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New supramolecular architectures based on polyfunctional organotin tetrazoles: synthesis and characterisation of phenylene-bridged bis(organotin tetrazoles)†

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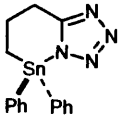
Seven bis(organostannyltetrazoles), $R_3SnN_4C–X–CN_4SnR_3$ (R = Et, Bu or Pr^i; X = 1,2-, 1,3- or 1,4-C_6H_4), have been synthesised by a cycloaddition reaction involving SnR_3N_3 and NC–X–CN. All of the products formed incorporate a *trans*-N_2SnC_3 stereochemistry about tin, though the co-ordination mode of the tetrazole has been found to vary in the combinations of ligating nitrogen atoms used. The crystal structure of 1,3-(2-$Bu_3SnN_4C)_2C_6H_4$·2MeOH showed that the preferred co-ordination site for tin on the tetrazole is the less-hindered N^2 position. The crystal structures of 1,2-(2-$Et_3SnN_4C)_2C_6H_4$ and 1,2-(2-$Bu_3SnN_4C)_2C_6H_4$, respectively showed that these compounds are either two- or three-dimensional supramolecular arrays, the arrangements of which are dictated by the organic groups on tin.

We have been interested in cycloaddition reactions of organotin azides, using both RNCS[1] and RCN[2,3] as dipolarophiles. In the latter case we have shown that the organotin tetrazoles that are produced are fluxional with respect to the bonding of tin to the heterocycle, and that the organotin moiety enhances the nucleophilicity of the ring towards pendant electrophiles. We have published the structure of the bicyclic species **I**, which, like all the known organotin tetrazoles,[4] adopts a *trans*-N_2SnC_3 stereochemistry about tin. Compound **I**, however, is the only crystallographically characterised organotin tetrazole, the structures of these compounds in general being inferred from spectroscopic data.[4,5] The structural chemistry of the organotin tetrazoles is thus still unresolved with regard to the favoured location of tin on the tetrazole ring (N^1 *vs.* N^2) in non-cyclic species, a situation complicated by several possible combinations of bridging, bidentate co-ordination chemistry for the ligand, *viz.* $N^1 + N^2$, $N^1 + N^3$, $N^1 + N^4$ and $N^2 + N^3$ (see **II** for numbering scheme used in connection with tetrazole co-ordination; note that from a structural point of view positions 1 and 4 are equivalent, as are 2 and 3, thus only N^1 and N^2 are used in the following text to describe the co-ordination of tin with respect to the heterocycle). Surprisingly few metallotetrazole crystal structures deal with bidentate behaviour,[6] though of the four possibilities above, all but the $N^1 + N^3$ combination have been observed. The remaining modes are exemplified by $AgNO_3$·2(1,5-pmtta) ($N^1 + N^2$; pmtta = pentamethylenetetrazole),[7] **I** ($N^1 + N^4$)[3] and $[Mn_2(CO)_6(N_4CCF_3)_3]^-$ ($N^2 + N^3$).[8]

Historically, interest in tetrazoles has been stimulated by their application in agricultural preparations and explosives and the realisation that the tetrazole subunit, with comparable acidity yet increased metabolic stability, could function as a carboxylic acid isostere. Analogues of amino acids and many other natural carboxylic acids have been synthesised and tetrazole-containing compounds have been employed as anti-allergic, -inflammatory and -convulsant agents. For example, pentamethylenetetrazole (Metrazole) is used as a stimulant for the central nervous system and to counteract the effects of barbiturate overdose. Detailed reviews of the chemistry of tetrazoles are available.[9,10] We now initiate a series of reports on an entirely new area of tetrazole chemistry, namely their ability to form supramolecular assemblies. The renaissance of co-ordination chemistry over the last half-decade has been largely due to the use of intermolecular metal–ligand interactions to generate lattice structures of tailored design.[11] The more favoured approach in this area is to use a polyvalent metal as the centre about which the lattice grows in two- or three-dimensions, with the metal centres linked by relatively rigid interconnects. This approach is preferred since the co-ordination number of a metal is a more versatile variable than the denticity of a ligand, and is exemplified by, for example, $Cd(CN)_2$-based frameworks.[12] Organometallic fragments, including tin, have been used as the rigid linking groups in such formulations, *e.g.* $[NBu^n_4][SnEt_3]_2[Cu(CN)_4]$,[13] but compounds in which the lattice construction is controlled by the ligand alone are much less common. In organotin tetrazoles the linear N–Sn–N array which is universally adopted is available to act as the linking group, which we now utilise in conjunction with ligands containing more than one multidentate tetrazole function. This paper deals with compounds containing two tetrazoles, both bearing organotin residues and linked by a rigid C_6H_4 group. Our work compliments a recent paper concerning a one-dimensional sodium co-ordination polymer which also incorporates a tetrazole moiety.[14]



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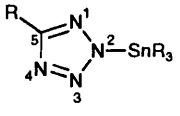


II

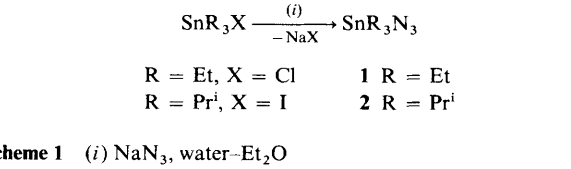
Results and Discussion

Synthesis and reactivity

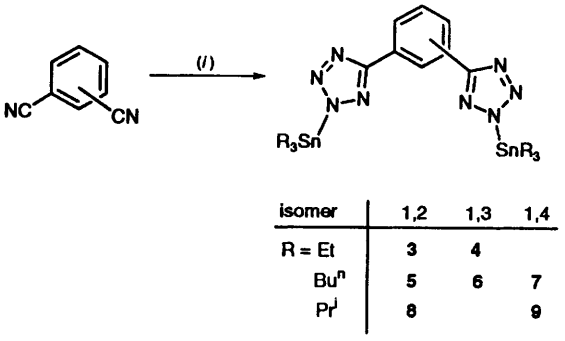
Organotin azides SnR_3N_3 (R = Bu, Et **1** or Pr^i **2**) were synthesised by literature methods (Scheme 1).[15,16] Compounds **1** and **2** are previously unreported, while to our knowledge $SnBu_3N_3$ has hitherto remained spectroscopically uncharacterised.

Seven 5,5′-phenylenebis(trialkylstannyltetrazoles) have been synthesised (Scheme 2) following established methodology[3,5] in which a triorganotin azide is heated with a slight excess of the chosen bis(nitrile) either neat or, in the case of **4**, in refluxing mesitylene. It was found that in most cases the reaction had

† *Non-SI unit employed:* mmHg ≈ 133 Pa.



Scheme 1 (*i*) NaN_3, water–Et_2O



isomer	1,2	1,3	1,4
R = Et	3	4	
Bu^n	5	6	7
Pr^i	8		9

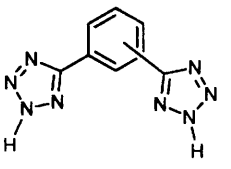
Scheme 2 (*i*) Heat, $2SnR_3N_3$

reached completion after less than 1 h, using temperatures in the range 100–190 °C. The extent of reaction was easily monitored by the disappearance of the IR bands due to ν(CN) at *ca.* 2250 cm^{-1} and $\nu_{asym}(N_3)$ at *ca.* 2060 cm^{-1}. The crude solid products were purified by recrystallisation from methanol, though some difficulty was encountered due to the low solubility of some of them, presumably because of their self-associated nature. The tributyltin derivative **6** crystallises from methanol as a bis-solvated adduct, which readily loses solvent on mild heating under vacuum to yield an amorphous, anhydrous material, and the spectroscopic data in Table 1 refer to this unsolvated form.

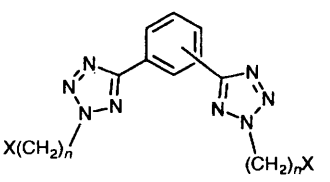
Organotin tetrazoles **3**–**9** all undergo the expected cleavage of the Sn–N bond on reaction with HCl to give protonated species **III**, and with bromoalkanes $Br(CH_2)_nX$ (X = Br or CN) to give functionalised tetrazoles **IV**. We will report fully on the structural characterisation of these compounds and their reaction chemistry in a subsequent publication.[17]

Spectroscopy

The IR [ν(N_3) 2066 and 2062 cm^{-1}] and ^{119}Sn chemical shifts (δ 79.4 and 43.8) for compound **1** and **2** compare well with data for the known compound $SnBu_3N_3$ (2060 cm^{-1}, δ 73.5) but are reported here for the first time. The ^1H and ^{13}C NMR spectra of all the tetrazole compounds studied are consistent with the proposed formulations, though structural inferences are complicated by the need to use Me_2SO as solvent due to the generally low solubility of the products. Thus, any co-ordination expansion could arise from bonding of either the tetrazole or the solvent to tin. The data presented in Table 1 could therefore reflect 1:1 or higher Me_2SO adducts (analogous to **6**·2MeOH) rather than the situation found in the solid state for **3** and **5**. Where spectra of sufficient signal-to-noise ratio allowed $^1J(^{13}C–^{119}Sn)$ coupling constants to be measured these were all over 450 Hz, implying a co-ordination number of >4 about tin.[18] Use of the semiempirical relationship derived by Holecek and Lycka[19] for correlating ^1J data and C–Sn–C angles suggests a value of 123.2° for the latter, consistent with a *trans*-N_2SnC_3 arrangement. The enhanced co-ordination about tin is further borne out by the ^{119}Sn NMR data where the chemical shifts (*ca.* δ −40 to −83, Table 1) are to low frequency of, for example, four-co-ordinated $SnBu_3(NMe_2)$ (δ 36).[20] In addition, the ^{119}Sn NMR signals of **3**–**9** at 25 °C are broad, typically 650 Hz at half-height, and parallel the spectra of fluxional organotin tetrazoles which we have studied previously.[3] Similar fluxional behaviour has been noted



III



IV

Table 1 Tin-119 NMR[a] and Mössbauer[b] data

Compound	δ(^{119}Sn)	i.s.	q.s.
1	79.4[c]	1.47	3.60
2	43.8[c]	1.27	3.39
3	−47.1	1.48	3.86
4	−49.8	1.50	3.82
5	−70.5	1.41	3.60
6	−54.0	1.41	3.65
7	−55.0	1.43	3.73
8	−81.3	1.55	3.73
9	−82.2	1.53	3.64

[a] All spectra recorded in $(CD_3)_2SO$ at 25 °C unless indicated otherwise; shifts in ppm relative to $SnMe_4$. [b] Data collected at 78 K and are given in mm s^{-1}. [c] In $CDCl_3$ solution.

previously for certain platinum tetrazoles[21] and recently *via* a ^{15}N NMR study of analogous cobalt systems.[22] Older quantum-mechanical calculations have shown that N^1 and N^2 binding are essentially energetically equivalent.[23]

The Mössbauer data for the triorganotin-substituted bis(tetrazoles) (Table 1) reveal quadrupole splittings in the range 3.60–3.86 mm s^{-1}, which are also consistent with a *trans*-C_3SnN_2 trigonal-bipyramidal co-ordination sphere about tin. The only way this can occur is through intermolecular N–Sn interactions, a tendency supported by previous structural investigations[3] and the solution-state ^{119}Sn NMR data reported above. That this is even the case for the sterically hindered triisopropyltin compounds indicates the strength and invariance of this interaction.

Crystal structures

The structural analysis of this family of compounds has proved difficult, partly due to the tendency for many of the samples to crystallise as twins but primarily due to the disordered nature of the molecules. As will be discussed subsequently, the packing arrangements adopted by compounds of this type are dictated by the alkyl groups on tin, which have to be accommodated in the cavities generated by the tin–tetrazole arrays. This process inevitably leads to a disordering of these alkyl groups within the lattice, a problem which proved particularly acute for **5**, and to a lesser extent for **6**·2MeOH. However, our prime objective in these crystal structure determinations was to identify the lattice structure adopted, and despite the low quality of some of the data the supramolecular frameworks have been unambiguously authenticated.

Compound 6·2MeOH. The asymmetric unit of **6**·2MeOH, showing the geometry about tin, is illustrated in Fig. 1. The large ellipsoids for the equatorial carbon atoms of the butyl groups are representative of some disorder in the crystal despite data collection at low temperature, but do not affect interpretation of the gross structure. Atomic coordinates are given in Table 2, selected bond lengths and angles are given in Table 3.

Fig. 1 shows that compound **6** crystallises from methanol as a solvated adduct, each metal co-ordinating one molecule of methanol through oxygen to provide axial substituents in what

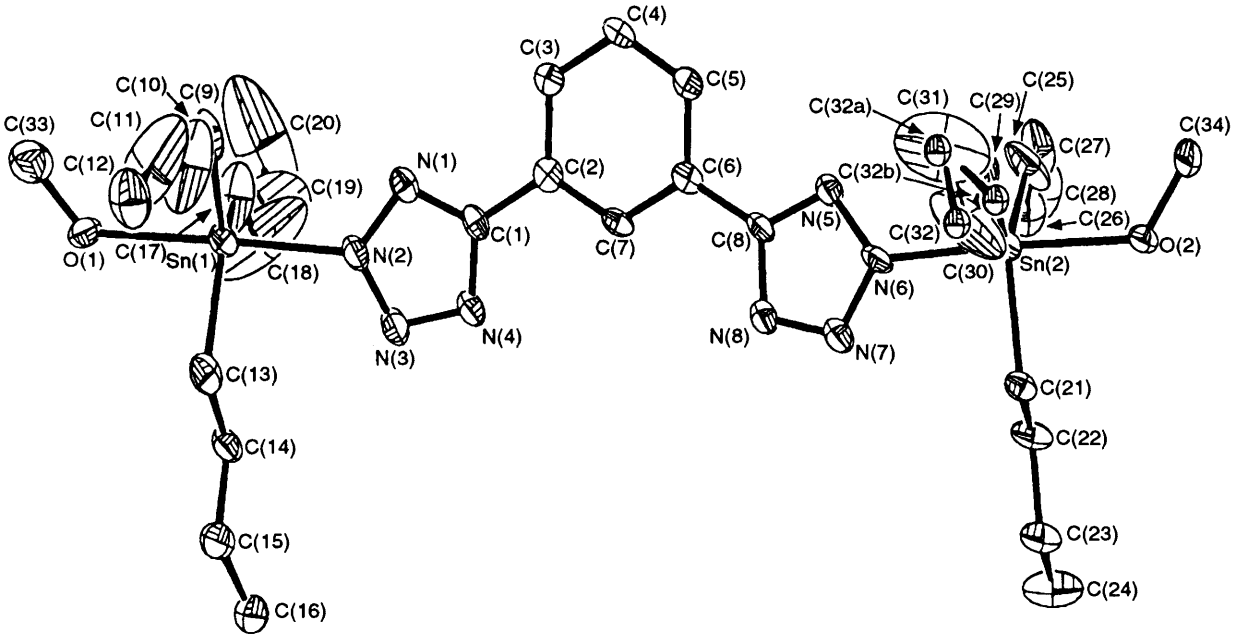


Fig. 1 The asymmetric unit of compound **6**·2MeOH showing the atomic labelling used

Table 2 Fractional atomic coordinates ($\times 10^4$) for compound **6**·2MeOH

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn(1)	2 717.8(4)	2 286(1)	1 699.6(4)	C(13)	2 338(6)	1 629(9)	2 649(6)
Sn(2)	−2 856(1)	9 825(1)	1 725.1(4)	C(14)	2 650(7)	2 156(8)	3 309(5)
O(1)	3 735(4)	9 98(6)	1 639(4)	C(15)	2 322(7)	1 687(10)	3 971(6)
O(2)	−3 883(4)	11 098(5)	1 645(3)	C(16)	2 517(8)	2 300(10)	4 639(6)
N(1)	1 467(5)	4 079(6)	1 268(4)	C(17)	3 741(9)	3 289(12)	1 600(10)
N(2)	1 800(5)	3 562(6)	1 801(5)	C(18)	3 982(15)	3 818(20)	2 006(13)
N(3)	1 614(6)	3 955(7)	2 405(5)	C(19)	4 678(17)	4 554(21)	1 904(17)
N(4)	1 127(5)	4 741(6)	2 272(4)	C(20)	5 064(18)	4 755(24)	1 487(21)
N(5)	−1 441(5)	8 277(7)	1 326(5)	C(21)	−3 162(6)	9 690(8)	2 794(5)
N(6)	−1 914(6)	8 581(7)	1 836(5)	C(22)	−2 611(6)	10 263(9)	3 307(4)
N(7)	−1 785(6)	8 052(8)	2 417(5)	C(23)	−2 872(7)	10 129(9)	4 062(5)
N(8)	−1 206(6)	7 383(7)	2 280(4)	C(24)	−2 349(9)	10 678(12)	4 585(6)
C(1)	1 053(6)	4 802(8)	1 580(6)	C(25)	−2 007(8)	10 830(12)	1 302(8)
C(2)	579(6)	5 581(7)	1 214(5)	C(26)	−1 404(8)	11 281(9)	1 787(8)
C(3)	637(6)	5 707(7)	489(5)	C(27)	−791(8)	11 958(11)	1 429(8)
C(4)	185(6)	6 449(8)	140(5)	C(28)	−189(9)	12 420(12)	1 891(9)
C(5)	−351(6)	7 040(7)	519(5)	C(29)	−3 581(10)	9 010(10)	990(6)
C(6)	−418(6)	6 914(8)	1 235(5)	C(30)	−4 073(16)	8 277(14)	1 231(10)
C(7)	46(6)	6 192(7)	1 577(5)	C(31)	−4 574(23)	7 766(24)	610(13)
C(8)	−1 009(7)	7 541(8)	1 607(5)	C(32)	−522(3)	724(4)	84(3)
C(9)	2 185(7)	1 741(8)	742(6)	C(32A)	−495(2)	718(3)	42(2)
C(10)	1 563(11)	947(14)	797(13)	C(32B)	−523(3)	781(4)	92(2)
C(11)	1 394(17)	220(14)	792(17)	C(33)	4 008(8)	453(11)	1 068(6)
C(12)	777(9)	−590(10)	837(8)	C(34)	−3 998(8)	11 737(8)	1 054(5)

Table 3 Bond lengths (Å) and angles (°) for compound **6**·2MeOH

O(1)–Sn(1)	2.398(9)	N(2)–Sn(1)	2.28(1)
C(9)–Sn(1)	2.14(1)	C(13)–Sn(1)	2.12(1)
C(17)–Sn(1)	2.16(2)	C(25)–Sn(2)	2.11(1)
O(2)–Sn(2)	2.393(9)	N(6)–Sn(2)	2.27(1)
C(21)–Sn(2)	2.12(1)	C(29)–Sn(2)	2.12(2)
N(2)–Sn(1)–O(1)	176.6(3)	C(9)–Sn(1)–O(1)	89.3(4)
C(9)–Sn(1)–N(2)	93.8(5)	C(13)–Sn(1)–O(1)	87.9(4)
C(13)–Sn(1)–N(2)	91.6(5)	C(13)–Sn(1)–C(9)	118.1(6)
C(17)–Sn(1)–O(1)	84.0(6)	C(17)–Sn(1)–N(2)	93.6(6)
C(17)–Sn(1)–C(9)	116.1(7)	C(17)–Sn(1)–C(13)	125.0(7)
N(6)–Sn(2)–O(2)	177.5(3)	C(29)–Sn(2)–C(25)	115.9(7)
C(21)–Sn(2)–O(2)	86.6(4)	C(21)–Sn(2)–N(6)	91.3(4)
C(25)–Sn(2)–O(2)	89.7(5)	C(25)–Sn(2)–N(6)	92.6(5)
C(25)–Sn(2)–C(21)	126.5(6)	C(29)–Sn(2)–O(2)	86.3(4)
C(29)–Sn(2)–N(6)	93.4(5)	C(29)–Sn(2)–C(21)	117.0(6)
C(33)–O(1)–Sn(1)	130.3(7)	C(34)–O(2)–Sn(2)	123.8(7)

are two marginally distorted *trans*-$NOSnC_3$ trigonal-bipyramidal tin sites [N(2)–Sn(1)–O(1) 176.6(3), N(6)–Sn(2)–O(2) 177.5(3)°]. The second axial sites are provided by the N^2 nitrogens [N(2) and N(6) of Fig. 1] of the respective tetrazole rings. This is the first example of an organotin tetrazole which is not a co-ordination polymer, the methanol solvate effectively blocking the development of such an array. Furthermore, this structure allows us to determine the preferred location of the tin on the tetrazole ring (without the complication of having both intra- and inter-molecular tin–tetrazole bonds about the same metal centre) and thus confirms the original assertion of Kozima *et al.*[5] that tin is covalently attached to the less sterically hindered site. Both N^1 and N^2 modes of metal co-ordination are known for C^5-substituted tetrazoles, as is isomerism between the two.[24] However, steric factors particularly favour N^2 co-ordination where the ring substituent

Table 4 Comparative Sn–N bond lengths (Å) for compounds **3**, **5**, **6**·2MeOH and related species

Compound*	Co-ordination number	*d*(Sn–N)/Å Intramolecular	Intermolecular	Ref.
6·2MeOH	5	2.28(1), 2.27(1)	—	This work
3	5	2.354(6), 2.364(6)	2.553(7), 2.415(9)	This work
5	5	2.24(5)–2.42(5)	2.44(7)–2.47(6)	This work
$Ph_2Sn(CH_2)_3CN_4$	5	2.339	2.371	3
$SnMe_3N_3$	5	2.390	2.390	26
$SnMe_3N_3{\cdot}SnMe_3(OH)$	5	2.442	2.612	27
$SnMe_3(NCN)$	5	2.470	2.470	28
$Sn(C_6H_{11})_3(tz)$	5	2.290	2.350	29
$Sn(CH{=}CH_2)_2Cl_2(Hpz)_2$	6	2.322	—	30
$SnMe_2Cl_2(Him)_2$	6	2.312	—	31
$[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2Sn(N_3)_2]$	4	2.158	—	32

* tz = Triazolyl, Hpz = pyrazole, Him = imidazole.

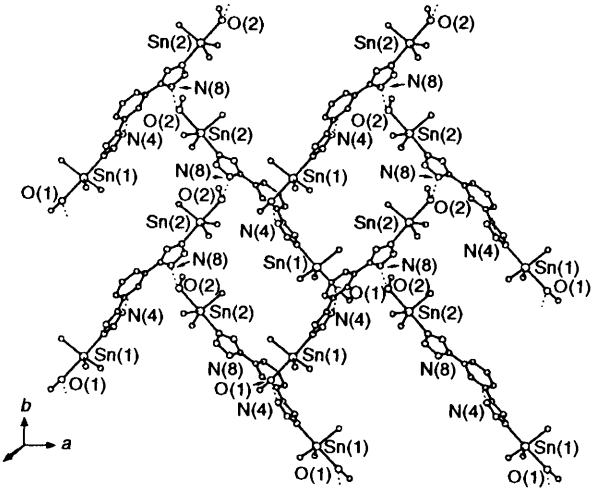


Fig. 2 The lattice structure of compound **6**·2MeOH viewed perpendicular to the *ab* plane. Dotted lines represent hydrogen bonds

is large or if the metal co-ordination site is crowded. For example, in the case of a tetrazole-substituted indium(III) porphyrin,[25] N^2 substitution is enforced because of the need to minimise steric interactions between the C^5-phenyl group of the tetrazole and the co-ordinated macrocycle. Several monodentate tetrazolate complexes containing N^2-bound metals have been crystallographically authenticated.[6]

The Sn–N bond lengths of compound **6**·2MeOH are equivalent [Sn(1)–N(2) 2.28(1), Sn(2)–N(6) 2.27(1) Å] and are comparable to those in related systems (Table 4). The Sn–O bonds to the co-ordinated alcohol [Sn(1)–O(1) 2.398(9), Sn(2)–O(2) 2.393(9) Å] are shorter than that reported for co-ordinated ethanol in $[N(C_6H_{11})_2H_2]_2[(SnBu_3)_4(C_2O_4)_3]\cdot 2EtOH$ [Sn–O 2.465(4) Å] but are notably longer than typical Sn–O covalent bonds typified by the tin–oxalate linkage in the same species [Sn–O 2.191(3) Å].[33]

The lattice structure of compound **6**·2MeOH is shown in Fig. 2, and comprises two-dimensional sheets of molecules parallel to the *ab* plane as a result of hydrogen bonding. Specifically, the H(1) and H(2) hydroxyl protons of the co-ordinated solvent molecules interact with N(4) and N(8) of neighbouring molecules [N(4) · · · H(1) 1.71(8), N(8) · · · H(2) 1.69(7) Å]. The net result of these intermolecular bonds is an array of molecules along the *b* axis as a result of N(8) · · · H(2) linkages, further cemented together along the *a* axis as a consequence of cross-links through N(1) and H(1). The O–H · · · N units are distinct and in one case non-linear [O(1)–H(1)–N(4) 162(6), O(2)–H(2)–N(8) 173(9)°], such that the N(4) · · · H(1) and N(8) · · · H(2) linkages are *ca.* 0.4 Å longer than the midpoints of the N(4)–O(1) and N(8)–O(2) vectors (2.68 Å) indicating that the hydrogen bonds are weaker than suggested by the O · · · N separation. The resultant sheet-like array is distinctly

Table 5 Fractional atomic coordinates (× 10^4) for compound **3**

Atom	*x*	*y*	*z*
Sn(1)	2378.7(4)	4251.6(2)	−2407.2(2)
Sn(2)	−2732.6(4)	2439.7(2)	−16.8(2)
N(1)	−2653(5)	3908(2)	−3663(3)
N(2)	−1779(5)	3473(2)	−4073(3)
N(3)	−266(5)	3570(2)	−3852(3)
N(4)	−106(5)	4089(2)	−3278(3)
N(5)	−3555(5)	3388(2)	−836(3)
N(6)	−4996(5)	3623(2)	−880(3)
N(7)	−5009(5)	4187(2)	−1338(3)
N(8)	−2586(5)	3790(2)	−1248(3)
C(1)	−1587(6)	4283(2)	−3180(3)
C(2)	−3525(6)	4276(2)	−1550(3)
C(3)	−2962(5)	4873(2)	−1948(3)
C(4)	−1961(5)	4872(2)	−2685(3)
C(5)	−1366(6)	5452(3)	−2967(4)
C(6)	−1771(6)	6021(3)	−2568(4)
C(7)	−2797(6)	6019(3)	−1858(4)
C(8)	−3375(6)	5450(2)	−1558(4)
C(9)	3077(6)	3337(2)	−2862(4)
C(10)	2416(6)	2791(3)	−2309(4)
C(11)	1437(6)	4445(3)	−1089(4)
C(12)	1655(7)	5143(3)	−801(4)
C(13)	3019(7)	5059(3)	−3226(4)
C(14)	2727(12)	4964(4)	−4295(5)
C(15)	−3442(7)	2840(3)	1264(4)
C(16)	−2175(9)	3027(5)	2008(5)
C(17)	−434(6)	2566(2)	−449(4)
C(18)	682(6)	2948(3)	240(4)
C(19)	−4402(6)	1853(3)	−849(4)
C(20)	−5798(7)	1675(3)	−317(4)

Table 6 Selected bond lengths (Å) and angles (°) for compound **3**

N(4)–Sn(1)	2.354(6)	N(7′)–Sn(1)	2.553(7)
C(9)–Sn(1)	2.126(7)	C(11)–Sn(1)	2.138(7)
C(13)–Sn(1)	2.150(7)	N(5)–Sn(2)	2.364(6)
N(2′)–Sn(2)	2.415(9)	C(15)–Sn(2)	2.134(7)
C(17)–Sn(2)	2.136(7)	C(19)–Sn(2)	2.132(7)
N(7′)–Sn(1)–N(4)	167.8(1)	C(9)–Sn(1)–N(4)	88.9(3)
C(9)–Sn(1)–N(7′)	82.7(3)	C(11)–Sn(1)–N(4)	94.2(3)
C(11)–Sn(1)–N(7′)	83.6(3)	C(11)–Sn(1)–C(9)	125.2(3)
C(13)–Sn(1)–N(4)	96.0(3)	C(13)–Sn(1)–N(7′)	95.6(3)
C(13)–Sn(1)–C(9)	116.8(3)	C(13)–Sn(1)–C(11)	117.2(3)
C(15)–Sn(2)–N(5)	89.0(3)	C(17)–Sn(2)–N(5)	89.5(3)
C(19)–Sn(2)–N(5)	94.2(3)	C(15)–Sn(2)–N(2′)	87.6(3)
C(17)–Sn(2)–N(2′)	89.4(3)	C(19)–Sn(2)–N(2′)	90.5(3)
N(2′)–Sn(2)–N(5)	175.0(3)	C(17)–Sn(2)–C(15)	123.2(3)
C(19)–Sn(2)–C(15)	116.9(3)	C(19)–Sn(2)–C(17)	119.8(3)

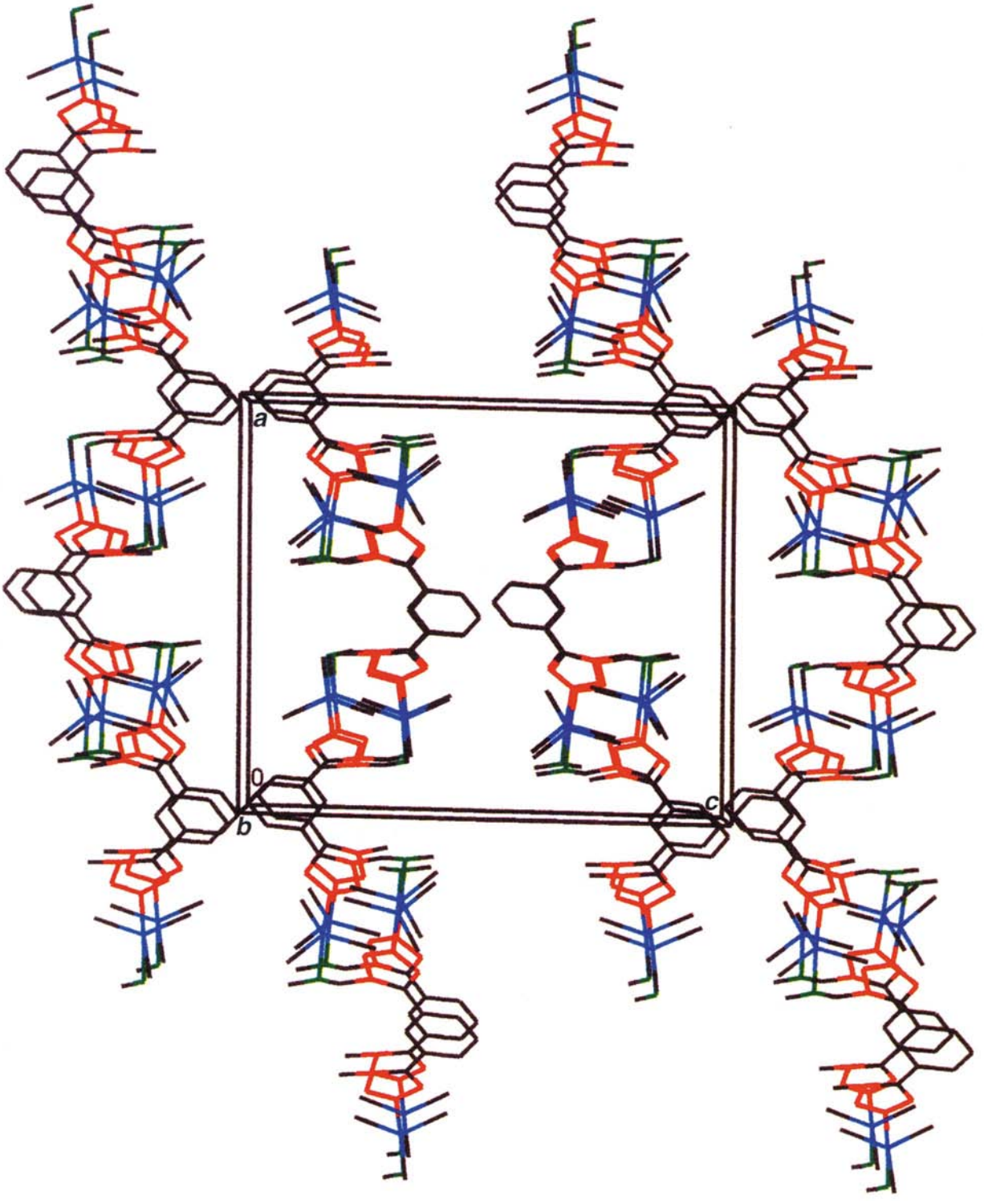


Plate 1 View of the lattice structure of compound **6**·2MeOH along *b* showing the non-planar nature of the layers (blue, tin; red, nitrogen; green, oxygen)

non-planar, adopting a 'corrugated' structure illustrated along *b* in Plate 1.

Compound 3. The asymmetric unit of compound **3** is illustrated in Fig. 3, atomic coordinates are given in Table 5 and selected geometric data in Table 6. There are two distinct trigonal-bipyramidal *trans*-N_2SnC_3 tin environments in **3**. The first, centred on Sn(1), is the more distorted of the two with an asymmetric co-ordination to the two nitrogen atoms [Sn(1)–N(4) 2.354(6), Sn(1)–N(7′) 2.553(7) Å] resulting in a relatively non-linear N(4)–Sn(1)–N(7′) unit [167.8(1)°]. Around Sn(2) both the bond lengths [Sn(2)–N(5) 2.364(6), Sn(2)–N(2′) 2.415(9) Å] and N(5)–Sn(2)–N(2′) fragment [175.0(3)°] are more regular. In both cases, however, it is possible to identify the nominal covalent and co-ordinative Sn–N linkages, in contrast to the only previously published polymeric tin-substituted tetrazole[3] where all Sn–N bond lengths were essentially identical. It is apparent from Table 6 that the Sn(1)–N(7′) [2.553(7) Å] and Sn(2)–N(2′) [2.415(9) Å] bonds are to the high end of the range associated with intermolecular Sn–N bonds.

It is interesting that with regard to the co-ordination mode

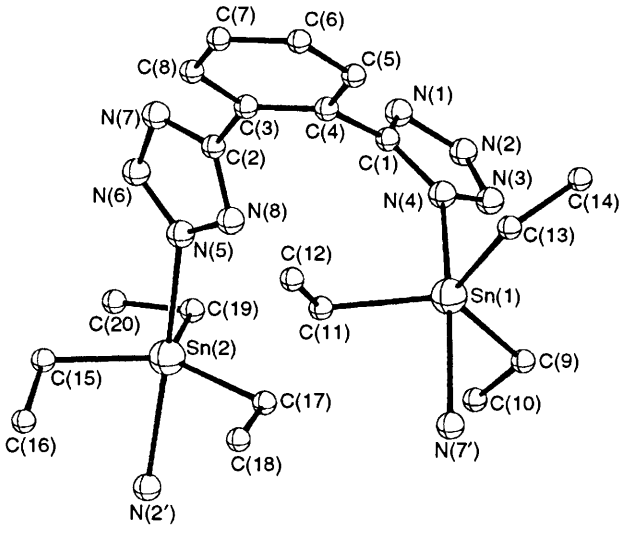


Fig. 3 The asymmetric unit of compound **3** showing the atomic labelling used

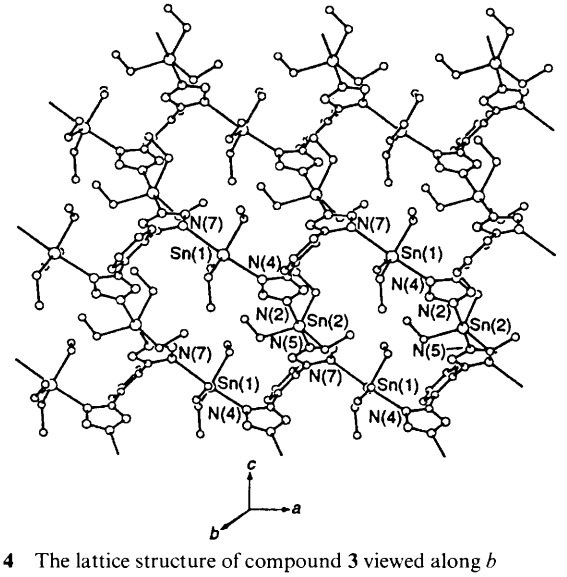


Fig. 4 The lattice structure of compound **3** viewed along *b*

of the tetrazole with respect to tin, $N^1 + N^1$ bonding [N(4)–Sn(1)–N(7')] coexists with the $N^2 + N^2$ mode [N(5)–Sn(2)–N(2')] originally proposed,[5] the two patterns also serving to distinguish Sn(1) from Sn(2). Moreover, the greater extent of distortion occurs about Sn(1), which is involved with the most sterically sensitive co-ordination sites for the tetrazole (N^1). With respect to the bidentate action of the tetrazole rings, each individual CN_4 ring is substituted in the least sterically hindered $N^1 + N^3$ fashion ($N^2 + N^4$ substitution is identical) by Et_3Sn groups. Such an observation is consistent with previous assertions,[5] although this is the first crystallographically confirmed example of such bonding in metal-substituted tetrazole derivatives.

In contrast to the essentially monomeric structure of solvated compound **6** described above, **3** crystallises from methanol without solvation as a supramolecular array dominated by polymeric two-dimensional sheets of molecules stacked along the *b* axis. Fig. 4 illustrates the manner in which the two-dimensional framework is constructed, generating large heterocycles comprising four tins, two complete ligands and two further tetrazole groups. Each twenty four-membered $C_8N_{12}Sn_4$ ring can be thought of as comprising two complete asymmetric units (Fig. 3) joined head-to-tail by two tetrazoles from adjacent rings. Each $C_8N_{12}Sn_4$ ring has six identical rings fused to it. It is also noteworthy that the sheet polymers are not flat but zigzagged, as illustrated by the view perpendicular to

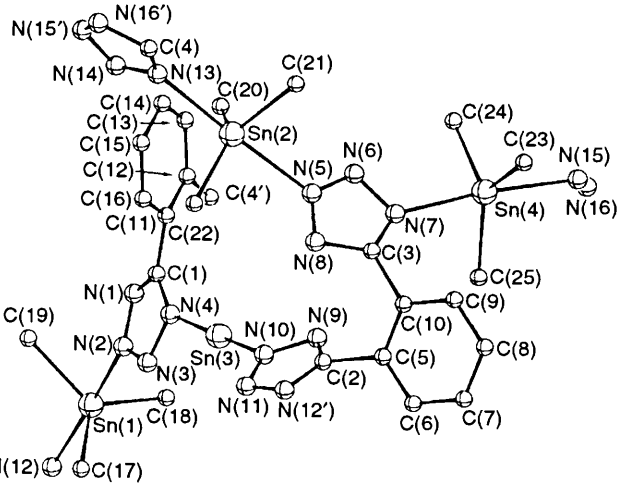


Fig. 5 The asymmetric unit of compound **5** showing the atomic labelling used. The carbon atoms of the butyl groups on Sn(3) and the β-, γ- and δ-carbons of the butyl groups on Sn(1), Sn(2) and Sn(4) are omitted (see text). Selected bond lengths (Å) and angles (°): N(2)–Sn(1) 2.24(5), N(12)–Sn(1) 2.45(4), N(5)–Sn(2) 2.46(5), N(13)–Sn(2) 2.42(5), N(4)–Sn(3) 2.47(6), N(10)–Sn(3) 2.32(5), N(7)–Sn(4) 2.40(4), N(15)–Sn(4) 2.44(7); N(12)–Sn(1)–N(2) 178(2), N(13)–Sn(2)–N(5) 175(2), N(10)–Sn(3)–N(4) 179(2), N(15)–Sn(4)–N(7) 174(2)

the *bc* plane (Plate 2). Crests and troughs of adjacent layers are defined by the phenyl groups of the 1,2-tetrazolyl-substituted ligand and lie convex face to concave face. Interlamellar packing is provided by protruding ethyl groups to produce a mean perpendicular interlayer spacing between the interlaced peaks and troughs of 6.18 Å.

Recently, similar two-dimensional networks have been reported for tetrazole analogues of poly(pyrazolyl)borate co-ordinated to cobalt, zinc and cadmium.[34] In these cases the individual tetrazole sub-units are linked in a $N^1 + N^4$ bonding combination to boron and metal, respectively.

Compound 5. The asymmetric unit of compound **5** is illustrated in Fig. 5 along with selected bond lengths and angles. Compounds **5** and **3** are related and differ only in the alkyl groups bonded to tin. The structural differences that arise between these species must result from the need to accommodate the alkyl groups within the supramolecular structure and in the case of **5** the nature of this packing coupled to the flexibility of the C_4H_9 unit causes severe disorder of the butyl groups. The asymmetric unit in Fig. 5 thus includes only the α-carbons of the butyl groups attached to Sn(1), Sn(2) and Sn(4), these being the only atoms of this type that refine reasonably. Carbon atoms in the β, γ and δ positions and all the constituents of the butyl groups on Sn(3) could not be located and/or refined at chemically sensible and consistent positions. This in no way negates our analysis of the overall lattice structure and bonding of the metal–tetrazole units.

Fig. 5 consists of two unique 1,2-phenylene substituted bis(tetrazole) ligands and four tri-*n*-butyltin centres, the latter adopting the ubiquitous *trans*-trigonal-bipyramidal N_2SnC_3 co-ordination. Each tetrazole acts in a bidentate manner and is uniformly substituted by the Bu_3Sn groups in the 1, 3 positions, as noted for the tetrazole ligands in **3**. Each tin is axially bound to two nitrogen atoms, one from the N^1 position of a tetrazole ring and the other from the N^2 position of a second tetrazole from an alternative bis(tetrazole) ligand within the asymmetric unit [Sn(1) bonds to N(2) and N(12); Sn(2) to N(5), N(13); Sn(3) to N(4), N(10); Sn(4) to N(7), N(15)].

In contrast to the two-dimensional lattice of compound **3** is the completely three-dimensional array adopted by **5** (Figs. 6 and 7, Plate 3). Along the *b* axis propagation is achieved *via* N(2)–Sn(1)–N(12) and N(4)–Sn(3)–N(10) linkages. In this

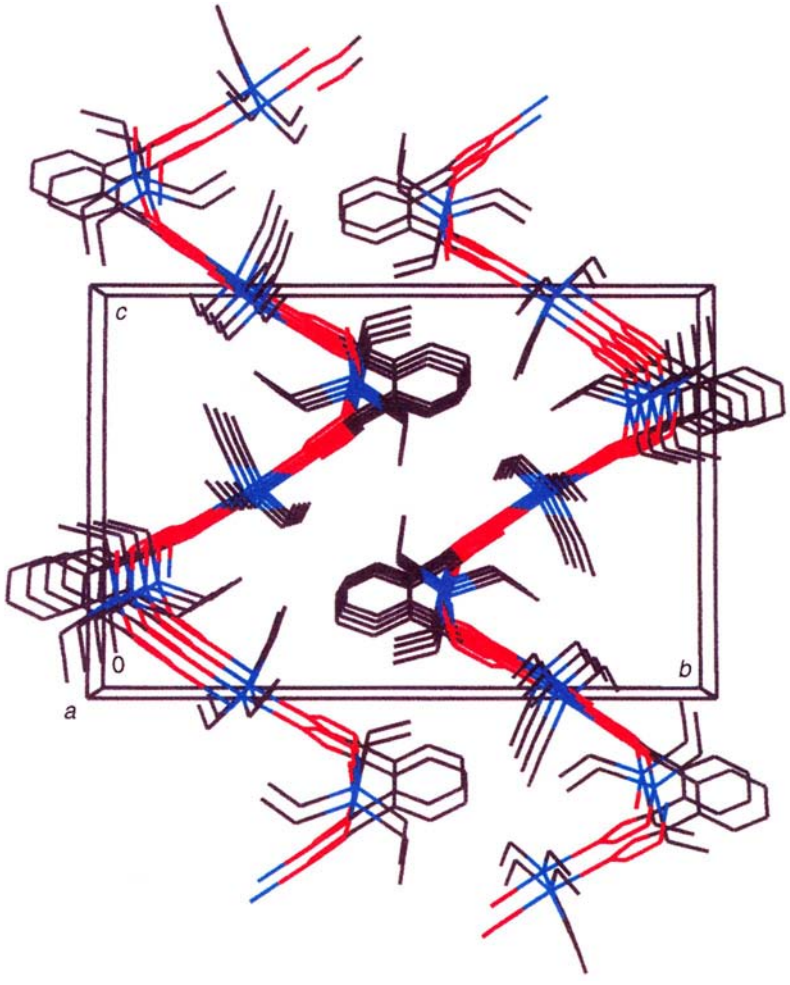


Plate 2 The lattice structure of compound **3** viewed perpendicular to the *bc* plane, showing the zigzag nature of the sheet structure

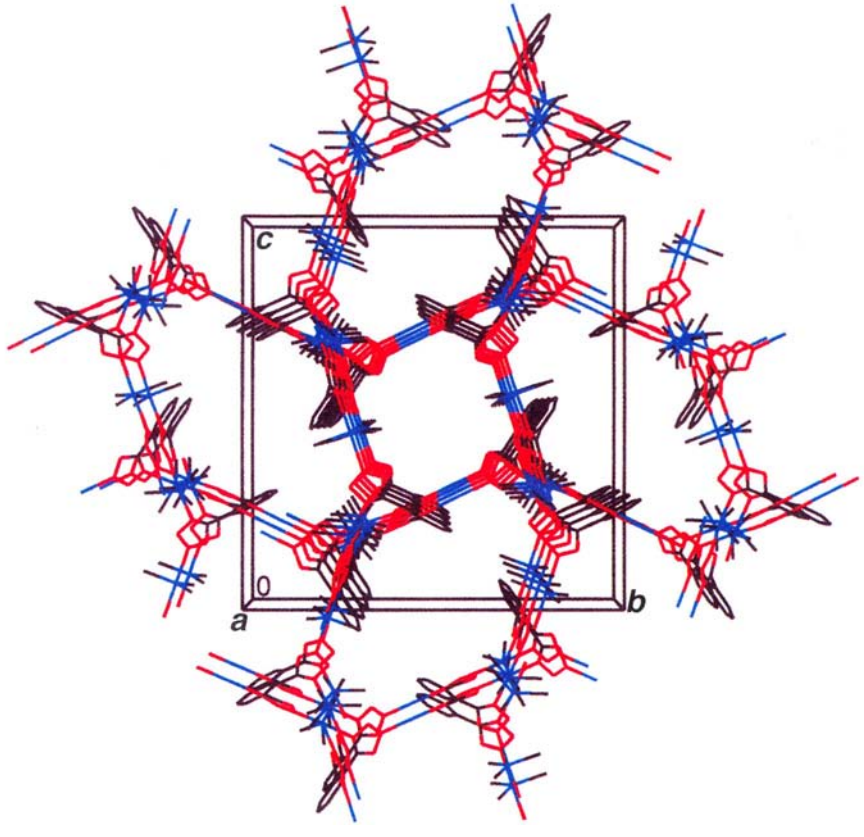


Plate 3 Channel formation in the lattice of compound **5**

manner a zigzag polymer evolves, constructed from a single tetrazole ring of each bis(tetrazole) ligand linked through its N^1 and N^3 centres by tributyltin units. A similar arrangement prevails along the *c* axis where polymer propagation occurs *via* N(5)–Sn(2)–N(13) and N(7)–Sn(4)–N(15) bridging interactions and involving the tetrazole rings not involved in propagation along the *b* axis. The net result of both these interactions is the evolution of a two-dimensional array bearing pseudo-four-fold symmetry (Fig. 6) parallel to the *bc* plane. The resultant sheets are intermolecularly linked along the *a* axis by N(12)–Sn(1)–N(2) and N(13)–Sn(2)–N(5) interactions, bridging now involving both the two complete phenyl-bridged bis(tetrazole) ligands (Fig. 7). Polymer propagation in this manner is made possible by free rotation of each of the tetrazole rings about their respective C^5-phenyl ring bonds. In this respect the tetrazoles centred on C(2) and C(3) subtend angles of 56.6 and 125.1° with the C(5)–C(10) phenyl ring while the ligands which incorporate C(1) and C(4) make angles of 52.2 and 66.2° with the C(11)–C(16) aromatic plane. In particular, it is the twist provided by the ligand which allows the propagation involving Sn(1) and Sn(3) to run approximately orthogonal to that based on Sn(2) and Sn(4).

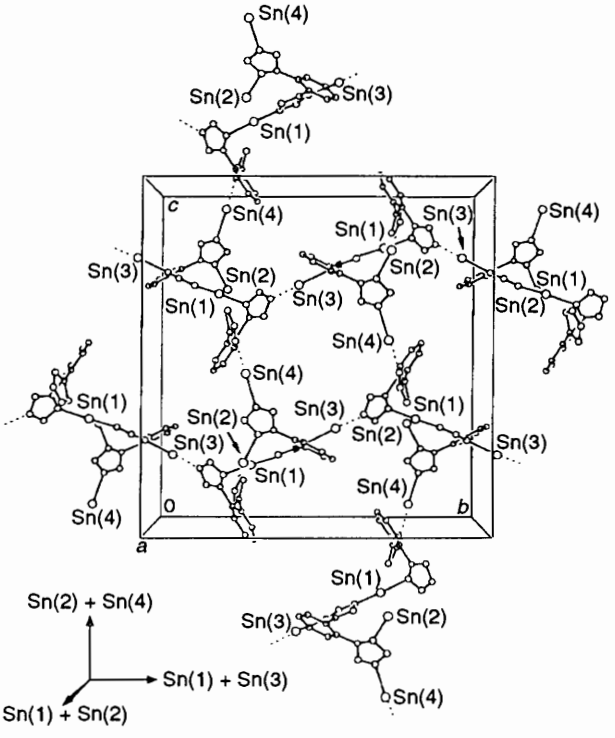


Fig. 6 The sheet-like nature of compound **5** viewed perpendicular to the *bc* plane

Co-ordination along *a* thus serves to arrange the sheets lying in the *bc* plane above each other to form open channels which run throughout the entire lattice (Plate 3). It should be recognised, however, that the large cavities provided by this apparently open framework are in fact entirely filled by the butyl groups bonded to tin of which only the α-carbons are shown. It is also apparent that it is the increase in the relative space-filling capacity of the tributyltin groups of **5** over the triethyltin groups of **3** that is the sole origin of the differing co-ordination mode adopted by the 1,2-phenylenebis(tetrazole) ligand and the dramatic contrast in the lattice packing adopted in both structures.

Conclusion

We have demonstrated that organotin-functionalised poly(tetrazole)ligands can be readily synthesised by conventional [3 + 2] cycloaddition reactions, and that these molecules form complex supramolecular arrays, the structure of which is dependent on the alkyl groups attached to tin.

Experimental

Spectra were recorded on the following instruments: JEOL GX270 (^{1}H, ^{13}C NMR), GX60Q and GX400 (^{119}Sn NMR), Perkin-Elmer 599B (IR). The NMR spectra were recorded in Me_2SO unless indicated otherwise. Details of our Mössbauer spectrometer and related procedures are given elsewhere.[35] The compound $SnBu_3N_3$ was prepared according to the method of Reichle[16] and employed without further purification. All nitriles and 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 screen.

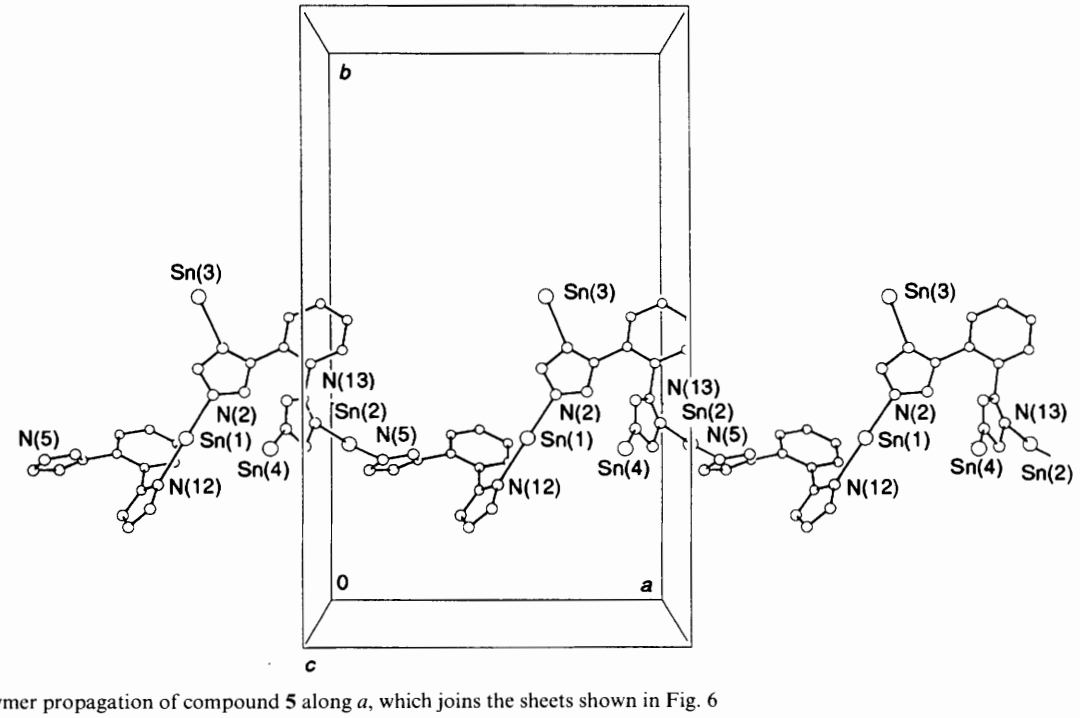


Fig. 7 Polymer propagation of compound **5** along *a*, which joins the sheets shown in Fig. 6

Syntheses

Triethyltin azide 1. Triethyltin chloride (4.5 g, 1.9 mmol) in diethyl ether (50 cm^3) and sodium azide (2.5 g, 3.8 mmol) in distilled water (20 cm^3) were shaken together as a two-phase system. The organic layer was separated and the aqueous layer extracted with further diethyl ether (50 cm^3). The combined ether washings were combined and dried over magnesium sulfate before *in vacuo* removal of the solvent. This yielded a pale brown oil which solidified on standing. Distillation on a Kügelrohr apparatus gave compound **1** as a colourless oil (3.6 g, 78%), b.p. 105 °C (1.5 mmHg), which subsequently solidified [Found (Calc. for $C_6H_{15}N_3$): C, 29.4 (29.2); H, 6.35 (6.10); N, 15.8 (16.8)%]. NMR ($CDCl_3$): ^1H, δ 1.07 (q, 6 H, CH_2CH_3) and 1.24 (t, 9 H, CH_2CH_3); ^{13}C, δ 10.2 (CH_2CH_3) and 10.4 (CH_2CH_3); ^{119}Sn, δ 79.4. ^{119}Sn Mössbauer (mm s^{-1}): i.s. = 1.47, q.s. = 3.60. IR (cm^{-1}, liquid film): 2949, 2872, 2066 [$\nu_{asym}(N_3)$], 1456, 1421, 1379, 1348, 1265, 1234, 1192, 1016, 952 and 675.

Triisopropyltin azide 2. A solution of triisopropyltin iodide (31.6 g, 7.5 mmol) in diethyl ether was shaken with a five to one excess of sodium azide (26.9 g, 41 mmol) in distilled water (100 cm^3). The resulting yellow ether layer was separated and the aqueous layer washed with diethyl ether (50 cm^3). The combined washings were dried over sodium sulfate. *In vacuo* removal of the solvent afforded a greasy, low-melting off-white solid which was distilled at reduced pressure. The product, a colourless crystalline solid, boiled at 65–70 °C (0.3 mmHg). The ^{119}Sn NMR spectrum revealed small amounts of the starting iodide which proved inseparable by further distillation and attempted sublimation of the azide. Crude product collected, 16.2 g [Found (Calc. for $C_9H_{21}N_3Sn$): C, 32.5 (32.5); H, 6.65 (6.30); N, 11.1 (12.6)%]. NMR ($CDCl_3$): ^1H, δ 1.38 [d, 18 H, $(CH_3)_2CH$] and 1.85 [m, 3 H, $(CH_3)_2CH$]; $^3J[(C^1H_3)_2CH-^{117,119}Sn]$ 74.8, 88.4 Hz; ^{13}C, δ 20.7 [$(CH_3)_2CH$] and 21.5 [$(CH_3)_2CH$]; $^1J[(CH_3)_2{}^{13}CH-^{117,119}Sn]$ 304.0, 317.4 Hz; ^{119}Sn, δ 43.8. ^{119}Sn Mössbauer (mm s^{-1}): i.s. = 1.27, q.s. = 3.39. IR (cm^{-1}, liquid film): 2926, 2859, 2062 [$\nu_{asym}(N_3)$], 1462, 1379, 1341, 1202, 1156, 1001, 918, 874 and 634.

2,2′-Bis(triethylstannyl)-5,5′-*o*-phenylenebis(tetrazole) 3. Compound **1** (3.4 g, 1.3 mmol) and 1,2-dicyanobenzene (0.88 g, 0.7 mmol) were heated at 160 °C for 45 min, to yield a solid off-white mass. Recrystallisation from methanol yielded **3** as colourless cubic crystals (2.7 g, 63%), m.p. 230 °C (decomp.) [Found (Calc. for $C_{20}H_{34}N_8Sn_2$): C, 38.3 (38.5); H, 5.40 (5.45); N, 17.7 (17.8)%]. NMR [$(CD_3)_2SO$]: ^1H, δ 0.70–0.81 (m, 30 H, CH_2CH_3), 7.20 (dd, 2 H, *m*-H of C_6H_4) and 7.34 (dd, 2 H, *o*-H of C_6H_4); ^{13}C, δ 10.0 (CH_2CH_3), 10.0 (CH_2CH_3), 128.6 (*m*-C of C_6H_4), 129.8 (*o*-C of C_6H_4), 129.9 (*ipso*-C of C_6H_4) and 161.2 (CN_4); $^1J(^{13}CH_2CH_3-^{117,119}Sn)$ 470.6, 490.8 Hz; ^{119}Sn, δ −47.1. ^{119}Sn Mössbauer (mm s^{-1}): i.s. = 1.48, q.s. = 3.86. IR (cm^{-1}, KBr disc): 2950, 2870, 1458, 1441, 1423, 1352, 1224, 1013, 961, 756, 684, 527 and 442.

2,2′-Bis(triethylstannyl)-5,5′-*m*-phenylenebis(tetrazole) 4. Compound **1** (2.0 g, 0.8 mmol) and 1,3-dicyanobenzene (0.52 g, 0.4 mmol) were refluxed in mesitylene (20 cm^3) for 2 h. The insoluble product precipitated from solution as the reaction progressed and, on cooling, was filtered off and washed with diethyl ether. Attempted recrystallisation from methanol yielded **4** as an amorphous white powder (1.7 g, 68%), m.p. 208 °C (decomp.) [Found (Calc. for $C_{20}H_{34}N_8Sn_2$): C, 38.6 (38.5); H, 5.55 (5.45); N, 17.2 (17.8)%]. NMR [$(CD_3)_2SO$]: ^1H, δ 1.23 (t, 18 H, CH_2CH_3), 1.34 (m, 12 H, CH_2CH_3), 7.58 (t, 1 H, *m*-H of C_6H_4), 8.07 (d, 2 H, *o*-H of C_6H_4) and 8.76 (s, 1 H, *o*-H of C_6H_4); ^{13}C, δ 10.3 (CH_2CH_3), 10.3 (CH_2CH_3), 126.5 (*m*-C of C_6H_4), 126.8 (*o*-C of C_6H_4), 130.5 (*o*-C of C_6H_4), 137.1 (*ipso*-C of C_6H_4) and 162.3 (CN_4); $^2J(CH_2{}^{13}CH_3-^{117,119}Sn)$ 34.2 Hz (unresolved); ^{119}Sn, δ −49.8, ^{119}Sn Mössbauer (mm s^{-1}): i.s. = 1.50, q.s. = 3.82. IR (cm^{-1}, KBr disc): 2950, 2870, 1458, 1422, 1377, 1329, 1221, 1194, 1142, 1105, 1016, 961, 808, 761, 748, 683, 523 and 488.

2,2′-Bis(tributylstannyl)-5,5′-*o*-phenylenebis(tetrazole) 5. 1,2-Dicyanobenzene (5.61 g, 4.4 mmol) was heated at 170 °C under nitrogen with tributyltin azide (28.9 g, 8.7 mmol). After 10 min a viscous dark oil resulted which solidified to a glass on cooling. This was dissolved in boiling methanol and decolourised with activated charcoal. Filtration whilst hot afforded a yellow solution which on cooling yielded compound **5** as colourless cubic crystals (20.4 g, 60%), m.p. 175 °C [Found (Calc. for $C_{32}H_{58}N_8Sn_2$): C, 48.5 (48.6); H, 7.50 (7.45); N, 14.2 (14.1)%]. NMR [$(CD_3)_2SO$]: ^1H, δ 0.78 [t, 18 H, $(CH_2)_3CH_3$], 1.10–1.30 (m, 24 H, $SnCH_2CH_2CH_2CH_3$), 1.40 (m, 12 H, $SnCH_2CH_2CH_2CH_3$), 7.54 (m, 2 H, *m*-H of C_6H_4) and 7.62 (m, 2 H, *o*-H of C_6H_4); ^{13}C, 13.8 [$(CH_2)_3CH_3$], 18.0 [$SnCH_2(CH_2)_3CH_3$], 26.7 [$Sn(CH_2)_2CH_2CH_3$], 27.8 ($SnCH_2CH_2CH_2CH_3$), 128.0 (*m*-C of C_6H_4), 130.3 (*o*-C of C_6H_4), 133.2 (*ipso*-C of C_6H_4) and 160.9 (CN_4); $^2J(CH_2{}^{13}CH_2CH_3-^{117,119}Sn)$ 28.6 (unresolved); $^3J[(CH_2)_2{}^{13}CH_2CH_3-^{117,119}Sn]$ 83.8 Hz (unresolved); ^{119}Sn, δ −70.5, ^{119}Sn Mössbauer (mm s^{-1}): i.s. = 1.41, q.s. = 3.60. IR (cm^{-1}, KBr disc): 2959, 2922, 2870, 2856, 1464, 1444, 1423, 1354, 1080, 1012, 756, 680, 613 and 441.

2,2′-Bis(tributylstannyl)-5,5′-*m*-phenylenebis(tetrazole) 6. A suspension of 1,3-dicyanobenzene (4.3 g, 33.3 mmol) and tributyltin azide (22.0 g, 66.6 mmol) was heated to 190 °C for 1 h. During this time a homogeneous brown melt formed which set to a brittle glass upon cooling. This was dissolved in boiling methanol, decolourised with activated charcoal and filtered. Cooling to −20 °C produced compound **6** as a bis(methanol) solvate (20.2 g, 77%), m.p. 68 °C (decomp.) which could be converted into an amorphous, unsolvated form by gentle warming under vacuum, m.p. 177–179 °C (decomp.) [Found (Calc. for $C_{32}H_{58}N_8Sn_2$): C, 48.9 (48.6); H, 7.35 (7.45); N, 14.2 (14.1)%]. NMR [$(CD_3)_2SO$]: ^1H, δ 0.87 [t, 18 H, $(CH_2)_3CH_3$], 1.22–1.42 (m, 24 H, $SnCH_2CH_2CH_2CH_3$), 1.63 (m, 12 H, $CH_2CH_2CH_2CH_3$), 8.08 (t, 1 H, *m*-H of C_6H_4), 8.11 (d, 2 H, *o*-H of C_6H_4) and 8.77 (s, 1 H, *o*-H of C_6H_4); ^{13}C, δ 13.7 [$(CH_2)_3CH_3$], 18.4 [$CH_2(CH_2)_2CH_3$], 26.5 [$(CH_2)_2CH_2CH_3$], 27.8 ($CH_2CH_2CH_2CH_3$), 124.1 (*m*-C of C_6H_4), 126.4 (*o*-C of C_6H_4), 129.3 (*o*-C of C_6H_4), 130.6 (*ipso*-C of C_6H_4) and 162.2 (CN_4); $^1J[^{13}CH_2(CH_2)_2CH_3-^{117,119}Sn]$ 484.8 (unresolved); $^2J[CH_2{}^{13}CH_2CH_2CH_3-^{117,119}Sn]$ 28.6 (unresolved); $^3J[(CH_2)_2{}^{13}CH_2CH_3-^{117,119}Sn]$ 75.0 Hz (unresolved); ^{119}Sn, δ −54.0. ^{119}Sn Mössbauer (mm s^{-1}): i.s. = 1.41, q.s. = 3.65. IR (cm^{-1}, KBr disc): 2957, 2924, 2872, 2855, 1464, 1427, 1377, 1080, 879, 747, 696, 679 and 611.

For **6**·2MeOH [Found (Calc. for $C_{32}H_{58}N_8Sn_2{\cdot}2CH_3OH$): C, 47.3 (47.6); H, 7.75 (7.70); N, 12.9 (13.0)%]: ^{119}Sn Mössbauer (mm s^{-1}): i.s. = 1.47, q.s. = 3.73.

2,2′-Bis(tributylstannyl)-5,5′-*p*-phenylenebis(tetrazole) 7. 1,4-Dicyanobenzene (6.02 g, 4.7 mmol) and tributyltin azide (30.9 g, 9.3 mmol) were heated to 150 °C under nitrogen during which time the initial suspension became a solid mass. This was dissolved in boiling methanol, decolourised with activated carbon, filtered and cooled to −20 °C, affording compound **7** as a colourless crystalline solid (24.2 g, 70%), m.p. 220–222 °C (decomp.) [Found (Calc. for $C_{32}H_{58}N_8Sn_2$): C, 48.4 (48.6); H, 7.35 (7.45); N, 13.9 (14.1)%]. NMR [$(CD_3)_2SO$]: ^1H, δ 0.89 [t, 18 H, $(CH_2)_3CH_3$], 1.29–1.49 (m, 24 H, $SnCH_2CH_2CH_2CH_3$), 1.64 (m, 12 H, $SnCH_2CH_2CH_3$) and 8.20 (s, 4 H, *o*-H of C_6H_4); ^{13}C, δ 13.7 [$(CH_2)_3CH_3$], 18.4 [$SnCH_2(CH_2)_2CH_3$], 26.4 [$Sn(CH_2)_2CH_2CH_3$], 27.8 [$SnCH_2CH_2CH_2CH_3$], 126.6 (*o*-C of C_6H_4), 130.2 (*ipso*-C of C_6H_4) and 162.1 (CN_4); $^2J(CH_2{}^{13}CH_2CH_2CH_3-^{117,119}Sn)$ 30.8 (unresolved); $^3J[(CH_2)_2{}^{13}CH_2CH_3-^{117,119}Sn]$ 75.0 Hz (unresolved); ^{119}Sn,

δ −55.0. ^{119}Sn Mössbauer (mm s^{-1}): i.s. = 1.43, q.s. = 3.73. IR (cm^{-1}, KBr disc): 2959, 2924, 2870, 2855, 1464, 1443, 1427, 1010, 852, 752, 690, 615, 490 and 478.

2,2′-Bis(triisopropylstannyl)-5,5′-*o*-phenylenebis(tetrazole) 8. Compound **2** (4.8 g, 16.4 mmol) and 1,2-dicyanobenzene (1.1 g, 8.0 mmol) were heated as above to yield a pale brown oil after 1 h at 100 °C. Dissolution in methanol, decolourisation with activated carbon and subsequent removal of solvent yielded a yellow oil. Trituration with hexane–diethyl ether afforded **8** as an amorphous white powder (2.8 g, 48.3%), m.p. 192 °C (decomp.) [Found (Calc. for $C_{26}H_{46}N_8Sn_2$): C, 46.4 (44.1); H, 5.90 (6.50); N, 16.5 (15.8)%]. NMR [$(CD_3)_2SO$]: ^{1}H, δ 1.33 [d, 18 H, $(CH_3)_2CH$], 2.01 [br s, 3 H, $(CH_3)_2CH$], 7.73 (m, 2 H, *m*-H of C_6H_4), 8.08 (m, 2 H, *o*-H of C_6H_4); ^3J[$(C^1H_3)_2$-CH–^{117,119}Sn] 80.4, 84.4 Hz; ^{13}C, δ 21.3 [$(CH_3)_2CH$], 24.6 [$(CH_3)_2CH$], 128.8 (*m*-C of C_6H_4), 129.2, (*o*-C of C_6H_4), 132.4 (*ipso*-C of C_6H_4) and 160.1 (CN_4); ^2J[$(^{13}CH_3)_2$CH–^{117,119}Sn] 22.0 Hz (unresolved); ^{119}Sn, δ −81.3. ^{119}Sn Mössbauer (mm s^{-1}): i.s. = 1.55, q.s. = 3.73. IR (cm^{-1}, KBr disc): 2961, 2942, 2861, 1462, 1426, 1358, 1206, 1154, 1013, 779, 619, 499 and 476.

2,2′-Bis(triisopropylstannyl)-5,5′-*p*-phenylenebis(tetrazole) 9. Compound **2** (6.5 g, 2.3 mmol) and 1,4-dicyanobenzene (1.5 g, 1.2 mmol) were heated to 120 °C for 30 min. This resulted in a brown oil which solidified on cooling to a cream solid which was extracted into methanol using a Soxhlet apparatus to yield on cooling **9** as a white amorphous powder (2.6 g, 33%), m.p. 183 °C [Found (Calc. for $C_{26}H_{46}N_8Sn_2$): C, 42.4 (44.1); H, 6.50 (6.50); N, 15.3 (15.8)%]. NMR [$(CD_3)_2SO$]: ^{1}H, δ 1.33 [d, 18 H, $(CH_3)_2CH$], 2.01 [br s, 3 H, $(CH_3)_2CH$] and 8.17 (br m, *ca.* 4 H, *o*, *m*-H of C_6H_4); ^3J[$(C^1H_3)_2$CH–^{117,119}Sn] 81.0, 84.3 Hz; ^{13}C, δ 21.4 [$(CH_3)_2CH$], 24.4 [$(CH_3)_2CH$], 126.6 (*o*,*m*-C of C_6H_4), 130.1(*ipso*-C of C_6H_4) and 161.8 (CN_4); ^2J[$(^{13}CH_3)_2$-CH–^{117,119}Sn] 19.8 Hz (unresolved); ^{119}Sn, δ −82.2. ^{119}Sn Mössbauer (mm s^{-1}): i.s. = 1.53, q.s. = 3.64. IR (cm^{-1}, KBr disc): 2936, 2861, 1464, 1426, 1385, 1367, 1269, 1209, 1156, 1121, 1021, 1005, 874, 853, 747, 513 and 484.

Crystallography

Compound 3. A crystal of approximate dimensions 0.25 × 0.25 × 0.2 mm was used for data collection.

Crystal data. $C_{20}H_{34}N_8Sn_2$, M = 623.9, monoclinic, space group $P2_1/c$, a = 8.549(2), b = 20.952(4), c = 14.046(3) Å, β = 96.41(2)°, U = 2500.2 Å^3, Z = 4, D_c = 1.66 g cm^{-3}, μ(Mo-Kα) = 20.3 cm^{-1}, F(000) = 1240.

Data were measured at 170 K on a CAD4 automatic four-circle diffractometer in the range 2 ⩽ θ ⩽ 24°. 4318 Reflections were collected of which 3014 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz and polarisation but not for absorption. The structure was solved by Patterson methods and refined using the SHELX[36,37] suite of programs. In the final least-squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions. Final residuals after 10 cycles of least squares were R = 0.0321, R' = 0.0313, for a weighting scheme of w = 2.1396/[$\sigma^2(F)$ + 0.000 544(F)^2]. Maximum final shift/e.s.d. was 0.001. The maximum and minimum residual densities were 0.51 and −0.53 e Å^{-3}, respectively.

Compound 5. A crystal of approximate dimensions 0.3 × 0.3 × 0.2 mm was used for data collection.

Crystal data. $C_{32}H_{58}N_8Sn_2$, M = 790.2, orthorhombic, space group $P22_12_1$, a = 13.819(2), b = 23.075(3), c = 24.043(6) Å, U = 7666.4 Å^3, Z = 8 (two molecules per asymmetric unit), D_c = 1.37 g cm^{-3}, μ(Mo-Kα) = 12.21 cm^{-1}, F(000) = 3248.

Complete refinement of this structure was precluded due to severe disorder in the butyl groups, which resulted in a failure to locate some of the carbon atoms and unsatisfactory refinement of others. The best R value achieved (based on F) was 0.1503 (unit weights), though the maximum shift/e.s.d. for the tin and nitrogen atoms was 0.011 indicating that geometric parameters associated with the tin–tetrazole units are reasonably well defined.

Compound 6·2MeOH. A crystal of approximate dimensions 0.3 × 0.2 × 0.2 mm was used for data collection.

Crystal data. $C_{34}H_{66}N_8O_2Sn_2$, M = 856.3, monoclinic, space group $P2_1/n$, a = 16.414(3), b = 13.321(4), c = 19.114(5) Å, β = 91.18(2)°, U = 4178.4 Å^3, Z = 4, D_c = 1.36 g cm^{-3}, μ(Mo-Kα) = 12.4 cm^{-1}, F(000) = 608.

Data were measured as for compound **3**. 5607 Reflections were collected of which 3131 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz and polarisation and also for absorption[38] (maximum and minimum absorption corrections 1.168, 0.875, respectively). The structure was solved and refined as for **3**. In the final least-squares cycles all atoms were allowed to vibrate anisotropically except for the triply disordered C(32) positions. Hydrogen atoms were included at calculated positions except for the methoxy protons attached to C(33) and C(34). These hydrogens [H(1) and H(2)] were located in an advanced Fourier-difference map and refined at a distance of 0.98 Å from the relevant parent atoms. Final residuals after 10 cycles of least squares were R = 0.0500, R' = 0.0442, for w = 2.6333/[$\sigma^2(F)$ + 0.000 224(F)^2]. Maximum final shift/e.s.d. was 0.113, maximum and minimum residual densities 0.25 and −0.28 e Å^{-3}.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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