

Synthesis and supramolecular architectures of tetrakis(triorgano-stannyltetrazoles), including the crystal structure of hydrated 1,2,4,5-tetrakis(triethylstannyltetrazolyl)benzene

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Six tetrakis(triorganostannyltetrazolyl)-alkanes and -benzenes have been prepared by a cycloaddition reaction between SnR_3N_3 and either 1,2,4,5-(NC) $_4\text{C}_6\text{H}_2$, 1,1,3,3-(NC) $_4\text{C}_3\text{H}_4$ or 1,3,3,5-(NC) $_4\text{C}_5\text{H}_8$. All compounds contain tin in a *trans*-XYSnR $_3$ environment; in anhydrous compounds the axial co-ordination about tin is exclusively from the tetrazoles (X, Y = N), while hydrated materials may also contain less symmetrical arrangements (X = N; Y = O). The structure of 1,2,4,5-tetrakis(triethylstannyltetrazolyl)benzene dihydrate has been determined and displays a complex three-dimensional network in which each tetrazole acts as at least a bidentate unit. One molecule of water co-ordinates one of the metal centres while the other is embedded in the lattice as a guest.

Introduction

We have been investigating the structural chemistry of organotin tetrazoles, influenced primarily by the variety of supramolecular lattices which these species generate.¹⁻⁵ In such compounds the metal centre invariably adopts a *trans*-N $_2$ SnC $_3$ geometry with a near-linear N–Sn–N moiety (established both crystallographically and by Mössbauer spectroscopy) thus acting as a rigid connector between multifunctional azoles. The polydentate nature of each tetrazole leads to a wide variety of supramolecular structures, the nature of which appears to be dependent on the hydrocarbon groups bonded to the tin. Thus, while 1,2-(Et $_3$ SnN $_4$ C) $_2\text{C}_6\text{H}_4$ adopts a non-planar layer structure, its *n*-butyl analogue, 1,2-(Bu $_3$ SnN $_4$ C) $_2\text{C}_6\text{H}_4$, exhibits a three-dimensional architecture with pores filled by the hydrocarbon groups.⁴ Other arrangements we have identified include a two-dimensional network of hexamers [1,3,5-(Bu $_3$ SnN $_4$ C) $_3\text{C}_6\text{H}_3$, 1,3,5-(Bu $_3$ SnN $_4$ CCH $_2\text{CH}_2$) $_3\text{CNO}_2$]⁵ and a bilayer structure with channels running in all three directions.³ The latter arises when a flexible alkyl chain is used to link two organotin tetrazoles [1,6-(Bu $_3$ SnN $_4$ C)(CH $_2$) $_6$].

As the number of organometallic tetrazoles inherent in the molecular motif increases so, potentially, does the complexity of the lattice construct. We now report the syntheses of tetrakis(triorganostannyltetrazolyl)-alkanes and -benzenes as a natural extension of our earlier work on systems containing two and three organostannyl tetrazole moieties. The structure of 1,2,4,5-(Et $_3$ SnN $_4$ C) $_4\text{C}_6\text{H}_2\cdot 2\text{H}_2\text{O}$ is presented and is the most complex yet of this family of compounds.

Results and discussion

Synthesis

Six triorganotin-substituted tetra-tetrazoles **1–6** have been synthesized using the well established [3+2] cycloaddition route,² in which a tetranitrile is heated with a slight excess of the appropriate azide under nitrogen in the absence of any solvent (Scheme 1). Reactions usually reached completion at elevated temperatures (100–170 °C) over one hour. The course of the reaction was followed by the disappearance of the IR bands due to the $\nu(\text{N}_3)$ at $\approx 2060\text{ cm}^{-1}$ and $\nu(\text{CN})$ at $\approx 2250\text{ cm}^{-1}$. The crude products in all cases were recrystallised from methanol. Cooling

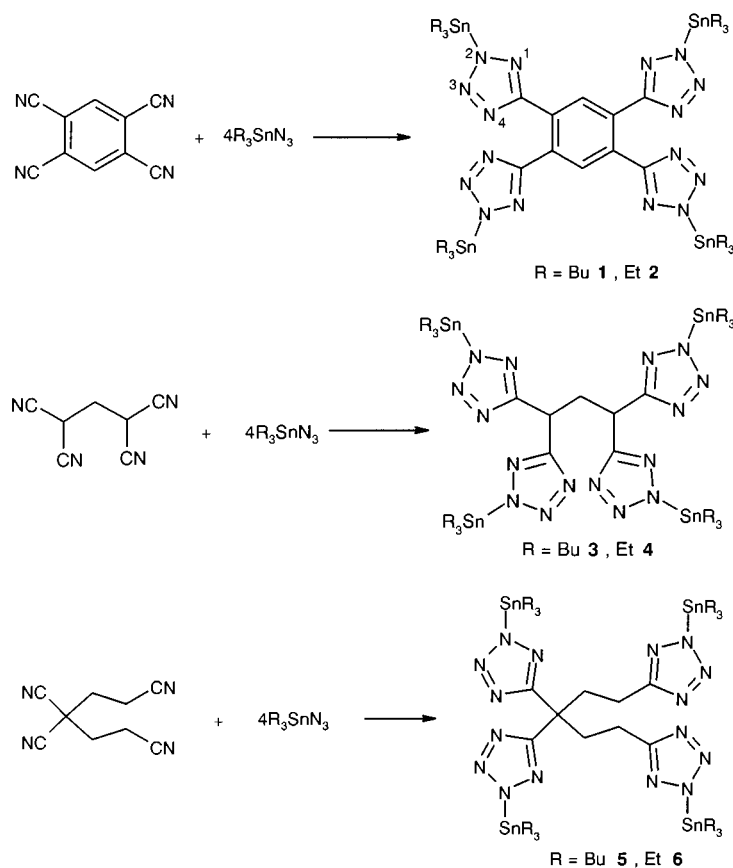
the methanolic solutions gave gummy materials for **1**, **3–6**, which needed trituration with hexane to give the respective products in a powder form. Compound **2** crystallised from methanol as a dihydrate in a form suitable for X-ray crystallography.

Spectroscopy

The ^1H and ^{13}C NMR data for compounds **1–6** are largely unexceptional but confirm the formulations shown in Scheme 1. The ^{13}C NMR spectra of all species clearly show the quaternary carbon of the tetrazole at δ ca. 160 confirming the result of the cycloaddition reaction; $^1J(\text{Sn–C}) \approx 480\text{ Hz}$ fall within the range for five-co-ordinate tin and the semiempirical relationship derived by Holecek and Lycka⁶ for correlating 1J and C–Sn–C angles in butyltin compounds suggests a value of 124° for compounds **1**, **3** and **5**, implying a *trans*-trigonal bipyramidal geometry about the metal centre.

The ^{119}Sn NMR spectra of compounds **1–6** exhibit resonances between δ –40 and –80. In comparison with previous work on organotin-substituted tetrazoles this indicates a five-co-ordinate tin.² For example, the ^{119}Sn chemical shifts of 1,2-[(R $_3$ Sn)N $_4$ C]C $_6\text{H}_4$ (R = Et, Buⁿ or Prⁱ), 1,3-[(R $_3$ Sn)N $_4$ C]C $_6\text{H}_4$ (R = Et or Buⁿ) and 1,4-[(R $_3$ Sn)N $_4$ C]C $_6\text{H}_4$ (R = Buⁿ or Prⁱ) fall within the range of δ –40 to –83 and are to low frequency of four-co-ordinated SnBu $_3$ (NMe $_2$) (δ 36).⁷ The five-co-ordination at tin could be achieved either *via* co-ordination of a solvent molecule (as for previously reported triorganostannyl tetrazoles, highly co-ordinating *d* $_6$ -DMSO was required for dissolution of NMR samples) or *via* formation of an oligomeric species. There is, however, no structural precedent for DMSO co-ordination in the solid state. In addition, the linewidths of the ^{119}Sn resonances are broad (half width at half height, HWHH, ca. 470 Hz). Simple R $_3$ SnN $_4$ CR' species exhibit similar spectral characteristics as a result of migration of the tin around the tetrazole nitrogens.²

The Mössbauer spectra for compounds **1–6** have isomer shifts (i.s.) in the range 1.30–1.55 mm s $^{-1}$ and quadrupole splitting (q.s.) between 3.5 and 3.9 mm s $^{-1}$. The former confirms the +4 oxidation state of the tin atom while the latter points towards a *trans*-trigonal bipyramidal geometry around tin, consistent with the NMR analysis. For comparison, q.s. values of 1,2-[(R $_3$ Sn)N $_4$ C]C $_6\text{H}_4$ (R = Et, Buⁿ or Prⁱ), 1,3-[(R $_3$ Sn)N $_4$ C]C $_6\text{H}_4$



Scheme 1

(R = Et or Buⁿ) and 1,4-[(R₃Sn)NC₄]C₆H₄ (R = Buⁿ or Prⁱ) fall within the narrow range of 3.60–3.86 mm s⁻¹.⁴ The *trans*-trigonal bipyramidal geometry about tin is achieved by axial co-ordination of the tetrazoles, a feature which is common in all published organotin tetrazole structures. Possible exceptions to this may occur, however, in the case of hydrated **2**, **4** and **6**. In these three cases, both *trans*-N₂SnC₃ and *trans*-NOSnC₃ coordinations are possible, the latter arising if the intermolecular N→Sn is replaced by H₂O→Sn, and both are consistent with the Mössbauer data. The quadrupole splittings for both possibilities (N₂SnC₃ vs. NOSnC₃) fall within the same range, e.g. q.s. for crystallographically characterised 1,3-bis(tributylstannyl-tetrazolyl)benzene bis(methanol) is 3.65 mm s⁻¹.⁴ A precedent for simultaneous observation of both tin environments in the same lattice exists in bis(trimethylstannyl)-5,5'-azotetrazole for which similar Mössbauer data have also been recorded (q.s. = 3.90 mm s⁻¹).⁸ Broad linewidths for **5** (*I* = 0.98, 1.07) and **6** (0.83, 1.05 mm s⁻¹) are possibly caused by the asymmetry inherent in the tetratetrazole ligands, which in turn may give rise to a combination of different co-ordination modes between tin and the tetrazole nitrogens, e.g. N¹ + N², N¹ + N³, N¹ + N⁴, etc. (see numbering in Scheme 1).

Crystallography

The asymmetric unit of compound **2** consists of three tins of unit occupancy [Sn(2), Sn(4), Sn(5)], two tins which coincide with inversion centres of half occupancy [Sn(1), Sn(3)], along with two separate ligand halves (Fig. 1). Selected bond lengths and bond angles are given in Table 1. The crystallographic symmetry at the two metal centres [Sn(1), Sn(3)] gives rise to disorder with respect to the attached ethyl groups such that only 2 of 6 β-carbons in these groups could be located with any certainty and refined. The overall structural analysis is in no way compromised by these difficulties.

All tin environments are trigonal bipyramidal with equatorial

ethyl groups. The asymmetric unit contains four *trans*-N₂SnC₃ [Sn(1)–Sn(4)] centres and one *trans*-NOSnC₃ centre [Sn(5)]. Both these trigonal bipyramidal tin environments have been found in previously examined tin tetrazoles and are consistent with the spectroscopic interpretation (see above). The axially ligating atoms for the five tins, the N–Sn–N/N–Sn–O bond angles and the modes of co-ordination of the tetrazole ring with respect to the tins are summarised in Table 1. The seven unique Sn–N bond lengths are essentially equivalent within experimental error and the strength of N–Sn bonding is reflected in the proximity of all the N–Sn–N to 180°. The co-ordination between tetrazole and tin can be described with respect to the metal atom as being either N¹ (see Scheme 1 for numbering; for tin, N¹, N⁴ are equivalent) or N² (N², N³ are similarly equivalent). The versatility of the tetrazole co-ordination is reflected in the occurrence of both N¹ + N² [Sn(2), Sn(4)] and N² + N² [Sn(1), Sn(3)] environments. The N¹ + N² co-ordination mode has been noted previously in 1,2-(Bu₃SnN₄C)₂C₆H₄ while the N² + N² mode has been found in 1,2-(Et₃SnN₄C)₂C₆H₄.⁴

The gross three-dimensional structure of compound **2** (Fig. 2) is complex but can be broadly described in terms of layers. Propagation along *c* takes place primarily through the *trans*-N₂Sn(3) [Sn(3) in the asymmetric unit as presented sits on an inversion centre at 0, 0.5, 0], while propagation along *a* takes place via *trans*-N₂Sn(2) and *trans*-N₂Sn(4). In addition, the lattice is extended in the *b* direction through the influence of the ligands, which are of two distinct types. The ligand based on C(1) (type A) has an inversion centre at the middle of the C₆ ring (0.25, 0.75, 1.0) and is oriented asymmetrically with respect to *b*. The ligand based on C(7) (type B) has a twofold rotation axis through C(7) and C(10) parallel to *b* (0, *y*, 0.25) and is thus symmetrically disposed with respect to this axis. Both ligand types, but particularly those of type A, orchestrate lattice propagation into a third dimension.

The pseudo-five-sided, 28-atom rings visible in Fig. 2 contain

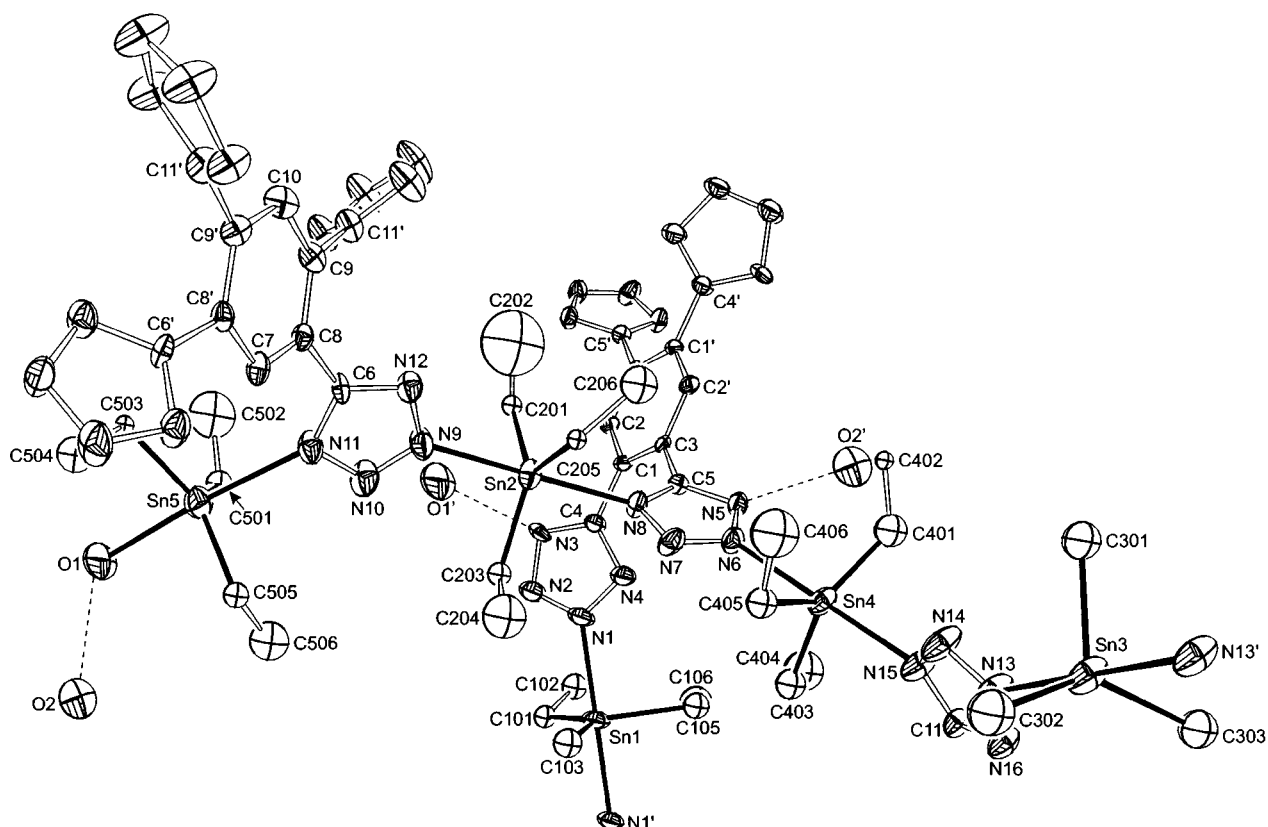
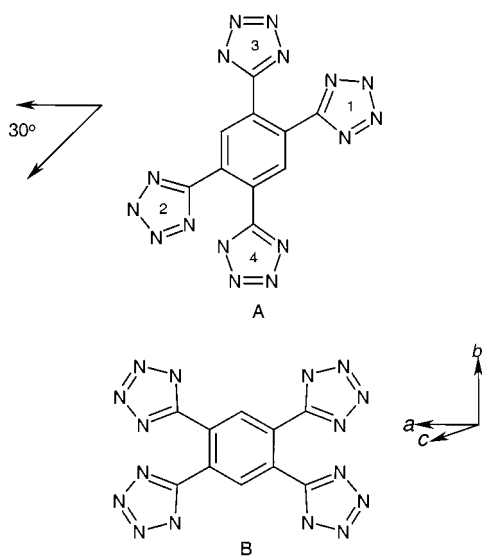


Fig. 1 The asymmetric unit of compound 2, showing the labelling scheme used in the text and Tables. Ellipsoids are at the 30% probability level.



three tin atoms [Sn(2)–Sn(4)] and lie approximately in the *ac* plane. However, these rings are not planar and are tilted with respect to the *b* axis. They can be viewed as starting and finishing at tetrazoles based on C(5) sharing a common phenylene bridge (type A) and are highlighted in orange in Fig. 3. The tetrazoles labelled 1 or 2 on either side of the type A tetrazole are oriented approximately 30° with respect to the *ac*-plane and facilitate the “top to bottom” nature of these rings in the superstructure.

The formation of the three-dimensional lattice is, however, complex as several features contribute to the propagation along *b*. First, there are two distinct types of ligands as described above. Secondly, the spirals associated with Sn(2) and Sn(4), the pseudo four-sided rings (Fig. 2), are not planar but are related by the screw axis at 0.25, *y*, 0.25 which propagates the lattice along *b*. Thirdly, there is a hydrogen-bonding interaction involving water [O(1)] which is co-ordinated to Sn(5) and N(3).

This effectively anchors the position of the two tetrazoles based on C(4) [via the nitrogens not co-ordinating Sn(1)] and generates a new 26-membered centrosymmetric macrocycle (Fig. 3; highlighted in green but sharing some common atoms with the 28-membered ring shown in orange). Finally, the lattice can also be viewed as an interpenetrating network. The pseudo-eight-sided rings comprising of 38 atoms, built from 6 *trans*-N₂Sn units and fragments of two type A and four type B ligands (Fig. 3, blue), have the *trans*-N₂Sn(1) bridge (generated by the inversion centre at 0.25, 0.25, 1.0) involving ligand type A threaded through them.

The hydrogen-bonding interactions discussed above result from an interaction between the water molecule [O(1)] co-ordinated to Sn(5) and N(3) of the lattice neighbour generated by the operation $1 - x, 1 - y, 2 - z$ [O(1)–N(3): 2.65(2) Å]. The distance Sn(5)–O(1) [2.27(1) Å] of compound 2 is comparable to Sn–O of hydrated 1,4-(Bu₃SnN₄C)₂C₆H₄·H₂O [2.368(6) Å].⁹ There is also a second water molecule [O(2)], not co-ordinated to tin but occupying an interstitial guest site within the lattice, which is hydrogen bonded to both O(1) and N(5) of the symmetry related molecule generated by the $0.5 - x, -0.5 + y, z$ transformation [O(2)···O(1) 2.72(2); O(2)···N(5) 2.84(2) Å]. This is the first example of a non-metal bound solvent guest in an organotin tetrazole lattice and suggests other inclusion species can be synthesized more rationally.

Finally, the hierarchy for nitrogen co-ordination within the tetrazole is evident in the behaviour of the four independent heterocycles within the asymmetric unit (Fig. 1). Tetrazoles based on C(6) and C(11) exhibit N¹ + N³ co-ordination (Table 1; see Scheme 1 for numbering), this being the least sterically demanding combination and the one we have most commonly observed in other organotin tetrazole structures. The tetrazole incorporating C(4) also adopts N¹ + N³ co-ordination, with tin bound to N³ (the primary binding site) and the weaker hydrogen bond relegated to the use of N¹. The tridentate tetrazole involving C(5) follows a similar pattern: primary co-ordination to tin using N¹ + N³, followed by the use of N⁴ for the hydrogen bonds. In summary, N¹ + N³ co-ordination imposes the least

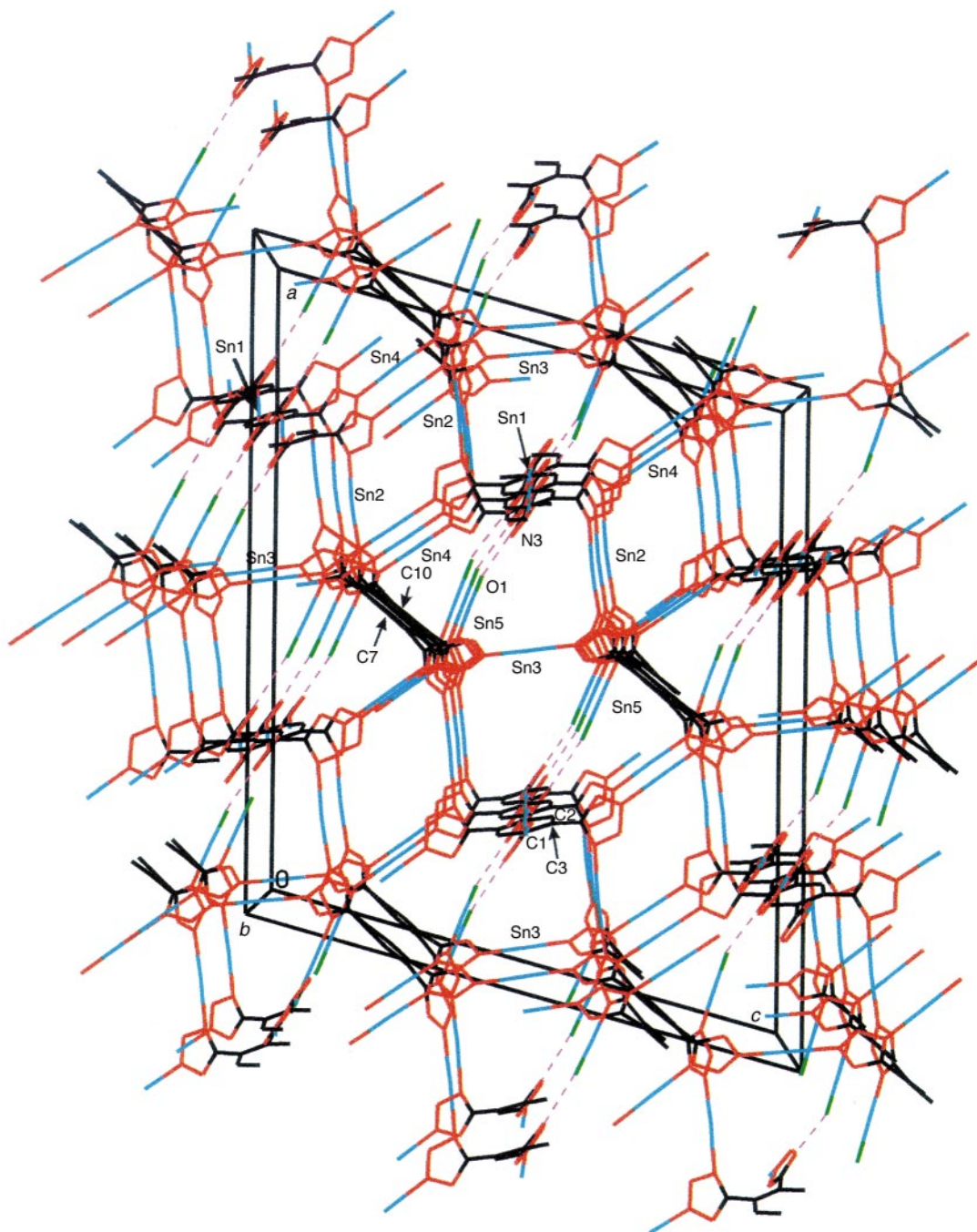


Fig. 2 The unit cell of compound 2 viewed along *b*. Colour code: Sn, blue; C, black; N, orange, O, green. Ethyl groups omitted for clarity.

steric clash between bulky metal centres, and is the primary mode of tetrazole co-ordination. The use of N¹ involves steric clashes with the hydrocarbon group attached to the adjacent carbon but these are less significant than metal–metal interactions which would arise from N² + N³ bonding. Hydrogen bonds are subservient to tin co-ordination and involve N¹, then N⁴, for their formation.

Conclusion

Polyfunctional tetrazoles incorporating four organotin tetrazole units can be synthesized and used to construct complex three-dimensional supramolecular lattice arrangements. The structure of 1,2,4,5-(Et₃SnN₄C)₄C₆H₂·2H₂O has been determined as an example and emphasises the structural versatility of tetrazoles in orchestrating supramolecular architectures. The utility of polytetrazoles in the development of such structures is, however, limited by the increasing lack of solubility which accrues as more tetrazoles are incorporated into the ligands.

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.¹⁰ Isomer shift data are relative to CaSnO₃. For all compounds, infrared spectra were recorded as Nujol mulls on KBr plates and all NMR data were recorded on saturated solutions in DMSO-*d*₆.

Syntheses

The tributyltin and triethyltin azides were prepared by the literature methods.¹¹ The method of Belsky¹² was used to prepare 1,3,3,5-pentatetrazocarbonitrile.¹² All other reagents were of commercial origin (*e.g.* Aldrich) and used without further purification.

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

Table 1 Selected structural data for compound **2**^a

Tin	Sn–N/Å	N–Sn–N/°		Tin co-ordination ^a	Tetrazole	Tetrazole co-ordination ^b
1	Sn(1)–N(1) 2.36(1)	N(1)–Sn(1)–N(1')	180	N ² + N ²	C(4)	N ¹ + N ³ ^c
2	Sn(2)–N(8) 2.43(1) Sn(2)–N(9) 2.37(1)	N(9)–Sn(2)–N(8)	176.3(4)	N ¹ + N ²	C(5)	N ¹ + N ² + N ⁴ ^c
3	Sn(3)–N(13) 2.40(1)	N(13)–Sn(3)–N(13')	180	N ² + N ²	C(6)	N ¹ + N ³
4	Sn(4)–N(6) 2.42(1) Sn(4)–N(15) 2.39(1)	N(6)–Sn(4)–N(15)	179.2(4)	N ¹ + N ²	C(11)	N ¹ + N ³
5 ^d	Sn(5)–N(11) 2.42(1) Sn(5)–O(1) 2.27(1)	N(11)–Sn(5)–O(1)	175.6(5)	N ¹		

^a See Scheme 1 for numbering; with respect to tin, N¹, N⁴ and N², N³ are equivalent pairs. ^b See Scheme 1 for numbering. ^c Atom N¹ involved in hydrogen bonding. ^d Tin co-ordinated to N, O.

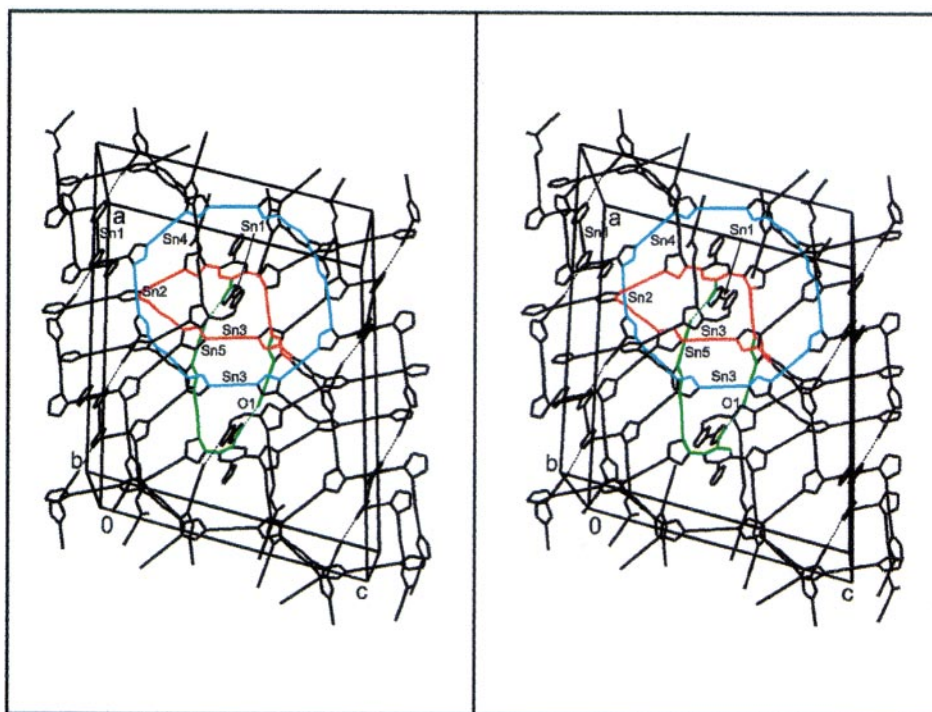


Fig. 3 A stereoscopic view of the unit cell of compound **2** highlighting the formation of 28- (orange), 26- (green) and 38-atom (blue) rings. Ethyl groups omitted for clarity.

screen. None of the tetrazoles synthesized showed any tendency to detonate at temperatures up to their melting points (*ca.* 200 °C).

Syntheses

1,2,4,5-Tetrakis(tributylstannyltetrazolyl)benzene 1. A mixture of tributyltin azide (2.89 g, 8.7 mmol) and 1,2,4,5-tetracyanobenzene (0.39 g, 2.12 mmol) was heated under N₂ at 120 °C for 45 min. The reaction mixture formed a white solid at this temperature, which was then dissolved in hot methanol. Hot filtration afforded a green solution, which on cooling produced a green gum, which was then washed with hexanes to give **1** as a green powder (0.99 g, 30%), mp 210 °C (decomp.) [Found (Calc. for C₂₉H₅₅N₈Sn₂): C, 46.2 (47.2); H, 7.30 (7.20); N, 14.9 (15.1)%]. NMR [(CD₃)₂SO]: ¹H, δ 8.49 (s, 1 H, H³ of C₆H₂), 8.10 (s, 1 H, H⁶ of C₆H₂), 1.45 (m, 24 H, SnCH₂CH₂CH₂CH₃), 1.20–1.30 (m, 48 H, SnCH₂CH₂CH₂CH₃) and 0.77 [m, 36 H, (CH₂)₃CH₃]; ¹³C, δ 159.9 (CN₄), 134.2 (C^{3,6} of C₆H₂), 117.7 (C^{1,2,4,5} of C₆H₂), 27.7 (SnCH₂CH₂CH₂CH₃), 26.5 [Sn(CH₂)₂CH₂CH₃], 18.4 [SnCH₂(CH₂)₂CH₃], 13.5 [(CH₂)₃CH₃], ²J[¹³CH₂–^{117,119}Sn] 77.2 (unresolved), ³J[¹³CH₂–^{117,119}Sn] 28.6 Hz (unresolved); ¹¹⁹Sn, δ –48.6. ^{119m}Sn Mössbauer (mm s^{–1}): i.s. = 1.50; q.s. = 3.67. IR (cm^{–1}, KBr disk): 3406, 2957, 2924, 2872, 2856, 1658, 1618, 1464, 1417, 1377, 1358, 1292, 1217, 1157, 1080, 1047, 1026, 879, 769, 700, 679, 524 and 432.

1,2,4,5-Tetrakis(triethylstannyltetrazolyl)benzene dihydrate 2. A mixture of triethyltin azide (0.92 g, 3.71 mmol) and 1,2,4,5-tetracyanobenzene (0.15 g, 0.84 mmol) was heated under N₂ at 105 °C for 30 min. The reaction mixture formed a white solid at this temperature, which was washed with hexanes and dried *in vacuo*. The resultant white powder, which was partially soluble in methanol, was extracted in this solvent using a Soxhlet apparatus. Hot filtration afforded a clear solution, which on cooling at room temperature produced colourless crystals (0.59 g, 56%), mp 200 °C [Found (Calc. for C₁₇H₃₃N₈OSn₂): C, 33.5 (33.9); H, 5.32 (5.53); N, 17.8 (18.6)%]. NMR [(CD₃)₂SO]: ¹H, δ 8.0 (s, 2 H, H^{3,6} of C₆H₂), 0.8–1.4 (m, 60 H, CH₂CH₃); ¹³C, δ 160.2 (CN₄), 131.1 (C^{3,6} of C₆H₂), 129.3 (C^{1,2,4,5} of C₆H₂), 9.7 (CH₂CH₃), 9.1 (CH₂CH₃), ¹J[¹³C–^{117,119}Sn] 478 (unresolved), ²J[¹³C–^{117,119}Sn] 34.9 Hz (unresolved); ¹¹⁹Sn, δ –43.2. ^{119m}Sn Mössbauer (mm s^{–1}): i.s. = 1.50; q.s. = 3.76. IR (cm^{–1}, KBr disk): 3661, 3061, 2924, 2870, 1637, 1479, 1460, 1427, 1377, 1190, 1074, 1057, 1022, 997, 729, 698, 661, 524 and 447.

1,1,3,3-Tetrakis(tributylstannyltetrazolyl)propane 3. A mixture of tributyltin azide (2.07 g, 6.23 mmol) and 1,1,3,3-tetrapropanecarbonitrile (0.18 g, 1.30 mmol) was heated while stirring under N₂ at 130 °C for half an hour. An orange-brown glass was formed at this temperature, which was dissolved in

hot methanol. Hot filtration resulted in a yellow solution, which, on cooling, gave a yellow gummy substance. The yellow gum, when washed with hexanes, gave compound **3** as a yellow powder (0.43 g, 24%), mp 195 °C [Found (Calc. for $C_{55}H_{112}N_{16}Sn_4$): C, 44.8 (44.0); H, 7.61 (7.58); N, 15.2 (14.9)%]. NMR [(CD₃)₂SO]: ¹H, δ 1.48 (m, 24 H, SnCH₂CH₂CH₂CH₃), 1.2–1.3 (m, 48 H, SnCH₂CH₂CH₂CH₃) and 0.78 [m, 36 H, (CH₂)₃CH₃]; ¹³C, δ 163.0 (CN₄), 27.7 (SnCH₂CH₂CH₂CH₃), 26.4 [Sn(CH₂)₂CH₂CH₃], 18.1 [SnCH₂(CH₂)₂CH₃], 13.5 [(CH₂)₃CH₃], ²J[¹³C–^{117,119}Sn] 76 Hz (unresolved); ¹¹⁹Sn, δ –50.2. ¹¹⁹Sn Mössbauer (mm s⁻¹): i.s. = 1.47; q.s. = 3.65. IR (cm⁻¹, KBr disk): 3420, 2957, 2924, 2872, 2855, 2073, 1653, 1635, 1464, 1377, 1342, 1292, 1155, 1126, 1026, 960, 879, 679 and 611.

1,1,3,3-Tetrakis(triethylstannyltetrazolyl)propane dihydrate **4**.

Prepared as for compound **3** using triethyltin azide (1.83 g, 7.38 mmol) and 1,1,3,3-tetrapropanecarbonitrile (0.26 g, 1.81 mmol). Yellow powder (1.75 g, 80%), mp 205 °C (decomp.) [Found (Calc. for $C_{31}H_{68}N_{16}O_2Sn_4$): C, 31.8 (31.8); H, 5.68 (5.86); N, 19.0 (19.1)%]. NMR [(CD₃)₂SO]: ¹H, δ 1.0–1.3 (m, 60 H, CH₂CH₃); ¹³C, δ 163.5 (CN₄), 10.1 (CH₂CH₃), 10.0 (CH₂CH₃), ¹J[¹³C–^{117,119}Sn] 478 Hz (unresolved); ¹¹⁹Sn, δ –45.1. ¹¹⁹Sn Mössbauer (mm s⁻¹): i.s. = 1.53; q.s. = 3.87. IR (cm⁻¹, KBr disk): 3406, 3182, 2949, 2870, 2735, 1458, 1421, 1379, 1199, 1126, 1016, 956 and 684.

1,3,3,5-Tetrakis(tributylstannyltetrazolyl)pentane **5**.

Prepared as for compound **3** using tributyltin azide (2.13 g, 6.42 mmol) and 1,3,3,5-tetracyanopentane (0.26 g, 1.5 mmol). Yellow powder (1.56 g, 70%), mp 209 °C [Found (Calc. for $C_{57}H_{116}N_{16}Sn_4$): C, 45.6 (44.1); H, 7.73 (7.46); N, 14.9 (14.7)%]. NMR [(CD₃)₂SO]: ¹H, δ 2.50–2.80 [m, 4 H, C(CH₂CH₂)₂], 1.48 (m, 24 H, SnCH₂CH₂CH₂CH₃), 1.20–1.25 (m, 48 H, SnCH₂CH₂CH₂CH₃) and 0.76 [m, 36H, (CH₂)₃CH₃]; ¹³C, δ 160.0 (CN₄), 27.7 (SnCH₂CH₂CH₂CH₃), 26.4 [Sn(CH₂)₂CH₂CH₃], 18.1 [SnCH₂(CH₂)₂CH₃], 13.5 [(CH₂)₃CH₃], ¹J[¹³C–^{117,119}Sn] 476 (unresolved), ²J[¹³C–^{117,119}Sn] 75.4 Hz (unresolved); ¹¹⁹Sn, δ –53.5. ¹¹⁹Sn Mössbauer (mm s⁻¹): i.s. = 1.47; q.s. = 3.59. IR (cm⁻¹, KBr disk): 3387, 2957, 2924, 2872, 2856, 1655, 1589, 1464, 1400, 1377, 1342, 1292, 1251, 1226, 1080, 1049, 1026, 962, 879, 771, 748, 679, 611, 515 and 453.

1,3,3,5-Tetrakis(triethylstannyltetrazolyl)pentane hydrate **6**.

Prepared as for compound **3** using triethyltin azide (1.72 g, 6.9 mmol) and 1,3,3,5-tetracyanopentane (0.25 g, 1.5 mmol). Yellow powder (1.17 g, 68%), mp 206 °C (decomp.) [Found (Calc. for $C_{33}H_{68}N_{16}Sn_4 \cdot H_2O$): C, 33.3 (33.5); H, 5.78 (5.92); N, 19.0 (18.9)%]. NMR [(CD₃)₂SO]: ¹H, δ 1.04–1.50 (m, 60 H, CH₂CH₃) and 2.48–2.55 [m, 4 H, C(CH₂CH₂)₂]; ¹³C, δ 161.5 (CN₄), 121.9 [(CN₄)₂C], 38.2 [(CN₄)₂C(CH₂)₂(CH₂)₂], 21.9 [(CN₄)₂C(CH₂)₂(CH₂)₂], 10.9 [CH₂CH₃], 10.8 (CH₂CH₃), ¹J[¹³C–^{117,119}Sn] 482 Hz (unresolved); ¹¹⁹Sn, δ –51.8. ¹¹⁹Sn Mössbauer (mm s⁻¹): i.s. = 1.43; q.s. = 3.63. IR (cm⁻¹, KBr disk): 2949, 2850, 1637, 1458, 1400, 1196, 1130, 1016, 962 and 682.

X-Ray crystallography

Suitable crystals of 1,2,4,5-tetrakis(triethylstannyltetrazolyl)benzene dihydrate **2** were grown from methanol at room tem-

perature. A crystal of approximate dimensions 0.25 × 0.25 × 0.3 mm was used for data collection.

Crystal data. $C_{34}H_{66}N_{16}O_2Sn_4$, $M = 1205.79$, monoclinic, $a = 30.070(3)$, $b = 14.241(2)$, $c = 25.259(2)$ Å, $\beta = 105.28(1)^\circ$, $U = 10434(2)$ Å³, space group $C2/c$, $Z = 8$, $D_c = 1.535$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.936$ mm⁻¹, $F(000) = 4784$.

Crystallographic measurements were made at 293(2) K on a CAD4 automatic four-circle diffractometer in the range $2.17 < \theta < 23.92^\circ$. Data (8368 reflections) were corrected for Lorentz-polarisation effects and also for linear decay of the crystal during data collection. In the final least squares cycles all Sn, O and N atoms along with carbons 1–11 were allowed to vibrate anisotropically. Ethyl carbons were refined isotropically as a consequence of disorder of these groups which naturally arises from the site symmetry of the associated centres [Sn(1) and Sn(3)]. Associated α -carbons were refined with half site occupancies but only two β -carbons could be reliably located and refined around these two metal centres. Hydrogen atoms were included at calculated positions where relevant on non-disordered ethyl groups. The hydrogen atoms on the water molecules could not be located with any reliability and were not modelled. The solution of the structure (SHELXS 86)¹³ and refinement (SHELXL 93)¹⁴ converged to a conventional [*i.e.* based on 4244 reflections with $F_o > 4\sigma(F_o)$] $R1 = 0.0628$ and $wR2 = 0.1451$. Goodness of fit = 1.043. The maximum and minimum residual densities were 0.944 and –1.086 e Å⁻³ respectively.

CCDC reference number 186/1442.

See <http://www.rsc.org/suppdata/dt/1999/1951/> for crystallographic files in .cif format.

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