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Synthesis of functionalised (triorganostannyl)tetrazoles: supramolecular structures of *n*-[2-(triorganostannyl)tetrazol-5-yl]-pyridine (*n* = 2, 3 or 4)†

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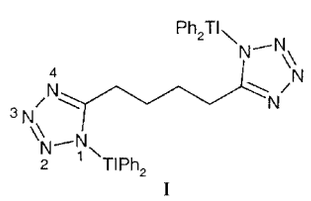
Six pyridine-substituted triorganostannyltetrazoles, *n*-[2-(triorganostannyl)tetrazol-5-yl]pyridine (*n* = 2, 3 or 4; R = Et or Bu), have been synthesized by a cycloaddition method involving R_3SnN_3 and *n*-cyanopyridine. 1,7-Bis[2-{(triorganostannyl)tetrazol-5-yl}phenyl]-1,4,7-trioxaheptane has been synthesized by the cycloaddition of tributyltin azide and 1,7-di(2-cyanophenyl)-1,4,7-trioxaheptane. The crystal structures of 3-$(Et_3SnN_4C)C_5H_4N\cdot H_2O$, 4-$(Et_3SnN_4C)C_5H_4N$ and 4-$(Bu_3SnN_4C)C_5H_4N\cdot 2H_2O$, have been determined. While the first and third are three-dimensional arrays held together by hydrogen bonds, the supramolecular structure of the anhydrous second consists of one-dimensional helical polymers.

Introduction

We have been investigating the structural chemistry of polyfunctional organotin tetrazoles, primarily because of the wide range of supramolecular architectures these species exhibit. The trigonal bipyramidal *trans*-N_2SnC_3 geometry at the tin centre with a near linear N–Sn–N component is universal in all triorgano-substituted tetrazoles known to date, which include organotin derivatives of mono-,[1] bis-,[2] tris-[3] and tetratetrazoles.[4] The supramolecular arrays exhibited by these species are a result of the multidentate nature of the tetrazole ring, in which each of the four ring nitrogens can act as a co-ordination site. This affords a variety of co-ordination modes *e.g.* $N^1 + N^2$, $N^1 + N^3$, $N^1 + N^2 + N^4$, *etc*. In the unique case of the solvated thallium derivative **I**·2MeOH all four ring nitrogens are involved in either metal binding or hydrogen bond formation.[5]



I

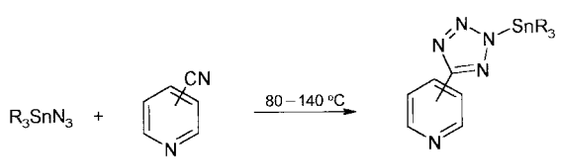
The nature of the hydrocarbon groups on the tin in these systems appears to determine the supramolecular architecture adopted as these groups need to be accommodated within the lattice, thereby generating cavities, channels, *etc*. Our earlier work has described polymeric chains [6-diphenylstannyl-2,3,4,5-tetraazabicyclonona-1,3-diene],[1] two-dimensional zig-zag sheets [1,2-bis{2-(triethylstannyl)tetrazol-5-yl}benzene][6] and three-dimensional arrays [1,2-bis{2-(tributylstannyl)-tetrazol-5-yl}benzene].[6] We have also noted that where the metal–tetrazole interactions provide too restrictive a framework for the hydrocarbon groups, the lattice expands through an additional network of hydrogen bonds generated by solvation [*e.g.* **I**·2MeOH, 1,3-$(Bu_3SnN_4C)_2C_6H_4\cdot 2MeOH$][6] or hydration from atmospheric moisture [*e.g.* 1,4-$(Bu_3SnN_4C)_2$-$C_6H_4\cdot H_2O$].[5]

In relation to possible applications as molecular hosts, we have become interested in the possibility of generating supramolecular arrays which embody additional functional groups capable of further metal complexation within the metallotetrazole framework. Pyridine-substituted tetrazoles were suggestive for this purpose, and we now report the synthesis of such species along with structural studies on three representative examples. A polyether functionalised derivative, 2-$(Bu_3$-$SnN_4C)C_6H_4O(CH_2)_2O(CH_2)_2O(CH_2)_2OC_6H_4(CN_4SnBu_3)$-2′, is also reported.

Results and discussion

Synthesis

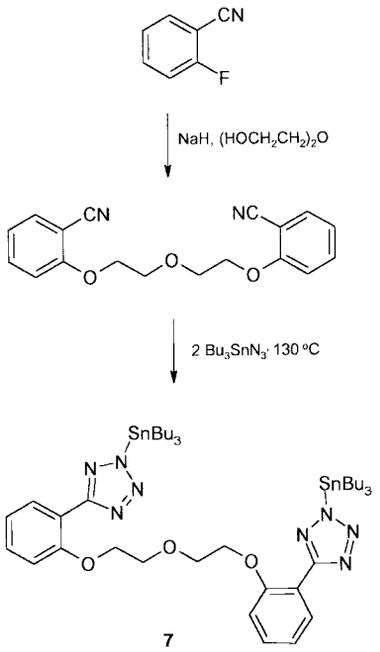
Six triorganotin-substituted 5-pyridyltetrazoles and 1,7-bis-[2-{(triorganostannyl)tetrazol-5-yl}phenyl]-1,4,7-trioxaheptane **1**–**7** have been synthesized (Schemes 1 and 2) using the well established cycloaddition route. The precursor to **7**, 1,7-di-(2-cyanophenyl)-1,4,7-trioxaheptane, was prepared by nucleophilic substitution of cyano-2-fluorobenzene using established methodology.[7] In a typical cycloaddition reaction the functionalised nitrile was heated with a slight excess of the appropriate organotin azide under N_2 in the absence of solvent. Reactions were heated over a temperature range of 80–140 °C for 30 to 60



isomer	2	3	4
R = Et	**1**	**3**	**5**
Bu	**2**	**4**	**6**

Scheme 1

† Electronic supplementary information (ESI) available: stereo-diagrams of unit-cell contents. See http://www.rsc.org/suppdata/dt/a9/a908380d/



Scheme 2

min to attain completion, which was monitored by the disappearance of the IR bands due to $\nu(N_3)$ at ≈2060 cm^{-1} and ν(CN) at ≈2250 cm^{-1}.

The crude products were recrystallised from methanol. Cooling the methanolic solution gave compounds **1**–**4**, **6** as white crystalline solids and **5**, **7** as white powders. Compound **3** has been isolated and crystallographically authenticated as a monohydrate, which is representative of the bulk material on the basis of elemental analysis. Compounds **1** and **6** are less clearly formulated, as the microanalysis data are intermediate between that of anhydrous and hydrated species. Furthermore, the crystal of **6** studied by X-ray diffraction had incorporated two molecules of water. Our previous work has shown that metallated polytetrazoles are prone to such solvation/hydration during crystallisation and it is plausible that a range of hydration levels are present in the bulk samples of these two species.

Spectroscopy

The ^1H and ^{13}C NMR data confirm the structures proposed in Schemes 1 and 2. The ^{13}C NMR spectra of compounds **1**–**7** show the quaternary carbon of the tetrazole ring at approximately δ 160; ^1J(Sn–C) is ≈480 Hz, which indicates a *trans*-trigonal bipyramidal N_2SnC_3 geometry about tin. The semi-empirical relationship derived by Holecek and Lycka [8] for correlating ^1J and angle C–Sn–C in butyltin compounds affords a range of 122–124° for compounds **2**, **4**, **6** and **7** consistent with this geometry. The ^{119}Sn NMR resonances appear in the narrow range of δ −42 to −53 and are comparable with those of other organotin-substituted tetrazoles reported previously.[3,4,6]

Mössbauer spectra for compounds **1**–**7** have isomer shifts (i.s.) in the range 1.43–1.48 mm s^{-1} and quadrupole splittings (q.s.) in the range 3.48–3.77 mm s^{-1}. The former confirms the +4 oxidation state of tin while the latter points towards a *trans*-$XYSnC_3$ trigonal bipyramidal geometry about tin, consistent with all published organotin tetrazole structures. The q.s. value of a related compound, 2-methyl-6-[2-(tributylstannyl)tetrazol-5-yl]pyridine, is 3.69 mm s^{-1}.[9] The geometric arrangement of ligands about tin can be achieved *via trans*-N_2SnC_3 type co-ordination which is also consistent with all organotin tetrazole structures known to date. Possible exceptions may arise in the case of **3**, **6** and **7** where both *trans*-N_2SnC_3 and *trans*-$NOSnC_3$ type co-ordinations are consistent with the Mössbauer data,

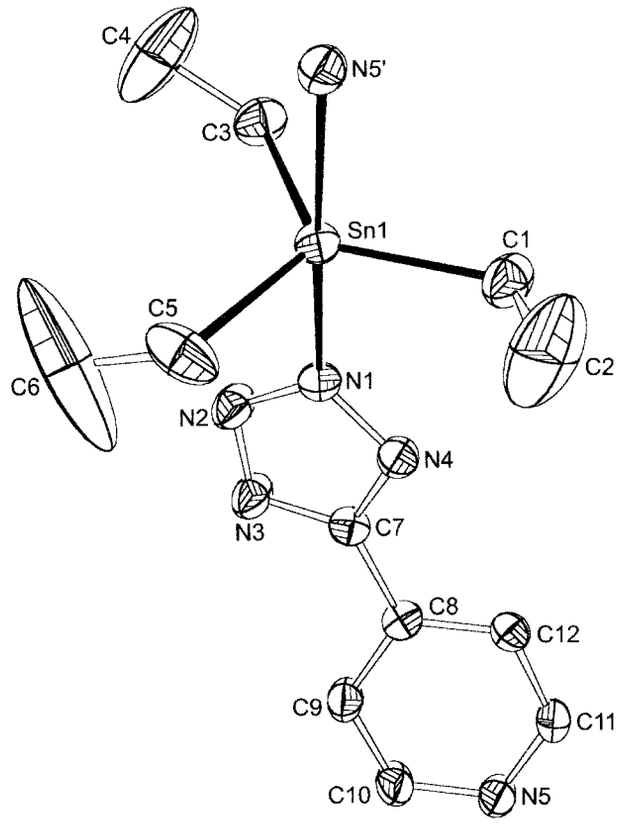


Fig. 1 The asymmetric unit of compound **5** showing the labelling used in the text. Thermal ellipsoids are at the 30% probability level (as in all Figures). Selected metric data: Sn(1)–C(5) 2.129(7), Sn(1)–C(3) 2.133(7), Sn(1)–C(1) 2.141(6), Sn(1)–N(1) 2.344(5) and Sn(1)–N(5′) 2.437(5) Å; C(5)–Sn(1)–C(3) 120.2(3), C(5)–Sn(1)–C(1) 114.8(3), C(3)–Sn(1)–C(1) 125.0(3), C(5)–Sn(1)–N(1) 89.6(3), C(3)–Sn(1)–N(1) 91.1(2), C(1)–Sn(1)–N(1) 90.1(2), C(5)–Sn(1)–N(5′) 91.7(3), C(3)–Sn(1)–N(5′) 89.2(2), C(1)–Sn(1)–N(5′) 88.3(2) and N(1)–Sn(1)–N(5′) 178.2(2)°.

the latter arising if the intermolecular N:→Sn interaction is replaced by H_2O:→Sn or, in the case of **7**, by donation from an ether oxygen. The quadrupole splittings for both possibilities (N_2SnC_3 *vs.* $NOSnC_3$) fall within the same range and thus Mössbauer spectroscopy is not capable of distinguishing between them. A precedent for the simultaneous existence of both tin environments in the same molecule exists in *E*-bis[2-(trimethylstannyl)tetrazol-5-yl]diazene monohydrate, *E*-$(Me_3SnN_4C)N{=}N(CN_4SnMe_3)\cdot H_2O$, for which similar Mössbauer data have been recorded (q.s. = 3.90 mm s^{-1}).[10]

Crystallography

For purposes of description, we number the tetrazole ring nitrogens as 1–4 for comparing the co-ordination mode of the tetrazole (*see* **I**), 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.

Compound 5. Crystals of compound **5** were grown from a dichloromethane solution at room temperature. The asymmetric unit of **5** contains one trigonal bipyramidal *trans*-N_2SnC_3 tin centre (Fig. 1), as found in all previously examined organotin tetrazoles, although in **5** this geometry is obtained in a unique way. Whereas in the previous cases the two nitrogens originate from two tetrazole moieties, in **5** one nitrogen comes from a tetrazole [N(1)] and another one from the pyridyl group [N(5)]. The N(1)–Sn(1)–N(5′) bond angle is close to 180° [178.2(2)°] though the covalent bond to the tetrazole [Sn(1)–N(1): 2.344(5) Å] is marginally stronger than that to the co-

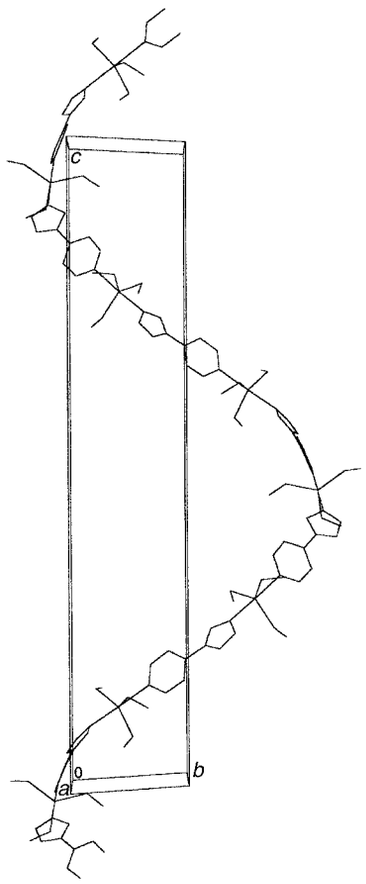


Fig. 2 Helical propagation of compound **5** along *c*.

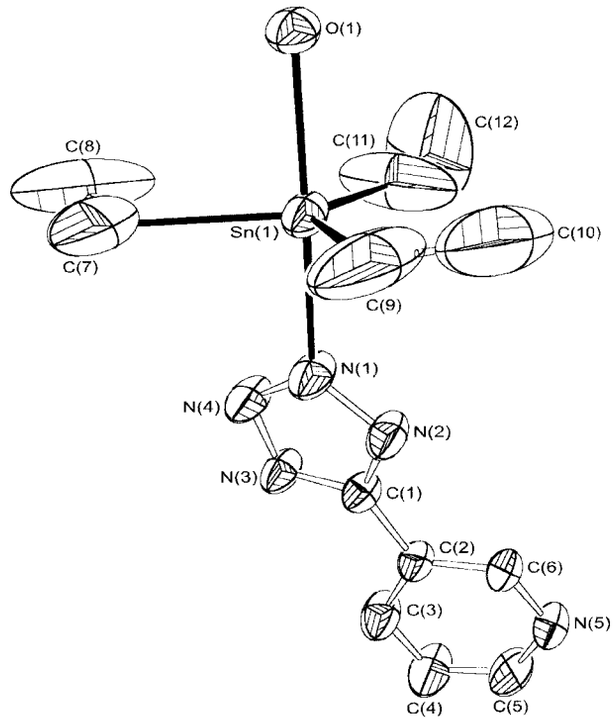


Fig. 3 The asymmetric unit of compound **3** showing the labelling used in the text. Selected metric data: Sn(1)–C(11) 2.02(2), Sn(1)–C(9) 2.23(2), Sn(1)–C(7) 2.240(14), Sn(1)–N(1) 2.333(6) and Sn(1)–O(1) 2.342(4) Å; C(7)–Sn(1)–N(1) 88.8(3), C(11)–Sn(1)–O(1) 88.6(5), C(9)–Sn(1)–O(1) 90.5(4), C(7)–Sn(1)–O(1) 90.0(3), N(1)–Sn(1)–O(1) 177.0(2), N(4)–N(1)–N(2) 112.2(5), C(11)–Sn(1)–C(9) 123.8(12), C(11)–Sn(1)–C(7) 128.2(11), C(9)–Sn(1)–C(7) 108.0(8), C(11)–Sn(1)–N(1) 89.9(5) and C(9)–Sn(1)–N(1) 92.6(4)°.

ordinated pyridine [Sn(1)–N(5′): 2.437(5) Å]. The competition between the pyridyl nitrogen and the tetrazole nitrogen to co-ordinate to tin is finely balanced, though the former has a marginal preference due to its higher basicity (pK_b: 8.6, 9–13, respectively).[11] Parallels can be drawn with diorganotin(IV) derivatives of pyridine carboxylic acids, since tetrazoles are isosteric and of comparable acidity with carboxylic acids.[12] Whereas IR and Mössbauer data for dimethyltin bis(3-pyridinecarboxylate) suggest a polymeric structure with bridging carboxylate groups, analogous data for diphenyltin bis(2-pyridinecarboxylate) suggest enhanced co-ordination to the tin through nitrogen.[13] The tetrazole moiety is monodentate and exhibits co-ordination through the less hindered N^2 site, the most common of the tetrazole bonding modes.

The supramolecular structure of compound **5** is dominated by one-dimensional helical polymers which develop as a consequence of the sixfold screw axis intrinsic to the space group symmetry. Typically, N(5) in the asymmetric unit interacts with Sn(1) of the lattice neighbour generated by $x - y + 1$, $x + 1$, $z + \frac{1}{6}$ and Sn(1) in the asymmetric unit interacts with N(5) of the lattice neighbour generated by $y - 1$, $-x + y$, $z - \frac{1}{6}$. Fig. 2 shows a view of the helical strand along the *c* axis. The long 'pitch' of the helix (40 Å) is due to the near-linear nature of the pyridyltetrazole moiety as a result of which only mild bending is possible.

Compound 3. Crystals of compound **3** were grown from a methanolic solution at room temperature and, in contrast to **5**, form as a monohydrate. The asymmetric unit (Fig. 3) contains a trigonal bipyramidal *trans*-$NOSnC_3$ centre which has been noted previously in 1,3-$(Bu_3SnN_4C)_2C_6H_4$·2MeOH and 1,2,4,5-$(Et_3SnN_4C)_4C_6H_2$·$2H_2O$.[4] The axial positions about Sn(1) are occupied by N(1) the tetrazole [Sn(1)–N(1): 2.333(6) Å] and O(1) of the water molecule [Sn(1)–O(1): 2.342(4) Å] at distances similar to those found in 1,2,4,5-$(Et_3SnN_4C)_4C_6H_2$·$2H_2O$ [Sn–N: 2.37(1)–2.43(1); Sn–O: 2.27(1) Å];[4] N(1)–Sn(1)–O(1) [177.0(2)°] is close to 180°.

The co-ordinated water molecule generates a number of intermolecular hydrogen-bonding interactions. In the molecule as shown in Fig. 3, H(1A) bonds to N(3) of the lattice neighbour generated by the transformation $-x$, $0.5 + y$, z [O(1)···N(3) 2.76(3) Å; O(1)–H(1A)–N(3) 172(6)°] and H(1B) bonds to the pyridine nitrogen N(5) after transformation by $0.5 + x$, $0.5 - y$, $0.5 + z$ [O(1)···N(5) 2.76(3) Å; O(1)–H(1B)–N(5) 173(3)°]. The O–N distances are comparable with those observed in 1,2,4,5-tetrakis[2-(triethylstannyl)tetrazol-5-yl]-benzene dihydrate [O(1)···N(3) 2.65(2) Å].[4] Fig. 4 depicts the overall view of the structure. Hydrogen bonding interaction involving H(1A) of the water and N(3) of the tetrazole results in the formation of a polymeric chain running parallel to *b* with pendant pyridine moieties. The hydrogen bonding interaction between the remaining hydrogen [H(1B)] and the pyridyl nitrogen N(5) further links these chains to generate an interpenetrating 3-D network. This arises due to the disposition of alternate pyridyl groups away from the polymeric chain which propagate the network in both the *a* and *c* directions (Fig. 4). The network can also be described as a series of interconnected spirals, analogous, though not identical, to the structure of **5**. The spirals in **3** do not consist of a number of repeat molecular units as in **5**, but a repeat unit of py–tet–Sn–O–tet–py–O–tet–Sn–O now involving the co-ordinated water. The number of atoms defining the pitch of the two structures is smaller in **3** (23, including hydrogens) than in **5** (48), the greater curvature (shorter pitch) being introduced into the structure of **3** as a result of the disposition of nitrogen within the pyridyl ring (3 *vs.* 4 isomer) and the tetrahedral angle at oxygen.

Taking into account both co-ordination to tin and hydrogen bonding, the tetrazole is bidentate and exhibits the commonly occurring $N^1 + N^3$ mode of co-ordination in which the less sterically hindered N^3 site is used first to bind the metal with N^1

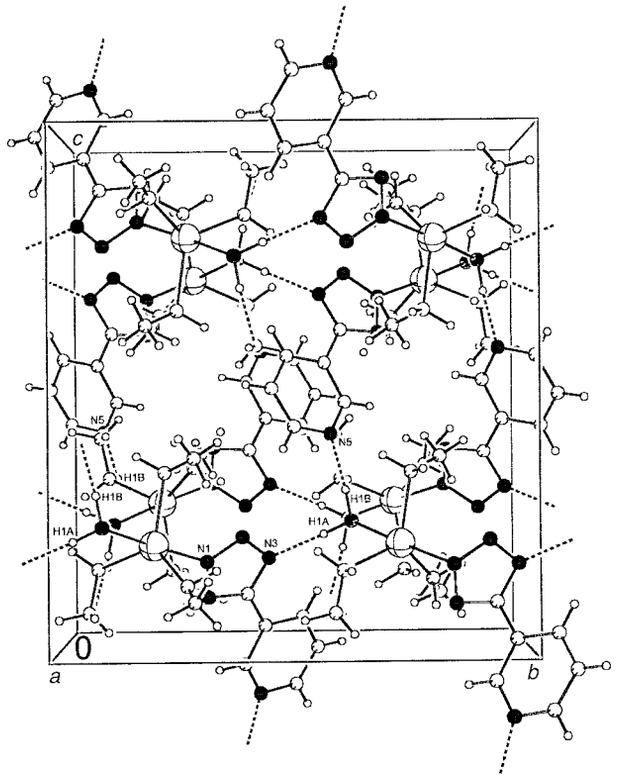


Fig. 4 The unit cell of compound **3** viewed along *a*.

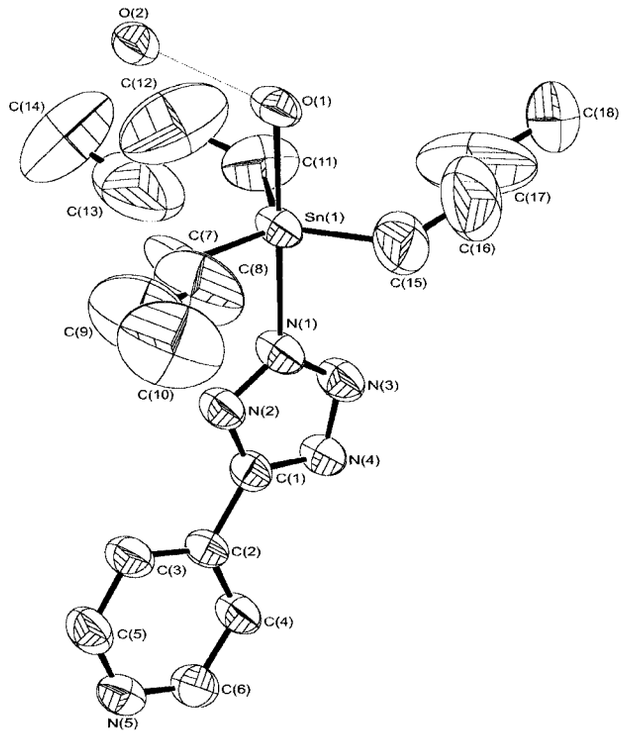


Fig. 5 The asymmetric unit of compound **6** showing the labelling used in the text. Selected metric data: Sn(1)–C(15) 2.091(12), Sn(1)–C(7) 2.103(9), Sn(1)–C(11) 2.105(14), Sn(1)–O(1) 2.340(5) and Sn(1)–N(1) 2.360(6) Å; C(15)–Sn(1)–C(7) 124.0(7), C(15)–Sn(1)–C(11) 115.2(7), C(7)–Sn(1)–C(11) 120.8(7), C(15)–Sn(1)–O(1) 89.3(4), C(7)–Sn(1)–O(1) 86.1(3), C(11)–Sn(1)–O(1) 92.1(5), C(15)–Sn(1)–N(1) 90.5(4), C(7)–Sn(1)–N(1) 91.4(3), C(11)–Sn(1)–N(1) 90.8(5) and O(1)–Sn(1)–N(1) 176.9(2)°.

subsequently used as the next available site for hydrogen bonding. These themes have been discussed elsewhere.[4]

Compound 6. On slow evaporation of a methanolic solution of compound **6** at room temperature, crystals were obtained of **6**·2H_2O. The asymmetric unit of **6** is shown in Fig. 5 and contains a trigonal bipyramidal *trans*-$NOSnC_3$ centre, as in the case of **3**. The co-ordination sphere about tin is analogous to that in **3**·H_2O and the N(1)–Sn(1)–O(1) bond angle is identical within error [176.9(2)°]; other key bond lengths are equally consistent between the two structures [Sn(1)–N(1): 2.360(6); Sn(1)–O(1): 2.340(5) Å].

As in compound **3**, hydrogen bonding dominates the intermolecular interactions inherent in the lattice of **6**, to form a structure which is closely related to that of the former. Again, the co-ordinated water O(1) hydrogen bonds to the pyridyl nitrogen N(5), generated by the symmetry operator $-1 + x$, $0.5 - y$, $-0.5 + z$ (Fig. 6) to form a molecular chain running approximately in the *a* direction. We have noted in our earlier studies the importance of the three alkyl groups bonded to tin in determining the overall lattice structure, as these need to be incorporated as hydrophobic domains within the tin–tetrazole framework. In essence, these groups act as templates around which the lattice is constructed. Although the change in form of the pyridyl moiety to the 4-isomer allows a spacial extension of the hydrogen-bonded network (and hence room to accommodate the alkyl groups) it is evidently insufficient to cope with the increased size of groups bonded to tin (**6**, Bu; **3**, Et). Thus, instead of O(1) hydrogen bonding directly with a neighbouring tetrazole as in **3**, a second water of crystallisation [O(2)] is incorporated which sits between O(1) and the tetrazole N(4), generated by the symmetry operator x, $0.5 - y$, $-0.5 + z$, thus enlarging the cavity size appropriately. The irregular manner in which the butyl groups are arranged in the cavities is manifest in the large thermal ellipsoids evident in Fig. 5, and is consistent with other organotin tetrazole structures. The sheet-like arrays in Fig. 6 are further linked into a three-dimensional network by hydrogen bonds between O(2) and N(3) of the lattice neighbour generated *via* the operator $1 - x$, $-0.5 + y$, $1.5 - z$. Bond

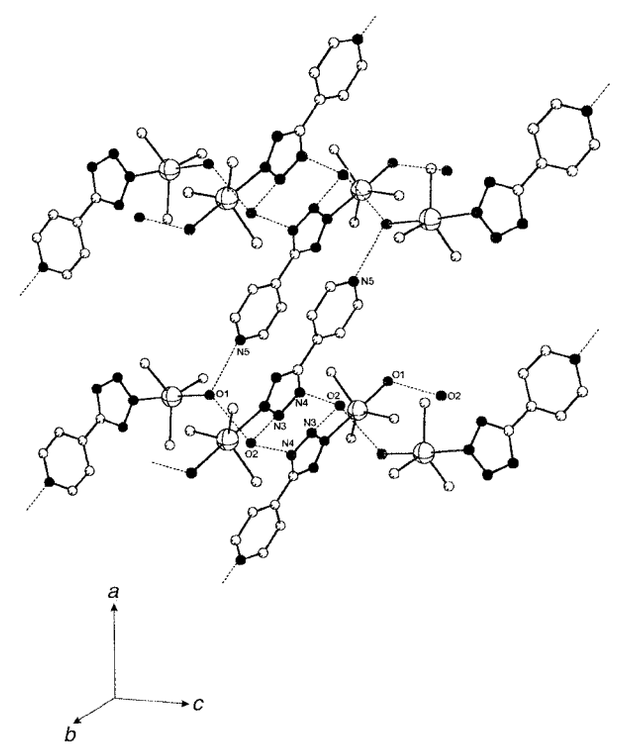
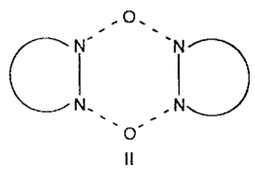


Fig. 6 Hydrogen bonding interactions in compound **6**.

lengths for the O···N interactions [O(1)···N(5′) 2.760(8); O(1)···O(2) 2.694(7) Å; O(2)···N(4′) 2.831(8) Å; O(2)···N(3′) 2.923(8) Å] are similar to the ones seen in **3**. Unlike **3**, however, the network in **6** is continuous and not made up of two interlocking components.

The lattice thus described incorporates one other notable feature: a six-membered ON_2ON_2 ring (**II**, dotted lines represent hydrogen bonds) analogous to a TlN_2TlN_2 heterocycle which is ubiquitous in the organothallium tetrazole structures we have studied to date.[5] Interestingly, the O(2) · · · N(3,4) distances are at the midpoint of the range of Tl–N separations (2.5–3.1 Å) which we have observed.



II

The composite co-ordination mode of the tetrazole ring in compound **6**, tridentate $N^1 + N^2 + N^3$, is unique and has not previously been reported. Another tridentate mode of co-ordination is, however, known and is of the type $N^1 + N^2 + N^4$, *e.g.* $[Rh_3(\mu_3\text{-}CN_4)(\mu\text{-}Cl)Cl(cod)_2(CO)_2]$,[14] $[Rh_3(\mu_3\text{-}CN_4)(\mu\text{-}Cl)\text{-}Cl(CO)_6]$,[14] $[Ag(NO_3)(1,5\text{-pmtta})_2]_2$ (pmtta = pentamethylenetetrazole)[15] and $[M\{H_2B(CHN_4)_2\}_2(H_2O)_2]\cdot 2H_2O$.[16]

Conclusion

The structures of three pyridyl-functionalised organotin tetrazoles have shown (i) that if pendant functionalities are to be embodied into an organotin tetrazole lattice then the functional group must be a weaker donor than the tetrazole otherwise it is involved in lattice construction and (ii) the nature of the lattice, including levels of solvation/ancillary hydrogen bonding, is fundamentally related to the spacial demands of the hydrocarbon groups bonded to tin and their templating effect.

Experimental

Spectra were recorded on the following instruments: JEOL GX270, Bruker AC270, AC400 (^{1}H, ^{13}C, NMR), JEOL GX400 (^{119}Sn NMR), Perkin-Elmer 599B (IR). Details of our Mössbauer spectrometer and related procedures are given elsewhere.[17] Isomer shift data are relative to $CaSnO_3$. For all compounds, infrared spectra were recorded as KBr discs and all NMR data on saturated solutions in $(CD_3)_2SO$, unless indicated otherwise.

Tributyltin azide, triethyltin azide and trimethyltin azide were prepared by literature procedures.[18] All other chemicals were obtained commercially (*e.g.* Aldrich) 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

2-[2-(Triethylstannyl)tetrazol-5-yl]pyridine 1. A mixture of triethyltin azide (2.25 g, 9.07 mmol) and 2-cyanopyridine (0.94 g, 9.038 mmol) was heated at 140 °C for 30 min under N_2. It was subsequently cooled to room temperature at which point it solidified into a colourless glass. The work-up of the reaction was similar to that for compound **2**. Compound **1** was obtained as colourless crystals (2.39 g, 75%) [Found (Calc. for $C_{12}H_{19}\text{-}N_5Sn$): C, 39.8 (40.9); H, 5.39 (5.45); N, 18.9 (19.9)%]. ^{1}H NMR: δ 8.70 (d, 1 H, *6*-C_5H_4N; ^3J 4.0), 8.13 (d, 1 H, *3*-C_5H_4N; ^3J 7.9), 7.93 (m, 1 H, *4*-C_5H_4N), 7.44 (ddd, 1 H, *5*-C_5H_4N; $^{3,3}J$ 7.8, 4.0 Hz), 0.8–1.4 (m, 15 H, CH_2CH_3). ^{13}C NMR: δ 160.7 (CN_4), 149.2 (*2*-C_5H_4N), 148.0 (*6*-C_5H_4N), 137.4 (*4*-C_5H_4N), 124.0 (*3*-C_5H_4N), 121.9 (*5*-C_5H_4N), 10.9 (CH_2CH_3) and 10.2 (CH_2CH_3), $^1J[^{13}C\text{–}^{117,119}Sn]$ 478, 500; $^2J[^{13}C\text{–}^{117,119}Sn]$ 33 Hz (unresolved). ^{119}Sn NMR: δ −42.0. IR (cm^{-1}, KBr disk): 3049, 2972, 2945, 2866, 1595, 1452, 1425, 1375, 1149, 1020, 995, 958, 800, 744, 734, 717, 679, 528 and 515. ^{119m}Sn Mössbauer (mm s^{-1}): i.s. = 1.48; q.s. = 3.77.

2-[2-(Tributylstannyl)tetrazol-5-yl]pyridine 2. Tributylin azide (4.66 g, 14 mmol) and 2-cyanopyridine (1.46 g, 14 mmol) were heated at 110 °C in a flask under N_2 for 30 min at which point a clear solution was obtained. As the reaction mixture was cooled to room temperature it formed into a white solid which was dissolved in hot methanol and filtered hot. The resultant colourless solution gave colourless crystals of compound **2** on cooling (4.91 g, 80%), mp 106–108 °C [Found (Calc. for $C_{18}H_{31}N_5Sn$): C, 49.1 (49.5); H, 7.00 (7.18); N, 15.8 (16.1)%]. ^{1}H NMR: δ 8.65 (d, 1 H, *6*-C_5H_4N; ^3J 4.4), 8.08 (d, 1 H, *3*-C_5H_4N; ^3J 7.8), 7.91 (m, 1 H, *4*-C_5H_4N), 7.42 (ddd, 1 H, *5*-C_5H_4N; $^{3,3,4}J$ 7.8, 4.4, 1.2 Hz), 1.45 (m, 6 H, $SnCH_2\text{-}CH_2CH_2CH_3$), 1.16–1.36 (m, 12 H, $SnCH_2CH_2CH_2CH_3$) and 0.79 [m, 9 H, $(CH_2)_3CH_3$]. ^{13}C NMR: δ 160.9 (CN_4), 149.2 (*2*-C_5H_4N), 148.2 (*6*-C_5H_4N), 137.2 (*4*-C_5H_4N), 123.9 (*3*-C_5H_4N), 121.9 (*5*-C_5H_4N), 27.7 ($SnCH_2CH_2CH_2CH_3$), 26.3 [$Sn(CH_2)_2CH_2CH_3$], 18.9 [$SnCH_2(CH_2)_2CH_3$] and 13.5 [$(CH_2)_3CH_3$], $^1J[^{13}C\text{–}^{117,119}Sn]$ 461, 484, $^2J[^{13}C\text{–}^{117,119}Sn]$ 27 (unresolved), $^3J[^{13}C\text{–}^{117,119}Sn]$ 79 Hz (unresolved). ^{119}Sn NMR: δ −46.1. IR (cm^{-1}, KBr disk): 3053, 2955, 2922, 2870, 2853, 1979, 1948, 1919, 1595, 1572, 1482, 1454, 1425, 1375, 1278, 1149, 742, 733 and 679. ^{119m}Sn Mössbauer (mm s^{-1}): i.s. = 1.47; q.s. = 3.75.

3-[2-(Triethylstannyl)tetrazol-5-yl]pyridine hydrate 3. A mixture of triethyltin azide (2.22 g, 8.95 mmol) and 3-cyanopyridine (0.93 g, 8.94 mmol) was taken in a flask under N_2 and heated at 140 °C for 30 min. The reaction mixture was cooled to room temperature at which point it solidified into a colourless glass. This was dissolved in hot methanol. Hot filtration afforded a colourless solution, which on cooling gave colourless crystals (2.64 g, 84%), mp 181 °C (decomp.) [Found (Calc. for $C_{12}H_{21}\text{-}N_5OSn$): C, 38.6 (38.9); H, 5.56 (5.73); N, 18.0 (18.9)%]. ^{1}H NMR: δ 9.21 (d, 1 H, *2*-C_5H_4N; ^4J 1.5), 8.59 (dd, 1 H, *6*-C_5H_4N; $^{3,4}J$ 4.7, 1.8), 8.34 (m, 1 H, *4*-C_5H_4N), 7.49 (ddd, 1 H, *5*-C_5H_4N; $^{3,3}J$ 7.9, 4.7 Hz) and 0.9–1.4 (m, 15 H, CH_2CH_3). ^{13}C NMR: δ 160.0 (CN_4), 149.5 (*2*-C_5H_4N), 147.0 (*6*-C_5H_4N), 133.3 (*4*-C_5H_4N), 126.0 (*3*-C_5H_4N), 124.2 (*5*-C_5H_4N), 10.2 (CH_2CH_3) and 10.2 (CH_2CH_3), $^1J[^{13}C\text{–}^{117,119}Sn]$ 496 Hz (unresolved). ^{119}Sn NMR: δ 48.3. IR (cm^{-1}, KBr disk): 2966, 2870, 1604, 1581, 1454, 1429, 1377, 1363, 1192, 1159, 1142, 1012, 962, 815, 752, 707, 636, 688 and 530. ^{119m}Sn Mössbauer (mm s^{-1}): i.s. = 1.45; q.s. = 3.63.

3-[2-(Tributylstannyl)tetrazol-5-yl]pyridine 4. A mixture of tributylin azide (2.41 g, 7.25 mmol) and 3-cyanopyridine (0.75 g, 7.21 mmol) was heated at 110 °C for 30 min in a flask under N_2 at which point a clear solution was obtained. As the reaction mixture was cooled to room temperature it formed into a white solid which was dissolved in hot methanol. Hot filtration gave a colourless solution, and on cooling colourless crystals of compound **3** (1.92 g, 61%), mp 91–93 °C [Found (Calc. for $C_{18}H_{31}\text{-}N_5Sn$): C, 49.1 (49.5); H, 7.19 (7.18); N, 15.5 (16.0)%]. ^{1}H NMR: δ 9.19 (d, 1 H, *2*-C_5H_4N; ^4J 1.2), 8.63 (dd, 1 H, *6*-C_5H_4N; $^{3,4}J$ 4.7, 1.8), 8.32 (ddd, 1 H, *4*-C_5H_4N; $^{3,4,4}J$ 7,9, 1.8, 1.2), 7.53 (dd, 1 H, *5*-C_5H_4N; ^3J 7.9, 4.7 Hz), 1.56 (m, 6 H, $SnCH_2CH_2\text{-}CH_2CH_3$), 1.29 (m, 12 H, $SnCH_2CH_2CH_2CH_3$) and 0.81 [m, 9 H, $(CH_2)_3CH_3$]. ^{13}C NMR: δ 160.0 (CN_4), 149.5 (*2*-C_5H_4N), 147.0 (*6*-C_5H_4N), 133.3 (*4*-C_5H_4N), 126.0 (*3*-C_5H_4N), 124.2 (*5*-C_5H_4N), 27.6 ($SnCH_2CH_2CH_2CH_3$), 26.3 [$Sn(CH_2)_2CH_2\text{-}CH_3$], 18.3 [$SnCH_2(CH_2)_2CH_3$] and 13.5 [$(CH_2)_3CH_3$], $^1J[^{13}C\text{–}^{117,119}Sn]$ 478 (unresolved), $^2J[^{13}C\text{–}^{117,119}Sn]$ 29 (unresolved), $^3J[^{13}C\text{–}^{117,119}Sn]$ 77 Hz (unresolved). ^{119}Sn NMR: δ −52.1. IR (cm^{-1}, KBr disk): 3080, 2955, 2922, 2870, 2863, 1583, 1464, 1427, 1186, 1082, 1055, 1008, 752, 709, 682 and 640. ^{119m}Sn Mössbauer (mm s^{-1}): i.s. = 1.46; q.s. = 3.53.

Table 1 Crystal data and structure refinement details for compounds **3**, **5** and **6**

	3	**5**	**6**
Empirical formula	$C_{12}H_{21}N_5OSn$	$C_{12}H_{19}N_5Sn$	$C_{18}H_{35}N_5O_2Sn$
Formula weight	370.03	352.01	472.20
T/K	293(2)	293(2)	293(2)
Space group	*Pbna* (no. 60)	$P6_1$	$P2_1/c$
Crystal symmetry	Orthorhombic	Hexagonal	Monoclinic
a/Å	13.781(2)	8.263(1)	10.120(2)
b/Å	14.764(2)	8.263(1)	14.269(2)
c/Å	16.227(3)	38.991(6)	16.788(3)
β/°			101.31(2)
V/Å^3	3301.6(9)	2305.5(5)	2377.1(7)
Z	8	6	4
μ/mm^{-1}	1.549	1.655	1.094
Reflections collected	2589	3933	3953
Independent reflections	2589 [*R*(int) = 0.0000]	1226 [*R*(int) = 0.0287]	3722 [*R*(int) = 0.0290]
Final *R*1, *wR*2			
[$I > 2\sigma(I)$]	0.0450, 0.1097	0.0188, 0.0426	0.0492, 0.1080
(all data)	0.0797, 0.1351	0.0284, 0.0467	0.1165, 0.1420
Absolute structure parameter		−0.02(4)	

4-[2-(Triethylstannyl)tetrazol-5-yl]pyridine 5. A mixture of triethyltin azide (3.33 g, 13.4 mmol) and 4-cyanopyridine (1.38 g, 13.3 mmol) was taken in a three-necked flask under N_2 and heated at 105 °C for one hour. The resultant white solid was dissolved in hot methanol. Hot filtration afforded a colourless solution, which on cooling gave a white powder (4.1 g, 88%), mp 178 °C (decomp.) [Found (Calc. for $C_{12}H_{19}N_5Sn$): C, 40.7 (40.9); H, 5.43 (5.39); N, 19.9 (19.9)%]. ^{1}H NMR: δ 8.70 (dd, m, *2,6*-C_5H_4N; ^3J 6), 8.00 (dd, 2 H, *3,5*-C_5H_4N; ^3J 6 Hz) and 0.8–1.5 (m, 15 H, CH_2CH_3). ^{13}C NMR: δ 160.5 (CN_4), 150.2 (*2,6*-C_5H_4N), 137.2 (*4*-C_5H_4N), 120.4 (*3,5*-C_5H_4N), 10.1 (CH_2CH_3) and 10.1 (CH_2CH_3). ^{119}Sn NMR: δ −50.9. IR (cm^{-1}, KBr disk): 2947, 2866, 1618, 1558, 1446, 1429, 1377, 1215, 1194, 1165, 1128, 1043, 1005, 956, 848, 758, 711, 682 and 534. ^{119m}Sn Mössbauer (mm s^{-1}): i.s. = 1.48; q.s. = 3.58.

4-[2-(Tributylstannyl)tetrazol-5-yl]pyridine 6. A mixture of tributyltin azide (2.30 g, 6.93 mmol) and 4-cyanopyridine (0.64 g, 6.15 mmol) in a three-necked flask under N_2 was heated while stirring at 80 °C for half an hour. The reaction mixture solidified at this temperature into a white solid, which was dissolved in boiling methanol. Hot filtration afforded a colourless solution, which, on cooling, gave compound **6** as a white crystalline solid (1.42 g, 47%), mp 134–136 °C [Found (Calc. for $C_{18}H_{31}N_5Sn$): C, 48.6 (49.5); H, 7.30 (7.11); N, 14.1 (16.0)%]. ^{1}H NMR: δ 8.70 (dd, 2 H, *2,6*-C_5H_4N, ^3J 6), 7.90 (dd, 2 H, *3,5*-C_5H_4N, ^3J 6 Hz), 1.58 (m, 6 H, $SnCH_2CH_2CH_2CH_3$), 1.31 (m, 12 H, $SnCH_2CH_2CH_2CH_3$) and 0.84 [m, 9 H, $(CH_2)_3CH_3$]. ^{13}C NMR: δ 160.4 (CN_4), 150.3 (*3,5*-C_5H_4N), 137.2 (*4*-C_5H_4N), 120.2 (*2,6*-C_5H_4), 27.7 ($SnCH_2CH_2CH_2CH_3$), 26.4 [$Sn(CH_2)_2CH_2CH_3$], 18.5 [$SnCH_2(CH_2)_2CH_3$] and 13.5 [$(CH_2)_3CH_3$]; ^1J[^{13}C–^{117,119}Sn] 466 (unresolved); ^3J[^{13}C–^{117,119}Sn] 74 Hz (unresolved). ^{119}Sn NMR: δ −49.4. IR (cm^{-1}, KBr disk): 2957, 2067, 1614, 1427, 1416, 1375, 1217, 1167, 1080, 1003, 962, 879, 841, 754 and 706. ^{119m}Sn Mössbauer (mm s^{-1}): i.s. = 1.43; q.s. = 3.48.

1,7-Di(2-cyanophenyl)-1,4,7-trioxaheptane. To a stirring mixture of NaH (0.53 g, 22 mmol) in dry THF (10 ml) was added a solution of diethylene glycol (0.95 ml, 10 mmol) in dry THF (5 ml). The mixture was allowed to stir at 0 °C for 30 min then to warm to room temperature whereupon a solution of 2-fluorobenzonitrile (2.13 ml, 20 mmol) in dry THF (5 ml) was added dropwise over a period of 30 min. The mixture was heated to 70 °C and allowed to reflux for 24 h under a N_2 atmosphere. After 24 h TLC (Merck glass plates, Keiselgel 60F254; eluent, 1:1 light petroleum–ethyl acetate, permanganate stain) confirmed that the starting material had completely been consumed. The mixture was then quenched with MeOH (20 ml) and water (20 ml) to destroy any remaining NaH. The product was extracted with ethyl acetate (3 × 30 ml), the organic phase washed with brine (2 × 20 ml), dried over $MgSO_4$ and evaporated to yield the crude product. Purification by flash chromatography (Merck silica gel, 230–400 mesh, eluent 1:1 light petroleum–ethyl acetate, R_f 0.64) afforded (2.06 g, 67%) of a white crystalline solid, mp = 77–79 °C [Found (Calc. for $C_{18}H_{16}NO_3$): C, 69.4 (70.1), H, 5.27 (5.24), N, 8.83 (9.08)%]. ^{1}H NMR ($CDCl_3$): δ 7.52 (4 H, m, CH), 7.02 (4 H, m, CH), 4.25 (4 H, m, OCH_2) and 4.07 (4 H, m, OCH_2). ^{13}C NMR ($CDCl_3$): δ 160.0 (*1*-C_6H_4), 133.9, 133.2 (*3,5*-C_6H_4), 120.5 (*4*-C_6H_4), 115.9 (CN), 112.1 (*6*-C_6H_4), 101.7 (*2*-C_6H_4), 69.3 (CH_2) and 68.5 (CH_2). IR (Nujol mull, cm^{-1}): 2800 (aliphatic CH), 2222 (CN) and 1430 (C–O).

1,7-Bis[2-{(triorganostannyl)tetrazol-5-yl}phenyl]-1,4,7-trioxaheptane 7. A mixture of tributyltin azide (1.60 g, 4.82 mmol) and 1,7-di(2-cyanophenyl)-1,4,7-trioxaheptane (0.50 g, 1.62 mmol) was heated at 130 °C for 30 min under N_2. On cooling to room temperature the reaction mixture solidified into a colourless glass. The reaction was worked up similarly to that of compound **2**. The product was collected as a white powder (1.0 g, 98%), mp 160–163 °C [Found (Calc. for $C_{18}H_{16}N_8O_3Sn_2$): C, 52.8 (51.9); H, 7.36 (7.20); N, 11.5 (11.5)%]. ^{1}H NMR: δ 7.54 (1 H, dd, *3*-C_6H_4, $^{3,4}J$ 7.5, 1.7), 7.38 (1 H, m, *5*-C_6H_4), 7.06 (2 H, m, *4*-C_6H_4, *6*-C_6H_4), 4.08 (t, 4 H, OCH_2CH_2O, ^3J 4.8), 3.70 (t, 4 H, OCH_2CH_2O, ^3J 4.8 Hz), 1.50 (12 H, m, $SnCH_2CH_2CH_2CH_3$), 1.25 (24 H, m, $SnCH_2CH_2CH_2CH_3$) and 0.80 [24 H, m, $(CH_2)_3CH_3$]. ^{13}C NMR: δ 159.3 (CN_4), 156.4 (*1*-C_6H_4), 130.6 (*3*-C_6H_4), 130.2 (*5*-C_6H_4), 120.8 (*4*-C_6H_4), 120.2 (*6*-C_6H_4), 114.1 (*2*-C_6H_4), 69.2 (OCH_2CH_2O), 68.6 (OCH_2CH_2O), 27.7 ($SnCH_2CH_2CH_2CH_2$), 26.5 ($SnCH_2CH_2CH_2CH_2$), 18.3 [$SnCH_2(CH_2)_2CH_3$] and 13.6 [$(CH_2)_3CH_3$], ^1J[^{13}C–^{117,119}Sn] 470 (unresolved), ^2J[^{13}C–^{117,119}Sn] 28 (unresolved), ^3J[^{13}C–^{117,119}Sn] 77 Hz (unresolved). ^{119}Sn NMR: δ −53.0. IR (cm^{-1}, KBr disk): 3414, 2959, 2670, 2229, 2066, 1612, 1522, 1466, 1450, 1433, 1342, 1284, 1255, 1223, 1147, 1126, 1103, 1057, 1026, 1014, 752 and 680. ^{119m}Sm Mössbauer (mm s^{-1}): i.s. = 1.47; q.s. = 3.72.

X-Ray crystallography

Experimental and crystallographic details relating to the structure determinations of compounds **3**·H_2O, **5**, and **6**·2H_2O are given in Table 1.

Compound 3·H_2O. Data were corrected for Lorentz-polarisation but not for absorption. In the final least squares

cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant except for H(1A) and H(1B) in the ligated water molecule. These protons were located and refined at a fixed distance of 0.98 Å from the parent atom, O(1).

Compound 5. Data were corrected for Lorentz-polarisation but not for absorption. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant.

Compound 6·2H$_2$O. Data were corrected for Lorentz-polarisation and 28% linear decay in the X-ray beam. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant on carbon atoms. The hydrogens of the water molecule could not be located and hence were not included in the refinement.

CCDC reference number 186/1798.

See http://www.rsc.org/suppdata/dt/a9/a908380d/ for crystallographic files in .cif format.

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