

Synthesis, characterisation and reaction chemistry of organotin-substituted bis(thiotetrazoles): supramolecular metallotetrazole structures containing hard and soft donors

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Four new organotin thiotetrazoles 1,4-(R₃SnSCN₄)₂C₆H₄ (R = Me, Et, Bu or Ph), along with their triphenyllead, diphenylthallium and phenylmercury analogues, have been synthesized. The supramolecular structure of 1,4-(Bu₃SnSCN₄)₂C₆H₄ has been found to consist of a 2-D sheet arrangement containing 32-membered (C₄NCSSnN₂CSSnN₃)₂ rings. In contrast, 1,4-(Me₃SnSCN₄)₂C₆H₄ crystallises as a bis(methanol) solvate in which 14-membered (SnSCN₂HO)₂ rings are linked through hydrogen bonds into a 1-D polymer.

Introduction

We have been interested for some time in the supramolecular architectures created by organotin derivatives of polyfunctional tetrazoles.^{1–3} The latter combine with various R₃Sn to yield products containing, without exception, the *trans*-N₂SnC₃ moiety, the linear N–Sn–N component of which acts as a rigid connector between azole units. The co-ordinatively versatile heterocycle, with four available donors all of which can be utilised in bonding in varying combinations, acts as a fulcrum about which lattice construction is orchestrated in two or more dimensions. Organotin tetrazoles thus represent an uncommon variant in supramolecular chemistry, where a combination of rigid ligands linking metals of various co-ordination numbers and stereochemistries *e.g.* Cd(CN)₂⁴ is a more common approach to lattice construction.

In our previous work we have been able to use organotin tetrazoles to construct zigzag sheets [*e.g.* 1,2-(Et₃SnN₄C)₂-C₆H₄],¹ planar sheets [*e.g.* 1,3,5-(Bu₃SnN₄C)₃C₆H₃],³ bilayers [*e.g.* 1,6-(Bu₃SnN₄C)₂(CH₂)₆]² and three-dimensional networks [*e.g.* 1,2-(Bu₃SnN₄C)₂C₆H₄].¹ In addition to ligand design, our experience suggests that the size of the hydrocarbon groups on tin also plays a crucial role in the way the lattice is constructed, by virtue of the fact that these groups need to be accommodated in any channels/cavities that are formed. The two variants of 1,2-(R₃SnN₄C)₂C₆H₄ cited above illustrate this point. Similar comments can be made about derivatives of the related ligand 1-phenyl-5-sulfanyl-1*H*-tetrazole (**I**), which we demonstrated some time ago preferentially co-ordinates through sulfur *via* its thiol (**Ia**), not thione (**Ib**), tautomer.⁵



Since we published the structure of SnBu₂(SCN₄Ph)₂, others have shown the ligand can act in a chelating [*e.g.* SnPh₃(SCN₄Ph)]⁶ or bridging manner, the latter generating both oligomers [*e.g.* (Me₃SnSCN₄Ph)₃]⁷ and polymers [*e.g.* [(PhCH₂)₃-SnSCN₄Ph]_n].⁸ More recently, several neutral and anionic transition metal derivatives have also been structurally characterised⁹ and we have discovered the first example of a

potentially π -co-ordinated tetrazole in PbPh₃SCN₄Ph-1.¹⁰ We now report our studies on the structural chemistry of 1,1'-*p*-phenylenebis[5(tributylstannylsulfanyl)tetrazole], 1,1'-*p*-phenylenebis[5(trimethylstannylsulfanyl)tetrazole] (solvated with methanol) and related organometallic species, in which a polyfunctional tetrazole-based ligand containing both hard (N) and soft (S) donors is used as a component of supramolecular assemblies.

Results and discussion

Synthesis

The cycloaddition of a triorganotin azide with 1,4-bis(isothiocyanato)benzene leads to the formation of **1** and **2** in yields in excess of 50% (Scheme 1). The course of the reactions was monitored by the disappearance of $\nu(\text{N}_3)$ and $\nu(\text{NCS})$ in the IR spectra at *ca.* 2076 and 2112 cm⁻¹, respectively. Compound **1** was recrystallised from hot methanol but, surprisingly, **2** proved insoluble in alcohols.

Compound **1** was converted into the metal-free tetrazole **II** by refluxing with aqueous HCl, and the absence of an IR band at *ca.* 2550 cm⁻¹ corresponding to $\nu(\text{SH})$ suggests **II** probably exists in the thione form. Indeed, a band assignable to $\nu(\text{C}=\text{S})$ was observed at 1049 cm⁻¹. The ammonium salt **III** was generated by bubbling ammonia through a solution of **II** for 30 min; **III** then enabled the synthesis of both trimethyl- and triphenyltin derivatives (**3**, **4**) by a salt elimination process, the former crystallising from methanol as a bis-solvate while the latter was unsolvated. Reaction of **1** with 2 equivalents of PbPh₃Cl resulted in elimination of SnBu₃Cl and formation of a bis-(organolead) derivative **5**. The bis(phenylmercury) analogue **6** was prepared similarly but proved difficult to characterise structurally due to its insolubility. A condensation reaction involving **II** and TlPh₂(OH) led to the diorganothallium analogue **7**, which crystallised as a dihydrate.

Spectroscopy

Table 1 gives the Mössbauer and NMR data for the triorganotin-substituted thiotetrazoles **1–4**. The quadrupole splittings (*q.s.*) for the three alkyltin species are in the range 3.32–3.39 mm s⁻¹ which are consistent with a polymeric, five-co-ordinate *trans*-XYSnC₃ trigonal bipyramidal geometry in the solid state.¹¹ The arrangement (X = N, Y = S) has been confirmed in

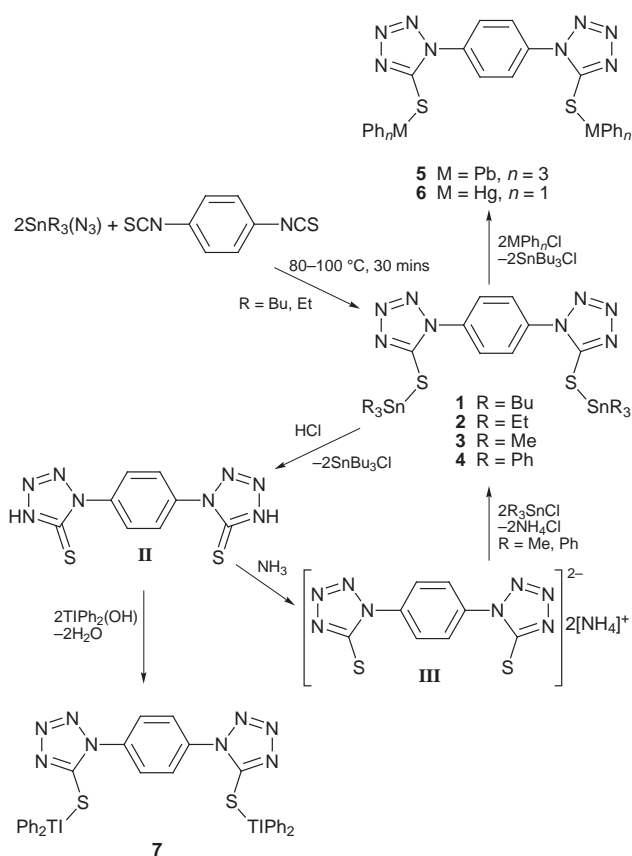


Table 1 The NMR^a and Mössbauer data^b

Compound	$\delta(^{119}\text{Sn})$	$^1J(\text{Sn}-^{13}\text{C})^c$	i. s.	q. s.	Ref.
$\text{SnBu}_3\text{SCN}_4\text{Ph}$	112.5	328	1.48	3.32	5
$\text{SnPh}_3\text{SCN}_4\text{Ph}$	-69.4		1.33	2.38	6
1	122.8	327	1.50	3.32	This work
2	-10.3	474	1.52	3.39	This work
3 ·2MeOH	-23.7	491, 515 ^d	1.38	3.35	This work
4	-65.0	—	1.22	2.29	This work
5	-235.5 ^e				This work

^a For $(\text{CD}_3)_2\text{SO}$ solutions at 25 °C except for compound **4** which was heated to 100 °C; δ in ppm relative to SnMe_4 , J in Hz. ^b Recorded at 78 K and data given as mm s^{-1} . ^c For unresolved $^{117,119}\text{Sn}$ couplings. ^d $^2J(^{117,119}\text{Sn}-^1\text{H})$ (unresolved): 68.5 Hz. ^e $\delta(^{207}\text{Pb})$.

$(\text{Me}_3\text{SnSCN}_4\text{Ph})_3$ (q.s. 3.15 mm s^{-1})⁷ while $\text{SnBu}_3(\text{SCN}_4\text{Ph})$, which has not been crystallographically characterised, has a q.s. of 3.32 mm s^{-1} .⁵ In **3**, which crystallises with two molecules of MeOH, both *trans*- NSSnC_3 and *trans*- OSSnC_3 arrangements are possible. A $\text{Me}(\text{H})\text{O} \rightarrow \text{Sn}$ co-ordination has been observed previously in $1,3\text{-}(\text{Bu}_3\text{SnN}_4\text{C})_2\text{C}_6\text{H}_4 \cdot 2\text{MeOH}$,¹ but literature precedent for a *trans*- SOSnC_3 tin environment, as well as related Mössbauer data, is scarce. The compound $\text{SnMe}_3[\text{O}(\text{S})\text{P}(\text{OMe})_2]$ has a q.s. of 3.89 mm s^{-1} ¹² and presumably adopts the same *trans*- OSSnC_3 structure as $\text{SnMe}_3[\text{O}(\text{S})\text{PMe}_2]$ ¹³ but there is no direct analogy for **3** where a co-ordinated solvent is incorporated, which, by its nature, is likely to be more weakly bound to tin and hence exhibit a lower q.s. Mössbauer spectroscopy is therefore not sufficient to distinguish unambiguously between the two possibilities but crystallography has confirmed a *trans*- SOSnC_3 centre (see below). The q.s. for **4** is 2.29 mm s^{-1} and is comparable with the value 2.38 mm s^{-1} for $\text{SnPh}_3(\text{SCN}_4\text{Ph})$ which is essentially tetrahedral at tin with only a very weak chelating interaction with a ring nitrogen [$3.275(3) \text{ \AA}$].⁶

The NMR data (Table 1), recorded in dmsO, indicate that any

Table 2 Selected metric data (bond lengths in Å, angles in °) for compound **1***

$\text{Sn}(1)-\text{C}(17)$	2.09(1)	$\text{Sn}(2)-\text{C}(29)$	2.11(1)
$\text{Sn}(1)-\text{C}(13)$	2.10(1)	$\text{Sn}(2)-\text{C}(21)$	2.13(1)
$\text{Sn}(1)-\text{C}(9)$	2.11(2)	$\text{Sn}(2)-\text{C}(25)$	2.13(1)
$\text{Sn}(1)-\text{S}(2)$	2.574(2)	$\text{Sn}(2)-\text{S}(1)$	2.554(3)
$\text{Sn}(1)-\text{N}(6')$	2.781(7)	$\text{Sn}(2)-\text{N}(2'')$	2.810(7)
$\text{S}(1)-\text{C}(1)$	1.716(9)	$\text{S}(2)-\text{C}(8)$	1.726(9)
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$\text{C}(17)-\text{Sn}(1)-\text{C}(13)$	125.0(8)	$\text{C}(29)-\text{Sn}(2)-\text{C}(21)$	122.2(5)
$\text{C}(17)-\text{Sn}(1)-\text{C}(9)$	110.8(8)	$\text{C}(29)-\text{Sn}(2)-\text{C}(25)$	117.6(6)
$\text{C}(13)-\text{Sn}(1)-\text{C}(9)$	118.4(5)	$\text{C}(21)-\text{Sn}(2)-\text{C}(25)$	114.5(5)
$\text{C}(17)-\text{Sn}(1)-\text{S}(2)$	92.9(4)	$\text{C}(29)-\text{Sn}(2)-\text{S}(1)$	101.1(4)
$\text{C}(13)-\text{Sn}(1)-\text{S}(2)$	101.9(3)	$\text{C}(21)-\text{Sn}(2)-\text{S}(1)$	89.5(3)
$\text{C}(9)-\text{Sn}(1)-\text{S}(2)$	98.8(4)	$\text{C}(25)-\text{Sn}(2)-\text{S}(1)$	103.2(3)
$\text{C}(17)-\text{Sn}(1)-\text{N}(6')$	79.7(4)	$\text{C}(29)-\text{Sn}(2)-\text{N}(2'')$	82.0(4)
$\text{C}(13)-\text{Sn}(1)-\text{N}(6')$	82.6(4)	$\text{C}(21)-\text{Sn}(2)-\text{N}(2'')$	80.4(3)
$\text{C}(9)-\text{Sn}(1)-\text{N}(6')$	83.9(4)	$\text{C}(25)-\text{Sn}(2)-\text{N}(2'')$	84.0(4)
$\text{S}(2)-\text{Sn}(1)-\text{N}(6')$	172.6(2)	$\text{S}(1)-\text{Sn}(2)-\text{N}(2'')$	169.4(2)
$\text{C}(1)-\text{S}(1)-\text{Sn}(2)$	104.0(3)	$\text{C}(8)-\text{S}(2)-\text{Sn}(1)$	101.8(3)

* Primed and double-primed atoms are related to their unprimed counterparts by $-x + 0.5, y + 0.5, -z$ and $-x + 1.5, y + 0.5, -z + 1$, respectively.

Table 3 Selected metric data (bond lengths in Å, angles in °) for compound **3**

$\text{Sn}(1)-\text{C}(2)$	2.132(7)	$\text{Sn}(1)-\text{O}(1)$	2.464(5)
$\text{Sn}(1)-\text{C}(1)$	2.133(6)	$\text{Sn}(1)-\text{S}(1)$	2.607(2)
$\text{Sn}(1)-\text{C}(3)$	2.141(7)	$\text{S}(1)-\text{C}(4)$	1.723(7)
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$\text{C}(1)-\text{Sn}(1)-\text{O}(1)$	82.2(2)	$\text{C}(4)-\text{S}(1)-\text{Sn}(1)$	101.1(2)
$\text{C}(3)-\text{Sn}(1)-\text{O}(1)$	85.0(2)	$\text{C}(2)-\text{Sn}(1)-\text{C}(1)$	115.2(3)
$\text{C}(2)-\text{Sn}(1)-\text{S}(1)$	91.1(2)	$\text{C}(2)-\text{Sn}(1)-\text{C}(3)$	120.9(3)
$\text{C}(1)-\text{Sn}(1)-\text{S}(1)$	99.3(2)	$\text{C}(1)-\text{Sn}(1)-\text{C}(3)$	120.3(3)
$\text{C}(3)-\text{Sn}(1)-\text{S}(1)$	98.5(2)	$\text{C}(2)-\text{Sn}(1)-\text{O}(1)$	83.7(2)
$\text{O}(1)-\text{Sn}(1)-\text{S}(1)$	174.7(1)		

intermolecular interactions in solid **1** are lost and that tin has a tetrahedral environment in solution. Similarly, a co-ordination number (c.n.) of 4 is maintained by compound **4** in solution. Both $\delta(^{119}\text{Sn})$ and 1J data are consistent with c.n. = 5 for both **2** and **3** in solution, but in both cases it is likely that this is achieved by dmsO co-ordination to tin. Similarly, $\delta(^{207}\text{Pb})$ for **5** (-235.5) is also indicative of a co-ordination number of 5 at the metal, and is comparable with data for other triphenyllead tetrazoles in dmsO (-251 to -360),¹⁴ where once again dmsO, as solvent, is probably involved in complexation.

The ^1H and ^{13}C NMR data are unremarkable, save for the occurrence of the quaternary ring carbon at *ca.* δ 160 in the ^{13}C spectra which confirms the presence of the tetrazole ring.

Crystallography

Selected metric data for compounds **1** and **3** are given in Tables 2 and 3, respectively. For purposes of comparison, the Sn-S, Sn-N, C-S bond lengths and the C-Sn-C bond angle of previously known organotin-substituted thiotetrazoles are summarised in Table 4. For descriptive purposes, we number the tetrazole ring nitrogens as 1-4 for comparing the co-ordination mode of the tetrazole, while with respect to tin we group the nitrogens into either N^1 (*i.e.* N^1 or N^4) or N^2 (*i.e.* N^2 or N^3) categories, these representing the two differing degrees of hindrance for metal binding. The system can equally well be applied to the thiotetrazoles, though here N^1 is arylated and cannot co-ordinate further to a metal.

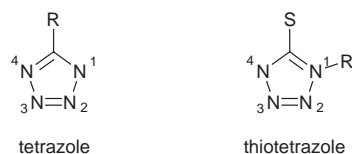


Table 4 Comparative geometric data for compounds **1** and **3** and related compounds

Compound	Sn–S/Å	Sn–N/Å	C–S/Å	C–Sn–C°	Ref.
1	2.574(2), 2.554(3)	2.781(7), ^a 2.810(7) ^a	1.716(9), 1.726(9)	110.8(8)–125.0(8)	This work
3	2.607(2)	2.464(5) ^b	1.723(7)	115.2(3)–120.9(3)	This work
SnBu ₂ (SCN ₄ Ph) ₂	2.477(4)	2.99 ^c	1.76(2)	130.7(4)	5
[(PhCH ₂) ₃ SnSCN ₄ Ph] _∞	2.565(4), 2.614(5)	2.68(1), ^a 2.56(1) ^a 3.16, ^c 3.20 ^c	1.72(1)	111.4(4)–126.1(5)	8
SnPh ₃ (SCN ₄ Ph)	2.482(1)	3.275(3) ^c	1.728(4)	113.6(1)–122.7(1)	6
(Me ₃ SnSCN ₄ Ph) ₃	2.565(4)	2.75(1), ^a 3.29(1) ^c	1.73(2)	115.8(8)–120(1)	7

^a Intermolecular. ^b Sn–O. ^c Intramolecular.

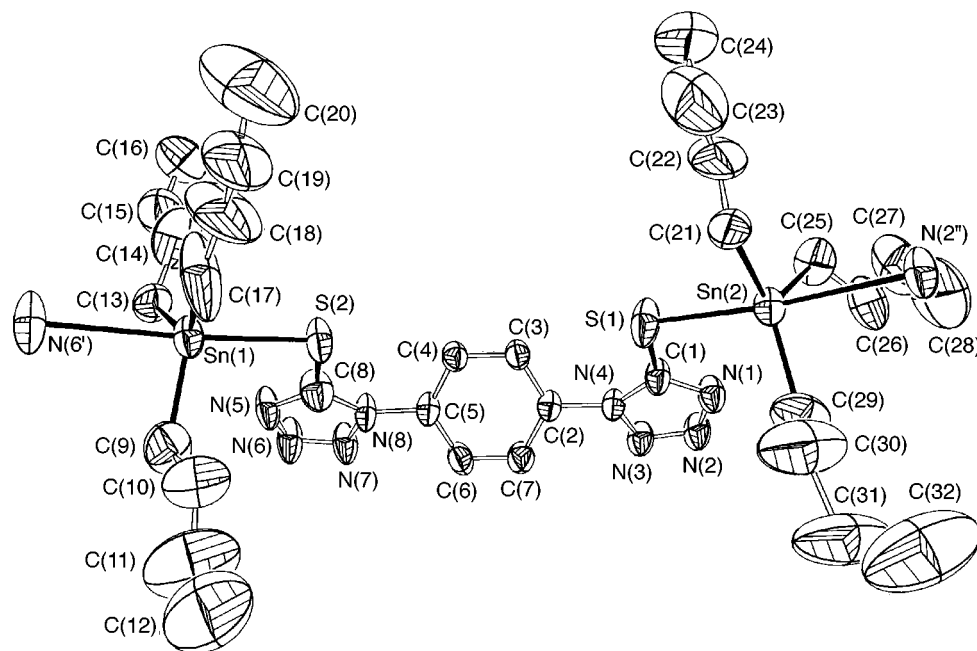


Fig. 1 The asymmetric unit of compound **1** showing the labelling scheme used in the text and tables. Thermal ellipsoids are at the 30% level.

Compound 1. The asymmetric unit of compound **1** contains two trigonal bipyramidal *trans*-NSSnC₃ centres (Fig. 1) consistent with the Mössbauer q.s. data (see above). Each tin is directly bonded to the sulfur of the attached ligand and is further coordinated intermolecularly by a nitrogen [either N(2') or N(6')] from the tetrazole of a neighbouring molecule. Both nitrogen and sulfur attached to a given tin form part of the same ligand group, *i.e.* the structure can be viewed as parallel chains, one based on Sn(1) and the ligand containing S(2), N(6) the other based on Sn(2), S(1), N(2) groupings. The arrangement can be seen as identical to that of Sn(CH₂Ph)₂(SCN₄Ph)⁸ but with the phenyl group attached to the tetrazole common to a pair of parallel strands (Fig. 2). The two Sn–S distances [Sn(1)–S(2) 2.574(2); Sn(2)–S(1) 2.554(3) Å] are comparable with the Sn–S bond lengths of previously known organotin thiotetrazoles (Table 4) although they are at the longer end of the range. The intermolecular Sn–N bonds [Sn(1)–N(6') 2.781(7); Sn(2)–N(2'') 2.810(7) Å] are similar to the intermolecular Sn–N bond lengths of [(PhCH₂)₃SnSCN₄Ph]_∞ and (Me₃SnSCN₄Ph)₃ (Table 4) but longer than the intermolecular Sn–N bond length of hydrated 2,2'-*p*-phenylenebis(tributylstannyltetrazole) [Sn(1)–N(6') 2.573(6) Å],¹⁴ presumably as a result of the lower Lewis acidity of tin arising from S, rather than N, primary bonding. Metal–ligand bonding thus takes place primarily through the sulfur exocyclic to the tetrazole rather than the nitrogen. The N–Sn–S bond angles approach 180° [N(6')–Sn(1)–S(2) 172.6(2); S(1)–Sn(2)–N(2'') 169.4(2)°].

The N³ co-ordination of the tetrazole with respect to the tin is that of lowest steric hindrance and is the mode adopted in both [(PhCH₂)₃SnSCN₄Ph]_∞⁸ and (Me₃SnSCN₄Ph)₃.⁷ For

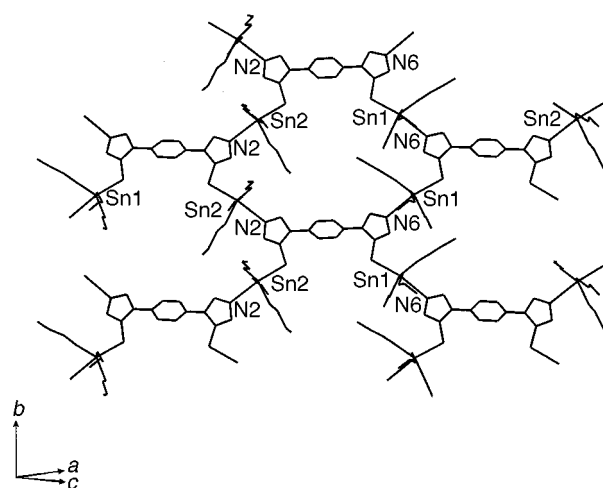


Fig. 2 The sheet structure of compound **1** viewed along the $-1, 0, 1$ direction.

comparison with known organotin tetrazoles, each tetrazole can be described as bidentate and exhibiting N¹ + N³ co-ordination, the N¹ site in the thiotetrazoles being occupied by the phenyl ring. The N¹ + N³ mode of co-ordination is the most common for organotin tetrazole and organotin thio-tetrazoles.¹⁵

The supramolecular structure of compound **1** is dominated by two-dimensional sheets as shown in Fig. 2. Atoms Sn(1) and Sn(2) in the asymmetric unit interact with N(6) and N(2) of

the lattice neighbours generated *via* the symmetry operators $0.5 - x, 0.5 + y, -z$ and $1.5 - x, 0.5 + y, 1 - z$, respectively. The axial nitrogens co-ordinated to the tin lie in the plane of the polymer sheets. These sheets are dominated by 32-membered rings containing four tins, four sulfurs, twelve tetrazole nitrogens, four tetrazole carbons and eight phenyl carbons. The interlayer region is filled by the equatorial *n*-butyl groups as shown Fig. 3. The supramolecular arrays of other organotin tetrazoles also include planar and puckered two-dimensional arrays. The closest analogies for **1** can be drawn with nitrotris[2-(2-tributylstannyltetrazol-5-yl)ethyl]methane and 1,3,5-tris(tributylstannyltetrazol-5-yl)benzene which are also two-dimensional sheet structures,³ though these are built to include only 24-atom (Sn_6N_{18}) rings. Indeed, the size of the rings in **1**, enlarged as they are by the phenylene groups inherent in the

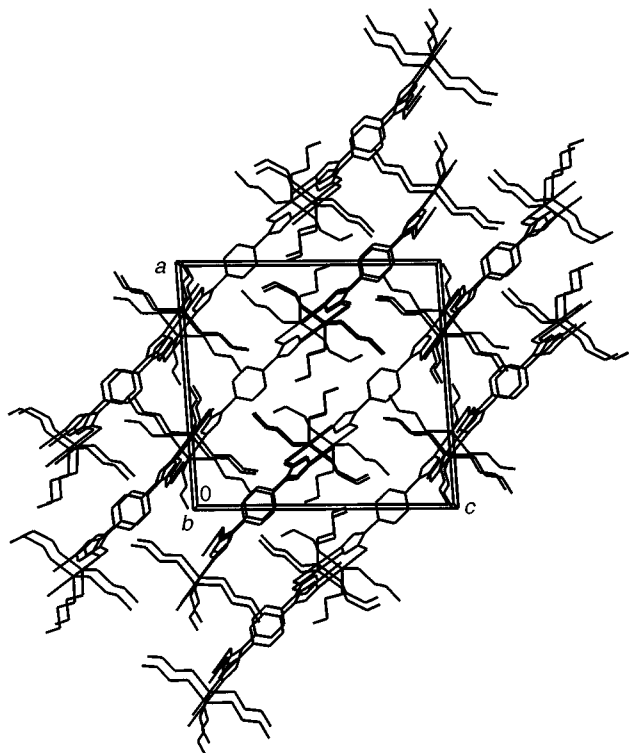


Fig. 3 The sheet structure of compound **1** viewed along *b* to illustrate the filling of the interlayer region by the butyl groups on tin.

ligand, is surprisingly large for accommodating only four of the butyl groups of the associated tin atoms. In contrast, both planar tris-substituted tetrazoles pack ten butyl groups from six tins into the cavity of the 24-atom ring. This suggests that with suitable ligand design far more porous structures than previously identified are achievable.

Compound 3·2MeOH. X-Ray quality crystals of compound **3** were obtained by slow evaporation of a methanolic solution at room temperature; data were collected at low temperature as the crystals desolvated at ambient temperatures in the absence of mother-liquor. The asymmetric unit (Fig. 4) was found to consist of one half of the molecule, the remainder being generated by an inversion centre at the midpoint of the C_6 ring. Each tin is trigonal bipyramidal *trans*- SOSnC_3 with the axial positions occupied by O(1) of the co-ordinated methanol molecule and S(1) of the thiotetrazole. The O–Sn–S bond angle is close to 180° [O(1)–Sn(1)–S(1) $174.7(1)^\circ$]. The Sn(1)–S(1) bond length [2.607(2) Å] is the longest such distance observed when compared with those of **1** and with other known organotin-substituted thiotetrazoles (Table 4). No other data for solvated organotin thiotetrazoles exist for comparison of the Sn(1)–O(1) bond length [2.464(5) Å], although it is longer than the analogous bond in related 1,3-($\text{Bu}_3\text{SnN}_4\text{C}$) $_2\text{C}_6\text{H}_4 \cdot 2\text{MeOH}$ [2.398(9) Å].¹ In addition, comparison can be made with data for ($\text{Me}_3\text{SnOSPM}_2$) $_x$ which also has a *trans*- SOSnC_3 centre where the Sn–O bond is, as expected, stronger [2.267(6) Å].¹³ The tetrazole adopts the common $\text{N}^1 + \text{N}^3$ co-ordination mode (N^1 bonded to the phenyl ring) seen in **1**.

The salient feature of the supramolecular structure of compound **3** is that of a one-dimensional hydrogen-bonded polymer, as shown in Fig. 5, in which the co-ordinated methanol hydrogen bonds to N(2) of a neighbouring tetrazole [O(1)⋯N(2) 2.801(8); H(1)⋯N(2) 1.84(3) Å; O(1)–H(1)–N(2) $173(5)^\circ$]. The polymers are, in effect, fourteen-membered (SnSCN_2HO) $_2$ rings linked by phenylene bridges. We have observed similar twelve-membered rings in the structure of 1-phenyl 5-diphenylthallium tetrazole which simply lacks the sulfurs of the thiotetrazole in **3**.¹⁴

Conclusion

Four organotin thiotetrazoles 1,4-(R_3SnSCN_4) $_2\text{C}_6\text{H}_4$ (R = Me, Et, Bu or Ph) along with the triphenyllead, diphenylthallium and phenylmercury analogues have been synthesized. The

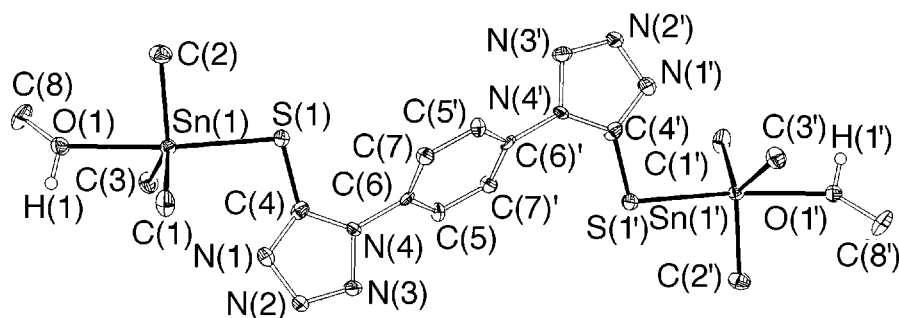


Fig. 4 The symmetric unit of compound **3** showing the labelling scheme used in the text and tables. Thermal ellipsoids are at the 30% level.

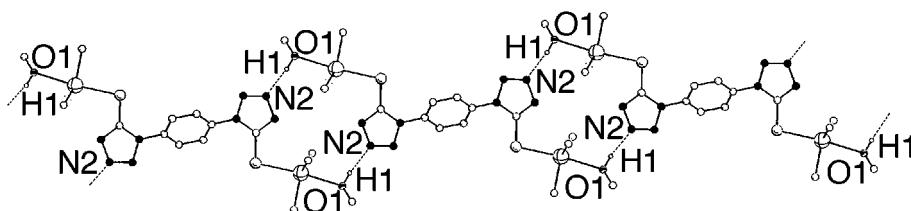


Fig. 5 The polymeric structure of compound **3** showing the intermolecular hydrogen bonds.

supramolecular structure of 1,4-(Bu₃SnSCN₄)₂C₆H₄ has been found to consist of a 2-D sheet arrangement containing 32-membered (C₄NCSSnN₂CSSnN₃)₂ rings. In contrast, 1,4-(Me₃-SnSCN₄)₂C₆H₄ crystallises as a bis(methanol) solvate in which 14-membered (SnSCN₂HO)₂ rings are linked through hydrogen bonds into a 1-D polymer.

Experimental

Spectra were recorded on the following instruments: JEOL GX270 (¹H, ¹³C NMR), GX400 (¹¹⁹Sn NMR), Perkin-Elmer 599B (IR). Details of our Mössbauer spectrometer and related procedures are given elsewhere.¹⁶ Isomer shift data are relative to CaSnO₃. For all compounds, infrared spectra were recorded as Nujol mulls on KBr plates and all NMR data on saturated solutions in (CD₃)₂SO unless indicated otherwise.

Organotin azides SnR₃(N₃) (R = Bu¹⁷ or Et¹) and TIPh₂(OH)¹⁸ were prepared by literature methods. Other reagents were obtained commercially and used without further purification.

CAUTION: Owing to their potentially explosive nature, all preparations and subsequent reactions with organotin azides were conducted under an inert atmosphere behind a rigid safety screen.

Syntheses

1,1'-*p*-Phenylenebis[(5-tributylstannylsulfanyl)tetrazole] 1. A mixture of tributyltin azide (6.96 g, 21.0 mmol) and 1,4-diisothiocyanatobenzene (2.04 g, 10.6 mmol) were heated while stirring under N₂ at 100 °C for half an hour. The resultant yellow-white solid was recrystallised from hexanes yielding compound **1** as a white microcrystalline solid (5.02 g, 55%), m.p. 122 °C [Found (Calc. for C₁₆H₂₉N₄SSn): C, 44.6 (44.9); H, 6.81 (6.83); N, 13.0 (13.1)%]. ¹H NMR: δ 8.01 (s, 4 H, C₆H₄), 1.62 [m, 12 H, SnCH₂CH₂CH₂CH₃]; 1.54 (m, 12 H, SnCH₂-CH₂CH₂CH₃), 1.48 (m, 12 H, SnCH₂CH₂CH₂CH₃) and 0.91 [t, 18 H, (CH₂)₃CH₃]. ¹³C NMR: δ 155.7 (CN₄), 135.1 (C^{1,4} of C₆H₄), 124.6 (C^{2,3,5,6} of C₆H₄), 28.5 (SnCH₂CH₂CH₂CH₃), 27.0 [Sn(CH₂)₂CH₂CH₃], 16.6 [SnCH₂(CH₂)₂CH₃] and 13.6 [(CH₂)₃CH₃]; ¹J[¹³C-^{117,119}Sn] 327 (unresolved), ³J[¹³C-^{117,119}Sn] 66 Hz (unresolved). ¹¹⁹Sn NMR: δ 122.8. IR (cm⁻¹, Nujol): 3457, 2924, 2855, 2363, 2340, 2168, 1653, 1601, 1509, 1464, 1418, 1375, 1300, 1277, 1219, 1080, 1039, 1011 and 837. ^{119m}Sn Mössbauer (mm s⁻¹): i.s. = 1.50; q.s. = 3.32.

1,1'-*p*-Phenylenebis[(5-triethylstannylsulfanyl)tetrazole] 2. A mixture of triethyltin azide (2.91 g, 11.73 mmol) and 1,4-diisothiocyanatobenzene (1.13 g, 5.87 mmol) was heated while stirring under N₂ at 88 °C for half an hour. The resultant yellow-white solid was washed with hexanes leaving the product as an analytically pure white powder (2.12 g, 53%); mp 184 °C (decomp.) [Found (Calc. for C₁₀H₁₇N₄SSn): C, 34.9 (34.9); H, 4.80 (4.94); N, 16.7 (16.3)%]. ¹H NMR: δ 8.06 (s, 4 H, C₆H₄) and 1.20–1.30 (m, 30 H, CH₂CH₃); ²J[¹H-^{117,119}Sn] 90 Hz (unresolved). ¹³C NMR: δ 163.0 (CN₄), 135.1 (C^{1,4} of C₆H₄), 124.7 (C^{2,3,5,6} of C₆H₄), 11.5 (CH₂CH₃) and 10.5 (CH₂CH₃); ¹J[¹³C-^{117,119}Sn] 237 Hz (unresolved). ¹¹⁹Sn NMR: δ -10.3. IR (cm⁻¹, KBr): 2947, 1606, 1518, 1446, 1371, 1300, 1277, 1218, 1120, 1082, 1039, 1010, 952, 839, 715 and 677. ^{119m}Sn Mössbauer (mm s⁻¹): i.s. = 1.52; q.s. = 3.39.

1,1'-*p*-Phenylenebis(5-thioxotetrazole)-methanol (1/1) II. Concentrated hydrochloric acid (1.50 mL, 18 mmol) was added dropwise to a well stirred solution of compound **1** (3.0 g, 3.5 mmol) in hot methanol (300 mL). The resultant colourless solution was refluxed for an hour. After cooling, methanol was removed *in vacuo* and the remaining white solid washed with hexanes to remove SnBu₃Cl and recrystallised from methanol to give the product as a white solid (0.96 g, 99%); mp 200 °C

(decomp.) [Found (Calc. for C₈H₆N₈S₂·CH₃OH): C, 34.9 (34.7); H, 2.05 (2.74); N, 38.5 (38.1)%]. ¹H NMR: δ 8.17 (s, 4 H, C₆H₄) and 3.18 (s, 3 H, CH₃OH). ¹³C NMR: δ 162.5 (CN₄), 134.5 (C^{1,4} of C₆H₄) and 125.4 (C^{2,3,5,6} of C₆H₄). IR (cm⁻¹, KBr disc): 3553, 3414, 3069, 2937, 2750, 1637, 1616, 1522, 1477, 1385, 1350, 1296, 1275, 1217, 1049, 989, 851, 767, 657 and 590.

Diammonium 1,1'-*p*-phenylenebis(tetrazole-5-thiolate) III.

Ammonia gas was bubbled through a solution of compound **II** in methanol (350 mL) for 30 min. The methanol was removed *in vacuo* to yield **III** in quantitative yield, mp 190 °C (decomp.) [Found (Calc. for C₄H₆N₈S): C, 31.4 (30.8); H, 3.90 (3.85); N, 44.2 (44.9)%]. ¹H NMR: δ 8.16 (s, 4 H, C₆H₄) and 7.30 (s, 8 H, NH₄⁺). ¹³C NMR: δ 167.5 (CN₄), 135.5 (C^{1,4} of C₆H₄) and 123.5 (C^{2,3,5,6} of C₆H₄). IR (cm⁻¹, Nujol): 3443, 2955, 2924, 2855, 2363, 2342, 1734, 1653, 1559, 1516, 1458, 1420, 1375, 1358, 1292, 1283, 1219, 1089, 1040 and 1013.

1,1'-*p*-Phenylenebis[(5-trimethylstannylsulfanyl)tetrazole]-methanol (1/2) 3. A solution of trimethyltin chloride (0.62 g, 3.12 mmol) in methanol (100 mL) was added dropwise to a well stirred solution of compound **III** (0.50 g, 1.56 mmol) in methanol (200 mL) and the reaction mixture refluxed for 3 h. Subsequently, the methanol was removed *in vacuo* and the white solid refluxed in acetone (300 mL) for 30 min. Hot filtration resulted in a yellow solution. The acetone was removed *in vacuo* and the resulting yellow-white solid recrystallised from methanol to yield **3** as a yellow crystalline product (0.73 g, 77%), mp 175 °C (decomp.) [Found (Calc. for C₇H₁₁N₄SSn·CH₃OH): C, 28.5 (28.7); H, 4.32 (4.49); N, 17.0 (16.8)%]. ¹H NMR: δ 8.06 (s, 4 H, C₆H₄), 3.16 (s, 6 H, CH₃OH), 0.64 (s, 12 H, SnCH₃); ²J[¹H-^{117,119}Sn] 68.5 Hz (unresolved). ¹³C NMR: δ 164.7 (CN₄), 135.1 (C^{1,4} of C₆H₄), 124.5 (C^{2,3,5,6} of C₆H₄), 48.7 (CH₃OH) and 0.9 (CH₃); ¹J[¹³C-^{117,119}Sn] 491, 515 Hz. ¹¹⁹Sn NMR: δ -23.7. IR (cm⁻¹, KBr disc): 3245, 2924, 2855, 2363, 2342, 1520, 1512, 1464, 1368, 1352, 1298, 1277, 1219, 1117, 1098, 1082, 1020, 1010, 837 and 789. ^{119m}Sn Mössbauer (mm s⁻¹): i.s. = 1.38; q.s. = 3.35.

1,1'-*p*-Phenylenebis[(5-triphenylstannylsulfanyl)tetrazole] 4. A solution of triphenyltin chloride (0.76 g, 1.97 mmol) in methanol (10 mL) was added dropwise to a well stirred solution of compound **III** (0.31 g, 0.99 mmol) in methanol (250 mL) and the reaction refluxed for 3 h. The reaction was worked up in the same way as for **3** to yield **4** as a white powder (0.42 g, 40%), mp 160–162 °C [Found (Calc. for C₂₂H₁₇N₄SSn): C, 53.2 (54.1); H, 3.46 (3.48); N, 11.5 (11.5)%]. ¹H NMR (100 °C): δ 7.89–7.42 (m, 34 H, phenyl). ¹³C NMR (100 °C): δ 141.7, 135.7, 134.9, 129.0, 128.3, 125.2, 124.0 and 118.0 (phenyl). ¹¹⁹Sn NMR (100 °C): δ -65.0. IR (cm⁻¹, KBr disc): 3414, 3067, 1637, 1618, 1522, 1479, 1429, 1379, 1238, 1226, 1091, 1074, 1016, 997, 837, 731, 696, 619, 574 and 453. ^{119m}Sn Mössbauer (mm s⁻¹): i.s. = 1.22; q.s. = 2.29.

1,1'-*p*-Phenylenebis[(5-triphenylplumbylsulfanyl)tetrazole]-toluene (2/1) 5. A solution of triphenyllead chloride (0.56 g, 1.18 mmol) in methanol (200 mL) was added dropwise to a well stirred solution of compound **1** (0.50 g, 0.58 mmol) also in hot methanol (150 mL). The resultant clear solution was refluxed for 10 h. Subsequently, methanol was removed *in vacuo* and the resulting white product washed with hexanes and recrystallised from toluene to give **5** as a white crystalline product (0.22 g, 33%), mp 218–220 °C (decomp.) [Found (Calc. for C₄₄H₃₄N₈Pb₂S₂·0.5CH₃C₆H₅): C, 47.7 (47.5); H, 3.32 (3.17); N, 9.48 (9.35)%]. ¹H NMR: δ 7.84, 7.74, 7.60–7.32 (phenyl) and 3.07 (s, CH₃C₆H₅). ¹³C NMR: δ 160.0 (CN₄), 135.8, 134.5, 129.4, 128.7 and 124.3 (phenyl). ²⁰⁷Pb NMR: δ -235.5 (100 °C). IR (cm⁻¹, Nujol): 2926, 2855, 1933, 1836, 1715, 1633, 1603, 1568, 1435, 1377, 1335, 1298, 1233, 1098, 1026, 1011, 997, 857, 760, 741 and 696.

Table 5 Crystallographic data for compounds **1** and **3***

	1	3
Empirical formula	C ₃₂ H ₅₈ N ₈ S ₂ Sn ₂	C ₈ H ₁₅ N ₄ OSSn
<i>M</i>	856.36	333.99
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> $\bar{1}$
<i>T</i> /K	293(2)	170(2)
<i>a</i> /Å	17.602(2)	6.755(2)
<i>b</i> /Å	12.639(2)	10.253(4)
<i>c</i> /Å	18.733(6)	10.452(4)
<i>a</i> °	—	70.44(4)
<i>β</i> °	93.79(1)	83.67(4)
<i>γ</i> °	—	70.84(3)
<i>U</i> /Å ³	4158(2)	644.3(4)
<i>Z</i>	4	2
μ (Mo-K α)/mm ⁻¹	1.332	2.128
Reflections collected	6015	2790
Goodness of fit on <i>F</i> ²	1.003	1.165
<i>R</i> 1, <i>wR</i> 2	0.0496, 0.1059	0.0347, 0.0978
[<i>I</i> > 2 σ (<i>I</i>)] (all data)	0.1341, 0.1524	0.0512, 0.1051

* Details in common; λ (Mo-K α) 0.70930 Å; full-matrix least-squares refinement on *F*².

1,1'-*p*-Phenylenebis[(5-phenylmercuriosulfanyl)tetrazole] **6**.

This was prepared in a similar manner to compound **5** from a methanolic solution (100 mL) of **1** (0.53 g, 0.61 mmol) and a solution of phenylmercury(II) chloride (0.38 g, 1.27 mmol) in methanol (130 mL). A white precipitate formed instantaneously, which was collected by washing with hexanes and filtering. The product was found to be insoluble in most commonly available solvents (0.40 g, 80%), mp 190–192 °C (decomp.) [Found (Calc. for C₁₀H₇HgN₄S): C, 28.2 (28.9); H, 1.74 (1.68); N, 13.0 (13.5)%], IR (cm⁻¹, Nujol): 3441, 2955, 2924, 2855, 1624, 1524, 1464, 1431, 1372, 1294, 1271, 1235, 1094, 1041, 1020, 997, 982, 843, 723 and 629.

1,1'-*p*-Phenylenebis[(5-diphenylthalliosulfanyl)tetrazole] dihydrate **7**.

A solution of diphenylthallium hydroxide (0.100 g, 0.267 mmol) in methanol (200 mL) was added dropwise to a well stirred solution of compound **II** (0.04 g, 0.134 mmol) in hot methanol (60 mL). After refluxing for 3 h the cloudy solution was cooled to room temperature and the volume of solvent decreased under reduced pressure, resulting in the precipitation of a white solid which was collected by filtration and dried *in vacuo* (0.06 g, 43%), mp 202 °C (decomp.) [Found (Calc. for C₁₁H₁₂N₄STl·H₂O): C, 38.7 (37.3); H, 2.42 (2.72); N, 11.3 (10.9%)]. ¹H NMR δ 8.28–7.29 (m, 24 H, phenyl). ¹³C NMR δ 164.0 (CN₄), 137.3, 136.9, 135.6, 130.9, 128.8, 126.5 and 123.9 (phenyl). IR (cm⁻¹, KBr): 3414, 3044, 2924, 1616, 1510, 1475, 1431, 1363, 1340, 1296, 1280, 1215, 1093, 1078, 1006, 997, 841, 723, 688 and 451.

X-Ray crystallography

Crystal data are summarised in Table 5.

Compound 1. A crystal of approximate dimensions 0.4 × 0.4 × 0.4 mm was used for data collection. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant. The C–C bond lengths in the butyl group containing carbons C(17)–C(20) were constrained to an ideal distance of 1.54 Å, as early refinement cycles indicated some instability in this region of the electron density map. This action was reflected in an improvement of residuals. The asymmetric unit is shown in Fig. 1.

Compound 3. A crystal of approximate dimensions 0.5 × 0.4 × 0.25 mm was used for data collection. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant, except for the methanolic proton [H(1)] which was located and refined at a distance of 0.98 Å from O(1). The asymmetric unit is shown in Fig. 4 (unprimed labels).

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