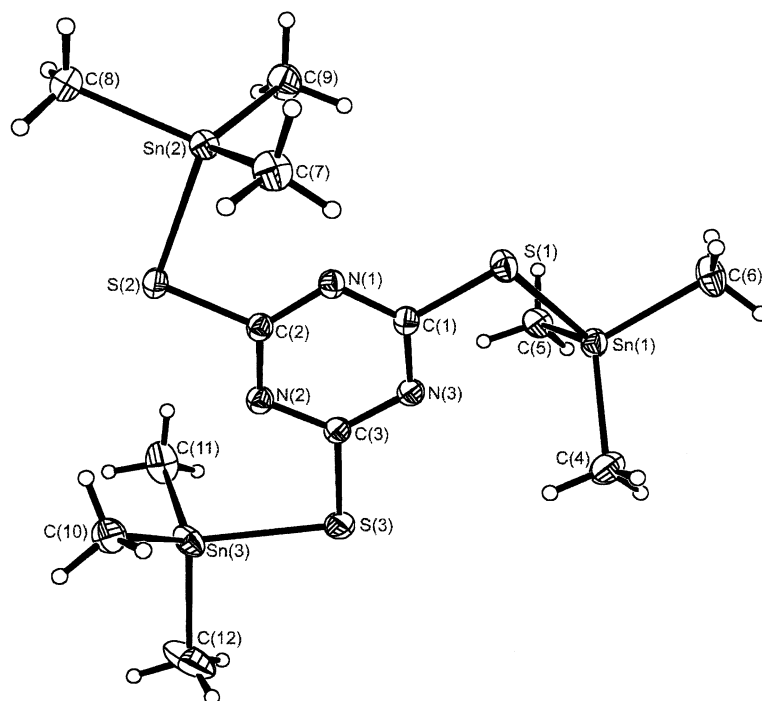


Fig. 2. The asymmetric unit of **3** showing the labelling scheme used in the text and tables. Thermal ellipsoids are at the 30% probability level.

[Sn(1): 95.8(2)–123.4(3); Sn(2): 97.3(3)–117.4(4); Sn(3): 96.6(3)–117.6(3)°]. In  $\text{Ph}_3\text{SnSPh}$  the bond angles at tin are more regular [106.4(1)–112.1(1)°] [22] suggesting that asymmetry in the angles about tin in **1** is largely a result of crowding of three bulky  $\text{Ph}_3\text{Sn}$  groups around the periphery of the heterocycle.

The structure of **3** (Fig. 2) is very similar to that of **1**. The three Sn–S bonds are marginally longer [2.4611(9), 2.4708(8), 2.4735(9) Å] while the angles about each tin are somewhat less distorted [Sn(1): 97.7(1)–114.7(2); Sn(2): 96.9(1)–115.4(2); Sn(3): 98.02–115.9(2)°], presumably due to decreased steric congestion.

In both structures, however, the three tins lie essentially in the plane of the  $\text{C}_3\text{N}_3$  ring and the  $\angle \text{C}–\text{S}–\text{Sn}$  is reduced to ca. 96–99°. This has the effect of bringing each tin into the proximity of a ring nitrogen (ca. 2.9–3.1 Å), which can be considered as reflecting the onset of very weak chelation. It should be noted, however, that the approach of nitrogen is only loosely *trans* to a Sn–C bond ( $\angle \text{N}–\text{Sn}–\text{C}$ : ca. 155°) and in more strongly chelating analogues the angle at sulphur is reduced to ca. 78° [14].

## 5. Experimental

Spectra were recorded on the following instruments: JEOL GX270 ( $^1\text{H}$ -,  $^{13}\text{C}$ -NMR), GX400 ( $^{119}\text{Sn}$ -NMR), Perkin–Elmer 599B (IR). Details of our Mössbauer spectrometer and related procedures are given elsewhere [23]. Isomer shift data are relative to  $\text{CaSnO}_3$ .

For all compounds, infrared spectra were recorded as nujol mulls on KBr plates and all NMR data were recorded on saturated solutions in  $\text{CDCl}_3$  at room temperature (r.t.); chemical shifts are in ppm relative to either  $\text{Me}_4\text{Si}$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or  $\text{Me}_4\text{Sn}$  ( $^{119}\text{Sn}$ ), coupling constants are in Hz.

Tribenzyltin chloride was prepared by a literature method [24]. Other organotin reagents and trithiocyanuric acid trisodium salt were purchased from Aldrich and used without further purification.

### 5.1. Synthesis of 1,3,5-( $\text{Ph}_3\text{Sn}$ ) $_3\text{C}_3\text{N}_3\text{S}_3$ (**1**)

A mixture of excess  $\text{C}_3\text{N}_3\text{S}_3\text{Na}_3 \cdot 9\text{H}_2\text{O}$  (0.20 g, 0.5 mmol) and  $\text{Ph}_3\text{SnCl}$  (0.46 g, 1.2 mmol) in methanol (40 ml) was stirred under  $\text{N}_2$  at r.t. for 2 h. The resultant white precipitate was washed with methanol and the product was extracted with ether and recrystallised from ether/hexane to yield **1** as a white microcrystalline solid (0.28 g, 58%). m.p. 177°C. Analysis: Found (Calc. for  $\text{C}_{57}\text{H}_{45}\text{N}_3\text{S}_3\text{Sn}_3$ ): C 55.7(55.9), H 3.71(3.71), N 3.41(3.43)%. IR ( $\text{cm}^{-1}$ ): 2924 vs, 2725 w, 1460 vs, 1377 vs, 1234 s, 1156 w, 1073 w, 1020 w, 996 w, 847 m, 788 w, 724 vs, 694 s. Mössbauer ( $\text{mm s}^{-1}$ ): i.s. 1.30, q.s. 2.21.  $^1\text{H}$ -NMR: 7.37 m (27H, *m*- and *p*- $\text{C}_6\text{H}_5$ ), 7.67 dd (18H, *o*- $\text{C}_6\text{H}_5$ );  $^3J = 6.5$ ,  $^4J = 3.0$ ;  $^3J(\text{SnH}) = 55.9$  (unresolved).  $^{13}\text{C}$ -NMR: 128.7 ( $\text{C}_p$ ), 129.6 ( $\text{C}_m$ ), 136.8 ( $\text{C}_o$ ), 138.8 ( $\text{C}_i$ ), 179.7 (C–S);  $^2J(\text{SnC}) = 45.1$  (unresolved).  $^{119}\text{Sn}$ -NMR: –100.5.

Also prepared by the same method were the following.

### 5.2. 1,3,5-(Bz<sub>3</sub>Sn)<sub>3</sub>C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> (**2**)

Ether as solvent, reaction time 4 h. Yield 57%, m.p. 96°C. Analysis: Found (Calc. for C<sub>66</sub>H<sub>63</sub>N<sub>3</sub>S<sub>3</sub>Sn<sub>3</sub>): C 58.7(58.7), H 4.70(4.77), N 3.24(3.11)%. IR (cm<sup>-1</sup>): 2928 vs, 1596 ms, 1490 vs, 1456 vs, 1377 vs, 1237 vs, 1206 s, 1180 w, 1094 w, 1048 w, 1028 w, 902 w, 847 s, 797 w, 788 w, 755 vs, 723 s, 696 vs. Mössbauer (mm s<sup>-1</sup>): i.s. 1.45, q.s. 1.86. <sup>1</sup>H-NMR: 2.59 s (18H, SnCH<sub>2</sub>), 6.77 d (18H, *o*-C<sub>6</sub>H<sub>5</sub>; <sup>3</sup>J = 7.3); 6.97 t (9H, *p*-C<sub>6</sub>H<sub>5</sub>; <sup>3</sup>J = 7.3); 7.10 dd (18H, *m*-C<sub>6</sub>H<sub>5</sub>; <sup>3</sup>J = 7.3, 7.3), <sup>2</sup>J(SnH) = 65.6 (unresolved). <sup>13</sup>C-NMR: 24.2 (SnCH<sub>2</sub>), 124.3 (C<sub>p</sub>), 127.9 (C<sub>m</sub>), 128.6 (C<sub>o</sub>), 139.9 (C<sub>i</sub>), 180.1 (C-S); <sup>2</sup>J(SnC) = 280.9 (unresolved). <sup>119</sup>Sn-NMR: -7.7.

### 5.3. 1,3,5-(Me<sub>3</sub>Sn)<sub>3</sub>C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> (**3**)

Reaction time 24 h, crude product washed with water before recrystallisation from methanol to give the product as colourless crystalline solid. Yield 53%, m.p. 118°C. Analysis: Found (Calc. for C<sub>12</sub>H<sub>27</sub>N<sub>3</sub>S<sub>3</sub>Sn<sub>3</sub>): C 21.7(21.7), H 4.08(4.09), N 6.26(6.31). IR (cm<sup>-1</sup>): 2928 vs, 1460 vs, 1377 vs, 1242 vs, 1188 w, 972 w, 892 w, 849 s, 771 s, 722 s. Mössbauer (mm s<sup>-1</sup>): i.s. 1.28, q.s. 1.84. <sup>1</sup>H-NMR: 0.57 s (27 H, SnCH<sub>3</sub>); <sup>2</sup>J(SnH) = 57.3 (unresolved). <sup>13</sup>C-NMR: -3.13 (SnCH<sub>3</sub>), 180.0 (C-S); <sup>1</sup>J(SnC) = 359, 377. <sup>119</sup>Sn-NMR: 74.4.

### 5.4. 1,3,5-(Bu<sub>3</sub>Sn)<sub>3</sub>C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> (**4**)

Reaction time 24 h. After filtration and solvent evaporation the product was obtained as an analytically pure oil in quantitative yield. Analysis: Found (Calc. for C<sub>39</sub>H<sub>81</sub>N<sub>3</sub>S<sub>3</sub>Sn<sub>3</sub>): C 45.0(44.9), H 7.83(7.82), N 4.04(4.02)%. IR (cm<sup>-1</sup>): 2923 vs, 2729 w, 1492 m, 1456 vs, 1377 s, 1340 w, 1319 w, 1292 w, 1238 vs (ν N<sub>2</sub>CS), 1181 w, 1152 w, 1074 mw, 1045 w, 1022 w, 961 w, 876 m, 846 vs, 790 mw, 770 w, 674 w. Mössbauer (mm s<sup>-1</sup>): i.s. 1.37, q.s. 2.27. <sup>1</sup>H-NMR: 0.90 t [27 H, Sn(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>], 1.29 m [18 H, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>], 1.35 m [18 H, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>], 1.60 m [18 H, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>]. <sup>13</sup>C-NMR: 13.6 [Sn(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>], 15.8 [SnCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>], 27.1 [Sn(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>], 28.8 [SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>], 180.4 [C-S]; <sup>1</sup>J(SnC) = 329, 345; <sup>3</sup>J(SnC) = 64 (unresolved). <sup>119</sup>Sn-NMR: 68.3.

### 5.5. 1,3,5-(Bu<sub>3</sub>Sn)<sub>3</sub>C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> (**4**): alternative strategy

Thiocyanuric acid (C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>H<sub>3</sub>) was prepared by the reaction of C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>Na<sub>3</sub>·9H<sub>2</sub>O (8.10 g, 20 mmol) in aqueous solution with the stoichiometric amount of a concentrated HCl (5.02 ml, 1.18 g cm<sup>-3</sup>). The resultant yellow precipitate was washed with water and dried at room temperature (3.10 g, 88%). Analysis: Found (Calc. for C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>H<sub>3</sub>): C 20.3(20.3), H 1.7(1.7), N 23.3(23.7). IR

(nujol, cm<sup>-1</sup>): 1576 m, 1537 s, 1258 m, 1125 s, 848 w, 785 w, 741 m.

A mixture of excess C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>H<sub>3</sub> (0.40 g, 2.3 mmol) and (Bu<sub>3</sub>Sn)<sub>2</sub>O (1.80 g, 3 mmol) in benzene (50 ml) was refluxed for 2 h and the water was removed azeotropically using a Dean and Stark apparatus. The solvent was removed in vacuo to yield the product as colourless oil (1.30 g, 62%). The product was identified as **4** by spectral comparison.

### 5.6. Synthesis of 1,3,5-(Ph<sub>2</sub>Sn)<sub>3</sub>(C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)<sub>2</sub> (**5**)

A mixture of C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>Na<sub>3</sub>·9H<sub>2</sub>O (0.30 g, 0.74 mmol, 20% excess) and Ph<sub>2</sub>SnCl<sub>2</sub> (0.31 g, 0.9 mmol) in methanol (30 ml) was stirred under N<sub>2</sub> at r.t. for 2 h. After removing the solvent, the resultant white precipitate was washed with methanol and water. Yield 0.16 g, 70%. **5** is insoluble in common organic solvents. Analysis: Found (Calc. for C<sub>42</sub>H<sub>30</sub>N<sub>6</sub>S<sub>6</sub>Sn<sub>3</sub>): C 40.7(43.2), H 2.65(2.59), N 5.93(7.20). IR (cm<sup>-1</sup>): 2922 vs, 2725 w, 1577 w, 1456 vs, 1377 vs, 1303 w, 1237 vs (ν N<sub>2</sub>CS), 1157 w, 1073 w, 1022 w, 996 w, 966 w, 856 s, 783 w, 722 s, 690 ms. Mössbauer (mm s<sup>-1</sup>): i.s. 1.27, q.s. 2.68.

Also prepared by the same method was the following.

### 5.7. 1,3,5-(Me<sub>2</sub>Sn)<sub>3</sub>(C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)<sub>2</sub> (**6**)

Reaction time 2 h, yield 62%. **6** is insoluble in common organic solvents. Analysis: Found (Calc. for C<sub>12</sub>H<sub>18</sub>N<sub>6</sub>S<sub>6</sub>Sn<sub>3</sub>): C 17.6(18.1), H 2.28(2.28), N 9.88(10.57)%. IR (cm<sup>-1</sup>): 2924 vs, 2725 w, 1460 vs, 1377 vs, 1307 w, 1275 w, 1240 vs, 1192 w, 972 w, 861 s, 783 s, 722 s. Mössbauer (mm s<sup>-1</sup>): i.s. 1.38, q.s. 2.96.

## 6. Crystallography

Suitable crystals of **1** and **3** for X-ray diffraction analysis were each obtained from ether/hexane by solvent diffusion over a period of one week. Crystal and experimental details are given in Table 1. Software used: SHELX86 [25], SHELX97 [26], ORTEP [27]. The asymmetric units of **1** and **3** are shown in Figs. 1 and 2, respectively; significant metrical data are given in Tables 2 and 3.

## 7. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 146550 and 146551 for compounds **1** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 1  
Crystal and experimental data

|                                                       | 1                                                                             | 3                                                                             |
|-------------------------------------------------------|-------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Empirical formula                                     | C <sub>57</sub> H <sub>45</sub> N <sub>3</sub> S <sub>3</sub> Sn <sub>3</sub> | C <sub>12</sub> H <sub>27</sub> N <sub>3</sub> S <sub>3</sub> Sn <sub>3</sub> |
| Crystal size                                          | 0.2 × 0.25 × 0.28                                                             | 0.25 × 0.17<br>× 0.05                                                         |
| Temperature (K)                                       | 293(2)                                                                        | 170(2)                                                                        |
| Diffractionmeter <sup>a</sup>                         | CAD-4                                                                         | Kappa CCD                                                                     |
| Wavelength (Å)                                        | 0.71069                                                                       | 0.71070                                                                       |
| Crystal system                                        | Monoclinic                                                                    | Monoclinic                                                                    |
| Space group                                           | Cc                                                                            | P2 <sub>1</sub> /a                                                            |
| Unit cell dimensions                                  |                                                                               |                                                                               |
| <i>a</i> (Å)                                          | 19.019(2)                                                                     | 12.742(1)                                                                     |
| <i>b</i> (Å)                                          | 28.301(3)                                                                     | 9.971(1)                                                                      |
| <i>c</i> (Å)                                          | 10.553(2)                                                                     | 18.617(1)                                                                     |
| β (°)                                                 | 108.62(1)                                                                     | 96.70(1)                                                                      |
| <i>Z</i>                                              | 4                                                                             | 4                                                                             |
| Absorption coefficient (mm <sup>-1</sup> )            | 1.536                                                                         | 3.429                                                                         |
| Crystal size (mm)                                     | 0.2 × 0.25 × 0.28                                                             | 0.25 × 0.17<br>× 0.05                                                         |
| Theta range (°)                                       | 2.11–25.02                                                                    | 3.52–30.08                                                                    |
| Reflections collected                                 | 4889                                                                          | 32566                                                                         |
| Independent reflections                               | 4889                                                                          | 6862                                                                          |
|                                                       | ( <i>R</i> <sub>int</sub> = 0.0000)                                           | ( <i>R</i> <sub>int</sub> = 0.0568)                                           |
| Absorption correction                                 | None                                                                          | Multiscan                                                                     |
| Max./min. transmission                                |                                                                               | 1.118 and 0.869                                                               |
| Data/restraints/parameters                            | 4889/2/595                                                                    | 6862/0/200                                                                    |
| Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]   | <i>R</i> <sub>1</sub> = 0.0371,<br><i>wR</i> <sub>2</sub> = 0.0883            | <i>R</i> <sub>1</sub> = 0.0299,<br><i>wR</i> <sub>2</sub> = 0.0737            |
| <i>R</i> indices (all data)                           | <i>R</i> <sub>1</sub> = 0.0506,<br><i>wR</i> <sub>2</sub> = 0.0932            | <i>R</i> <sub>1</sub> = 0.0443,<br><i>wR</i> <sub>2</sub> = 0.0823            |
| Largest difference peak and hole (e Å <sup>-3</sup> ) | 0.667 and<br>–0.764                                                           | 0.678 and<br>–1.082                                                           |

<sup>a</sup> Enraf–Nonius.Table 2  
Selected bond lengths (Å) and bond angles (°) for 1

|                     |           |                   |           |
|---------------------|-----------|-------------------|-----------|
| <i>Bond lengths</i> |           |                   |           |
| Sn(1)–C(10)         | 2.136(10) | Sn(3)–C(52)       | 2.108(12) |
| Sn(1)–C(4)          | 2.137(10) | Sn(3)–C(46)       | 2.114(10) |
| Sn(1)–C(16)         | 2.152(8)  | Sn(3)–C(40)       | 2.142(9)  |
| Sn(1)–S(1)          | 2.435(3)  | Sn(3)–S(2)        | 2.453(3)  |
| Sn(2)–C(28)         | 2.127(10) | S(1)–C(1)         | 1.730(9)  |
| Sn(2)–C(34)         | 2.139(9)  | S(2)–C(2)         | 1.726(9)  |
| Sn(2)–C(22)         | 2.140(9)  | S(3)–C(3)         | 1.744(8)  |
| Sn(2)–S(3)          | 2.457(3)  |                   |           |
| <i>Bond angles</i>  |           |                   |           |
| C(10)–Sn(1)–C(16)   | 107.7(3)  | C(22)–Sn(2)–S(3)  | 115.6(2)  |
| C(4)–Sn(1)–C(16)    | 107.7(4)  | C(52)–Sn(3)–C(46) | 112.6(4)  |
| C(10)–Sn(1)–S(1)    | 110.3(3)  | C(52)–Sn(3)–C(40) | 108.8(4)  |
| C(4)–Sn(1)–S(1)     | 123.4(3)  | C(46)–Sn(3)–C(40) | 108.5(4)  |
| C(16)–Sn(1)–S(1)    | 95.8(2)   | C(52)–Sn(3)–S(2)  | 117.6(3)  |
| C(28)–Sn(2)–C(34)   | 111.4(4)  | C(46)–Sn(3)–S(2)  | 111.2(3)  |
| C(28)–Sn(2)–C(22)   | 117.4(4)  | C(40)–Sn(3)–S(2)  | 96.6(3)   |
| C(34)–Sn(2)–C(22)   | 105.8(4)  | C(1)–S(1)–Sn(1)   | 98.6(3)   |
| C(28)–Sn(2)–S(3)    | 107.5(3)  | C(2)–S(2)–Sn(3)   | 95.5(3)   |
| C(34)–Sn(2)–S(3)    | 97.3(3)   | C(3)–S(3)–Sn(2)   | 96.6(3)   |

Table 3  
Selected bond lengths (Å) and bond angles (°) for 3

|                     |           |                   |           |
|---------------------|-----------|-------------------|-----------|
| <i>Bond lengths</i> |           |                   |           |
| Sn(1)–C(5)          | 2.128(3)  | Sn(3)–C(10)       | 2.124(3)  |
| Sn(1)–C(4)          | 2.131(4)  | Sn(3)–C(11)       | 2.134(4)  |
| Sn(1)–C(6)          | 2.135(3)  | Sn(3)–C(12)       | 2.140(5)  |
| Sn(1)–S(1)          | 2.4708(8) | Sn(3)–S(3)        | 2.4735(9) |
| Sn(2)–C(9)          | 2.122(3)  | S(1)–C(1)         | 1.742(3)  |
| Sn(2)–C(7)          | 2.129(3)  | S(2)–C(2)         | 1.743(3)  |
| Sn(2)–C(8)          | 2.143(3)  | S(3)–C(3)         | 1.743(3)  |
| Sn(2)–S(2)          | 2.4611(9) |                   |           |
| <i>Bond angles</i>  |           |                   |           |
| C(5)–Sn(1)–C(4)     | 114.7(2)  | C(7)–Sn(2)–S(2)   | 107.8(1)  |
| C(5)–Sn(1)–C(6)     | 113.1(1)  | C(8)–Sn(2)–S(2)   | 96.9(1)   |
| C(4)–Sn(1)–C(6)     | 112.9(2)  | C(10)–Sn(3)–C(11) | 115.9(2)  |
| C(5)–Sn(1)–S(1)     | 105.5(1)  | C(10)–Sn(3)–C(12) | 107.7(2)  |
| C(4)–Sn(1)–S(1)     | 111.5(1)  | C(11)–Sn(3)–C(12) | 113.6(2)  |
| C(6)–Sn(1)–S(1)     | 97.7(1)   | C(10)–Sn(3)–S(3)  | 115.0(1)  |
|                     |           | C(12)–Sn(3)–S(3)  | 98.0(2)   |
| C(9)–Sn(2)–C(7)     | 115.4(2)  | C(11)–Sn(3)–S(3)  | 105.3(1)  |
| C(9)–Sn(2)–C(8)     | 112.2(2)  | C(1)–S(1)–Sn(1)   | 99.3(1)   |
| C(7)–Sn(2)–C(8)     | 112.7(2)  | C(2)–S(2)–Sn(2)   | 97.7(1)   |
| C(9)–Sn(2)–S(2)     | 110.1(1)  | C(3)–S(3)–Sn(3)   | 96.2(1)   |

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