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FULL PAPER

Thallium(I)- and organothallium(III)-substituted mono-, bis- and tris-tetrazoles: synthesis and supramolecular structures

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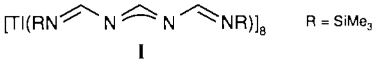
Six thallium(I) tetrazolates have been synthesized by either the addition of an alcoholic solution of the appropriate tetrazole to an ethanolic solution of thallium ethoxide, or from the sodium salt of the tetrazole with Tl_2SO_4. Seven diphenylthallium-substituted mono- and bis-tetrazoles have been synthesized by a condensation route involving the appropriate tetrazole and diphenylthallium hydroxide. 1-Diphenylthallyl-5-phenyltetrazole has also been prepared by a cycloaddition reaction between diphenylthallium azide and benzonitrile. The structures of $[Tl(18\text{-crown-}6)^+]_2[C_2N_{10}{}^{2-}]$, $Ph_2TlN_4CPh\cdot MeOH$, 1,4-$(Ph_2TlN_4C)_2C_4H_8\cdot 2MeOH$ and 1,2-$(Ph_2TlN_4C)_2C_6H_4\cdot Ph_2TlCl\cdot 2MeOH\cdot 2H_2O$ have been determined. The last three compounds generate supramolecular structures which incorporate six-membered Tl_2N_4 rings. The last two contain the first examples of tetrazoles which utilise all four available ring nitrogens for co-ordination.

Introduction

In recent years we have been interested in the supramolecular architectures created by organotin derivatives of polyfunctional tetrazoles. A universal feature of all organotin derivatives of mono-,[1] bis-,[2] tris-,[3] tetra-[4] and functionalised tetrazoles[5] known to date is the trigonal bipyramidal *trans*-N_2SnC_3 geometry at the tin with a linear N–Sn–N component which combines with the versatile, multidentate nature of the tetrazole ligand to result in a plethora of supramolecular arrays. Other determinants of the lattice structure are the nature of the R group on the metal and solvent molecule incorporation or hydration during the crystallisation process.

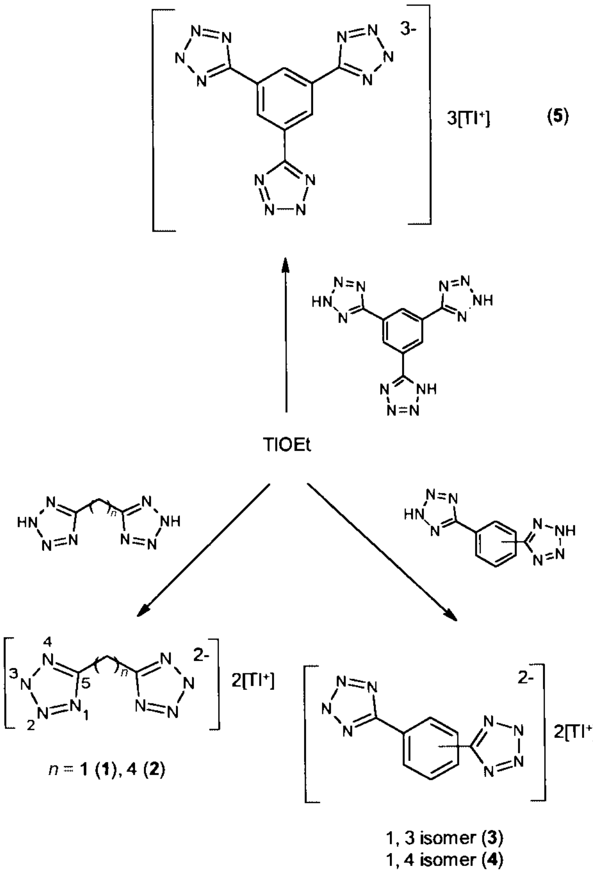
In this paper we turn our attention to the synthesis of thallium(I) and diphenylthallium(III) derivatives of tetrazoles. The wide range of co-ordination numbers which diorganothallium compounds are known to exhibit suggests that, in combination with the multidentate nature of the tetrazole, novel supramolecular structures should be forthcoming. In addition, relatively few thallium(I) or diorganothallium(III) derivatives of azoles have been reported. To our knowledge, the only such species structurally characterised to date are dimethyl(4-amino-5-sulfanyl-3-trifluoromethyl-1,2,4-triazolato)thallium(III),[6] (benzotriazolato)thallium(I)[7] and a number of hydrotris(pyrazolyl)borates.[8] Recently, the reaction of $TlN(SiMe_3)_2$ and 1,3,5-triazine has been shown to lead to the ring-opened product (**I**) which has been authenticated crystallographically.[9]



$[Tl(RN{=}N{=}N{=}NR)]_8$ R = $SiMe_3$

I

Along with synthetic studies, we now present the structures of one thallium(I) tetrazole and three novel diorganothallium tetrazoles of increasing complexity, as representatives of this family of compounds: $[Tl(18\text{-crown-}6)^+]_2[C_2N_{10}{}^{2-}]$, $Ph_2TlN_4CPh\cdot MeOH$, 1,4-$(Ph_2TlN_4C)_2C_4H_8\cdot 2MeOH$ and 1,2-$(Ph_2TlN_4C)_2C_6H_4\cdot Ph_2TlCl\cdot 2MeOH\cdot 2H_2O$.



Scheme 1

Results and discussion

Synthesis

Five thallium(I) tetrazolates have been synthesized following the method of McKillop and co-workers[10,11] (Scheme 1). In a typical experiment, a solution of thallium ethoxide in absolute ethanol was added dropwise to a solution of the appropriate tetrazole in absolute ethanol resulting in an almost immediate fine white precipitate. The reaction mixture was allowed to settle for 4–5 hours in each case, filtered and dried *in vacuo*. Products **1**–**4** were insoluble in commonly available solvents except dimethyl sulfoxide and hot water while **5** proved to be totally insoluble. Microanalysis revealed products **1**, **2** and **4** to

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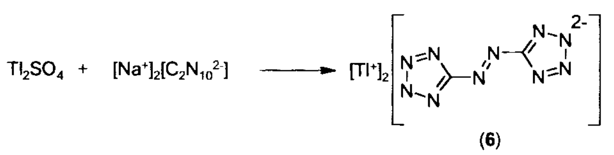
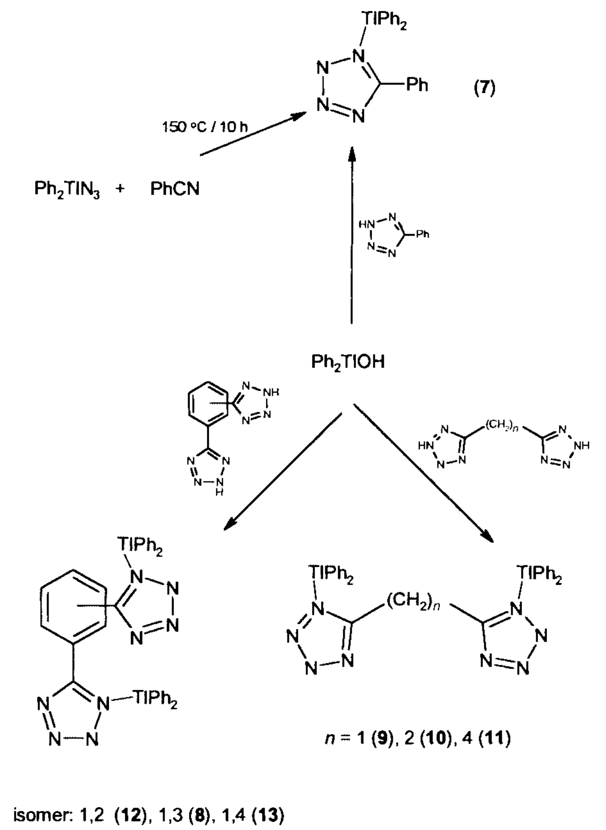
be anhydrous, and **3**, **5** to be dihydrates. Broad bands in the IR spectra of **3**, **5** at 3352 and 3414 cm^{-1} respectively confirmed the presence of water. Compound **6**, prepared from disodium 5,5′-azobis(tetrazolate) and isolated as a monohydrate (Scheme 2),[12]



Scheme 2

could be re-crystallised from ethanol in the presence of 18-crown-6 to yield $[Tl(18\text{-crown-}6)^+]_2[C_2N_{10}^{2-}]$ **6a**. **CAUTION**: an attempt to study the thermal decomposition of this product by TGA led to a violent explosion at *ca.* 200 °C. Similar observations have been made with respect to transition-metal dihydrobis(tetrazolyl)borates[13] and metal derivatives of $C_2N_{10}^{2-}$ have previously been investigated as detonators and stab-sensitive materials.[12,14]

The cycloaddition route used to prepare organotin-substituted tetrazoles has been used to synthesize one diphenylthallium-substituted mono-tetrazole (Scheme 3).



Scheme 3

Diphenylthallium azide was added to an excess of benzonitrile and stirred under N_2 for 10 hours at 150 °C, the reaction being monitored by the disappearance of ν(CN) and $\nu(N_3)$ at 2228 and 1989 cm^{-1}, respectively, of the starting materials. Recrystallisation from hot methanol yielded **7** as an anhydrous powder along with some crystals of a methanol solvate (**7a**). The disadvantage of this route is the necessity to heat diphenylthallium azide at high temperatures for prolonged periods of time, particularly in view of the high toxicity of thallium. Safety considerations have therefore led us to the search for a more convenient synthetic procedure for organothallium tetrazoles.

Seven diphenylthallium-substituted mono- and bis-tetrazoles, including **7**, have been prepared following the condensation route of Lee[15] (Scheme 3) in which a methanolic solution of the appropriate tetrazole is added to a refluxing methanolic solution of diphenylthallium hydroxide. Cooling for several days yielded **7**–**9**, **13** as white powders and **10**–**12** as brown crystals. Serendipitously, the incomplete conversion of Ph_2TlCl into Ph_2TlOH during part of this study has led to the isolation of **12** as a co-crystal with an equimolar amount of Ph_2TlCl (see below). The microanalysis data for **13**, prepared from the same batch of Ph_2TlOH starting material, are also consistent with a co-crystallised product. In all cases the products are susceptible to solvation, either by the crystallisation solvent (MeOH) and/or atmospheric moisture, in keeping with many of our findings with regard to analogous organotin compounds.[2,4]

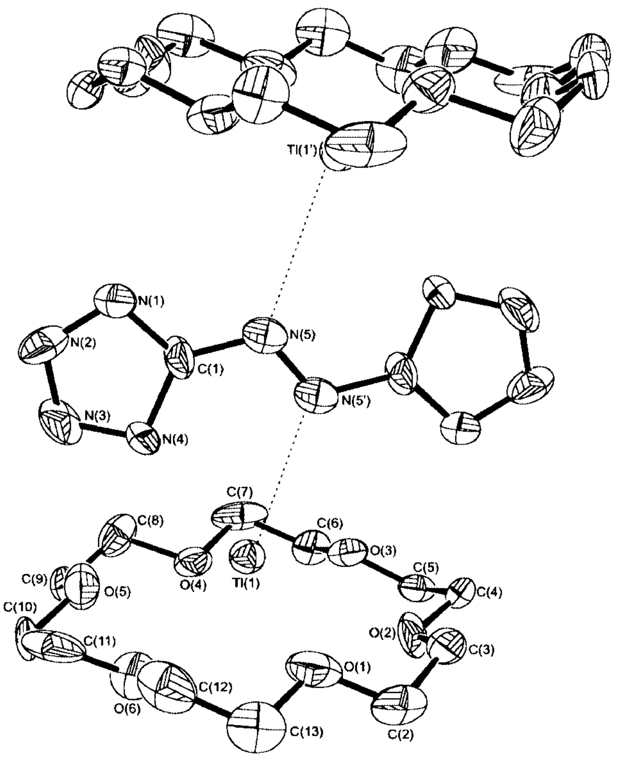
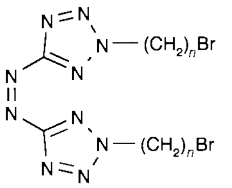


Fig. 1 The structure of compound **6a** showing the atomic labelling used in the text. Thermal ellipsoids are at the 30% probability level. Selected metric data: Tl(1)–O(1) 2.85(3), Tl(1)–O(2) 3.04(2), Tl(1)–O(3) 3.01(2), Tl(1)–O(4) 3.10(2), Tl(1)–O(5) 2.97(3), Tl(1)–O(6) 2.99(2), Tl(1)–N(5) 3.17(2) and N(5)–N(5′) 1.27(5) Å; N(5′)–N(5)–C(1) 115(3)°. Primed atoms are related to the equivalent unprimed atoms by the inversion centre midway along the N(5)–N(5′) bond.

Crystallography

In the following discussion the numbering of the tetrazole ring nitrogens is indicated in Scheme 1 for comparing the co-ordination mode of the tetrazole, while with respect to the metal centre 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 6a. The asymmetric unit of **6a**, which is one half of the molecule, is shown in Fig. 1. Thallium sits above the plane of the crown ether and makes six long contacts [2.85(3)–3.10(2) Å] to the ring oxygens. There is a long contact [3.17(2) Å] to N(5) of the diazenyl unit but no interactions with the tetrazole nitrogens. The structure is strongly reminiscent of $[Tl(18\text{-crown-}6)^+][TCNQ^-]$.[16] The two tetrazoles are disposed in the *E* isomeric form about N=N, as in the only other structure containing this ligand, $[Pb(OH)^+]_2[C_2N_{10}^{2-}]$,[17] though the anion, as its disodium salt, has been used to produce derivatives such as **II** which assume a *Z* stereochemistry.[18]



II

Compound 7a. Crystals of 1-diphenylthallyl-5-phenyltetrazole–methanol (1/1) **7a** were grown by slow evaporation of a methanolic solution at room temperature. The asymmetric unit of **7a** (Fig. 2) is half of a centrosymmetric dimer and contains a distorted trigonal bipyramidal *trans*-C_2TlN_2O thallium centre, in contrast to the *trans*-N_2 stereochemistry common to all organotin tetrazoles. The axial positions of Tl(1) are occupied by the two phenyl groups [C(8)–Tl(1)–C(14) 173.9(4)°] and the equatorial positions by two tetrazoles [Tl(1)–N(1) 2.512(9); Tl(1)–N(2′) 2.680(9) Å] and the oxygen of a co-ordinated methanol [Tl(1)–O(1) 2.691(7) Å]. The Tl–N bonds are shorter than those found in (benzotriazolato)thallium(I) [2.725, 2.732, 2.790 Å]. The $N^1 + N^2$ metal co-ordination mode of the tetrazole has been seen previously in 1,2-$(Bu_3SnN_4C)_2C_6H_4$,[2] [2-$(Bu_3SnN_4C)CH_2CH_2]_3CNO_2$[3] and 1,3,5-$(Bu_3SnN_4C)_3C_6H_3$[3] though in each of these cases the Sn–N bonds are sufficiently similar to render the N–Sn and N:→Sn interactions indistinguishable. The data for **7a** allow such a distinction and, surprisingly, it is the more hindered N^1 site [N(1)] which forms the stronger bond. However, AM1 calculations place the highest negative charge on the N^1 site[19,20] and, where steric factors allow *e.g.* $\{M(H_2O)_2[\mu\text{-}H_2B(N_4CH)_2]\}_n$,[13] this becomes the favoured position for metal binding.

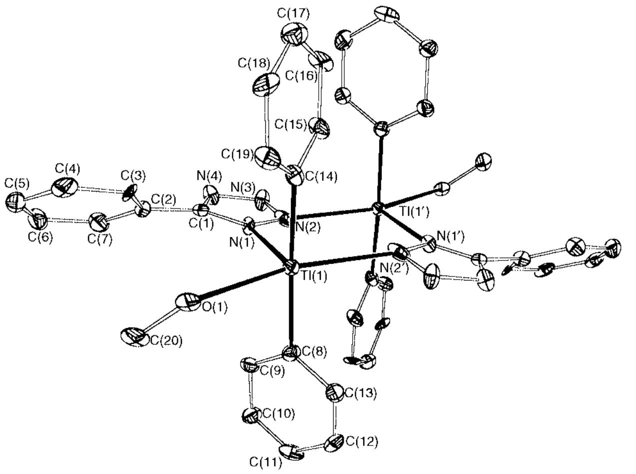


Fig. 2 The structure of compound **7a** showing the atomic labelling used in the text. Thermal ellipsoids are at the 30% probability level. Selected metric data: Tl(1)–C(8) 2.13(1), Tl(1)–C(14) 2.12(1), Tl(1)–N(1) 2.512(9), Tl(1)–N(2′) 2.680(9) and Tl(1)–O(1) 2.691(7) Å; C(8)–Tl(1)–C(14) 173.9(4), C(8)–Tl(1)–N(1) 94.1(3), C(14)–Tl(1)–N(1) 92.0(3), C(8)–Tl(1)–N(2′) 90.1(4), C(14)–Tl(1)–N(2′) 89.9(3), N(1)–Tl(1)–N(2′) 93.9(3), C(8)–Tl(1)–O(1) 88.6(3), C(14)–Tl(1)–O(1) 89.2(3), N(1)–Tl(1)–O(1) 106.8(2) and N(2′)–Tl(1)–O(1) 159.3(3)°.

The dominant feature of compound **7a** is the six-membered Tl_2N_4 ring generated by the dimerisation of asymmetric units. The six-membered Tl_2N_4 ring of **7a** adopts a slight chair conformation with a fold angle of 8.5°; the two thallium atoms are displaced 0.26(2) Å above and below the plane formed by the four nitrogens. One other structure, (benzotriazolato)thallium(I),[7] also incorporates this ring in alternating chair (fold angle: 46.2°) and boat (fold angle: 72.9°) conformations. The flexibility of the Tl_2N_4 ring is also manifest in the structures of **11** and **12**, described below. The only other relevant structure available for comparison is the eight-membered $(TlNCS)_2$ ring seen in tetrameric (4-amino-5-sulfanyl-3-trifluoromethyl-1,2,4-triazolato)dimethylthallium(III).[6]

The supramolecular structure of compound **7a** reveals that the dimers described above further interact to generate one-dimensional polymers along *a* due to intermolecular hydrogen bonding (Fig. 3), brought about by H(1A) bonding to N(4) of the residue generated by the transformation $x - 1, y, z$ [H(1A)–N(4) 1.9(2) Å]. One-dimensional chains build up further to generate a square grid arrangement with the centre of each square occupied by the various phenyl groups, which either stack (interplane separation *ca.* 3.5 Å) or are orthogonal to each other (C–H · · · ring plane *ca.* 3.0 Å). The view of **7a** projected in the *ac* plane consists of alternating six-membered (Tl_2N_4) and twelve-membered $(NTlOHN_2)_2$ rings. The equatorial ligands bonded to each thallium adopt a T arrangement [N(1)–Tl(1)–O(1) 106.8(2); N(1)–Tl(1)–N(2′) 93.9(3); N(2′)–Tl(1)–O(1) 159.3(3)°] and it is tempting to ascribe this to the formation of these two types of ring system. However, such distortions, previously termed pseudo-octahedral, are by no means unique amongst thallium compounds [*e.g.* dimethyl(tryptophanato)thallium][21] though no explanation of their general origin has been offered.

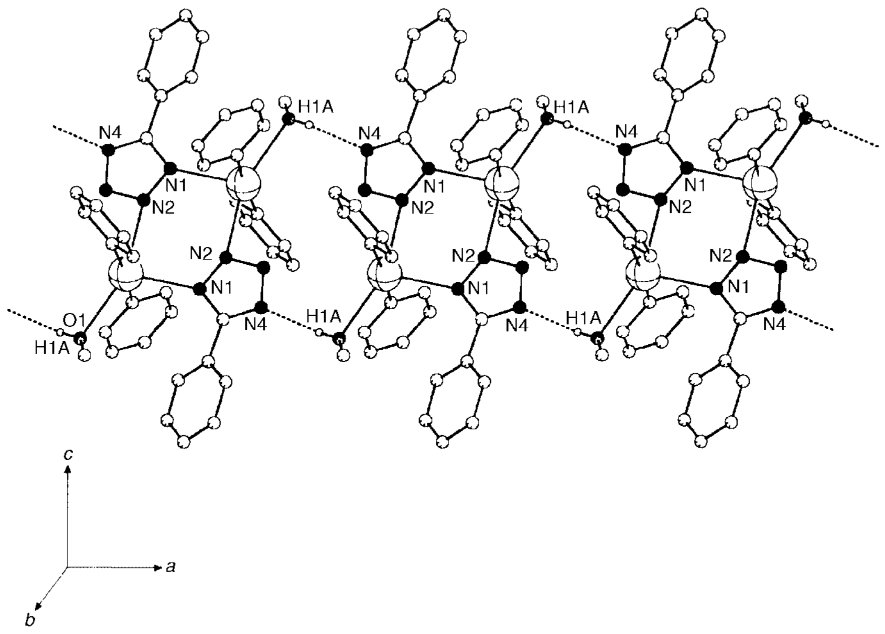


Fig. 3 The unit cell of compound **7a** shown perpendicular to the *ac* plane.

Including hydrogen bonding, the tetrazole unit is tridentate and exhibits $N^1 + N^2 + N^4$ co-ordination. Tridentate co-ordination of the tetrazole moiety has been observed in $\{M(H_2O)_2[H_2B(CN_4H)_2]_2\}\cdot 2H_2O$ (M = Co, Zn or Cd),[13,19] where N^1 and N^4 are co-ordinated to a boron and a metal atom respectively and N^2 is hydrogen bonded to a water of crystallisation.

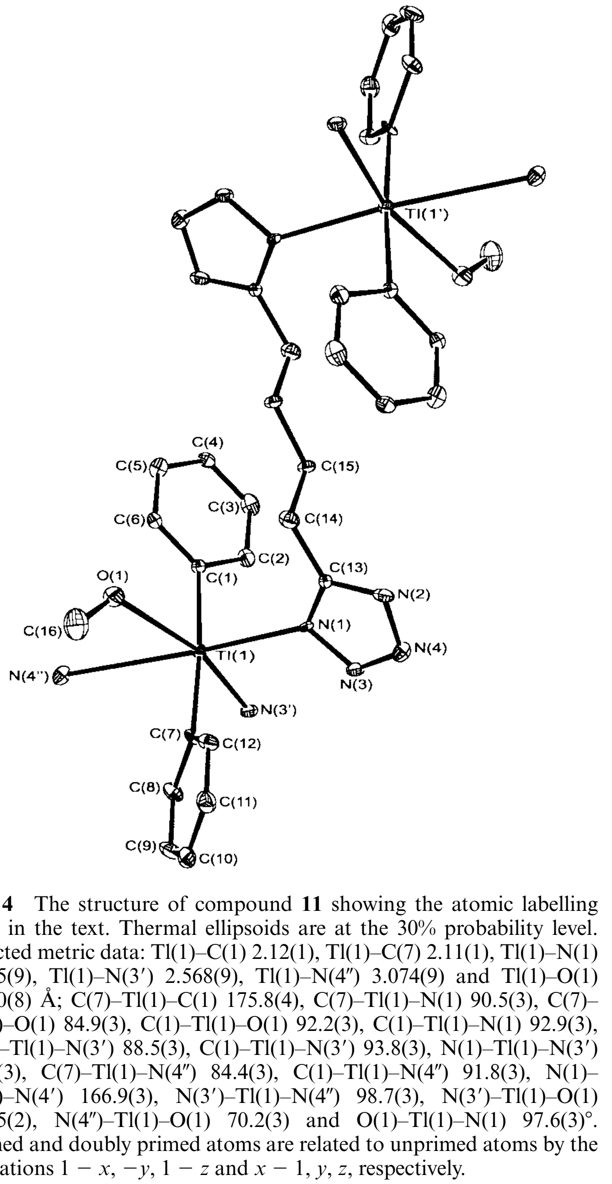


Fig. 4 The structure of compound **11** showing the atomic labelling used in the text. Thermal ellipsoids are at the 30% probability level. Selected metric data: Tl(1)–C(1) 2.12(1), Tl(1)–C(7) 2.11(1), Tl(1)–N(1) 2.535(9), Tl(1)–N(3′) 2.568(9), Tl(1)–N(4″) 3.074(9) and Tl(1)–O(1) 2.970(8) Å; C(7)–Tl(1)–C(1) 175.8(4), C(7)–Tl(1)–N(1) 90.5(3), C(7)–Tl(1)–O(1) 84.9(3), C(1)–Tl(1)–O(1) 92.2(3), C(1)–Tl(1)–N(1) 92.9(3), C(7)–Tl(1)–N(3′) 88.5(3), C(1)–Tl(1)–N(3′) 93.8(3), N(1)–Tl(1)–N(3′) 93.2(3), C(7)–Tl(1)–N(4″) 84.4(3), C(1)–Tl(1)–N(4″) 91.8(3), N(1)–Tl(1)–N(4′) 166.9(3), N(3′)–Tl(1)–N(4″) 98.7(3), N(3′)–Tl(1)–O(1) 167.5(2), N(4″)–Tl(1)–O(1) 70.2(3) and O(1)–Tl(1)–N(1) 97.6(3)°. Primed and doubly primed atoms are related to unprimed atoms by the operations $1 - x$, $-y$, $1 - z$ and $x - 1$, y, z, respectively.

Compound 11. Crystals of 1,4-bis[1-(diphenylthallyl)tetrazol-5-yl]butane–methanol (1/2) **11** were grown by slow evaporation of a methanolic solution at room temperature. The asymmetric unit of **11** is one half of the molecule (Fig. 4) the complete molecular unit being generated by an inversion centre lying halfway along the bridging butyl chain proximate to C(15). The thallium is in a distorted octahedral, *trans*-C_2TlN_3O environment, with the two phenyl groups axial [C(1)–Tl(1)–C(7) 175.8(4)°] and the equatorial positions occupied by three tetrazolic nitrogens [N(1), N(3), N(4)] and oxygen of the methanol [O(1)]. With one exception the four equatorial bond angles are close to 90° [N(1)–Tl(1)–N(3′) 93.2(3), N(3′)–Tl(1)–N(4″) 98.7(3), N(4″)–Tl(1)–O(1) 70.2(3), O(1)–Tl(1)–N(1) 97.6(3)°] while the dative Me(H)O:→Tl bond [Tl(1)–O(1) 2.970(8) Å] is longer than that in **7a** [Tl(1)–O(1) 2.691(7) Å]. The covalent Tl(1)–N(1) bond [2.535(9) Å] and bridging Tl(1)–N(3′) bond [2.568(9) Å] are similar to the covalent Tl–N bond length seen in **7a** [2.512(9) Å], however the bridging Tl(1)–N(4″) [3.074(9) Å] is distinctly longer. Although the distinction is less clear cut than in **7a**, N^1 again appears to be the preferred bonding site for thallium(III). The $N^1 + N^2 + N^3$ mode of co-ordination of the tetrazole ring with respect to the metal centre is unique.

The supramolecular structure reveals polymeric sheets of molecules at unit cell intervals along *b*, where all nitrogens play a role in bonding (Fig. 5). Viewed in the *ac* plane, each polymeric sheet consists of stacks of six-membered Tl_2N_4 connected by $-(CH_2)_4-$ moieties. Within each stack there are two kinds of these rings and these alternate with each other. The formation of the first ring is brought about by Tl(1) bonding to N(3′) of the tetrazole generated by the symmetry operator $1 - x$, $-y$, $1 - z$ and as such it resembles the Tl_2N_4 rings in compound **7a**. Like the latter, the rings in **11** are also chair-shaped but this conformation is now more pronounced: the two thallium atoms are displaced 0.89(2) Å above and below the plane of the four nitrogens and the fold angle of the chair is 30.4°. Whereas in **7a** the Tl_2N_4 rings further interact to form one-dimensional polymers *via* intermolecular hydrogen bonding, in **11** the Tl_2N_4 rings are held together by an additional long Tl–N bond. Thus, Tl(1) bonds to N(4″) in the lattice neighbour generated by $x - 1$, y, z and this leads to the formation of a second, flatter, six-membered Tl_2N_4 ring [Tl displacement from N_4 plane: 0.31(2) Å; fold angle 9.8°]. As noted above, the Tl(1)–N(4″) bond [3.074(9) Å] is much longer than the Tl(1)–N(3′) bridge and

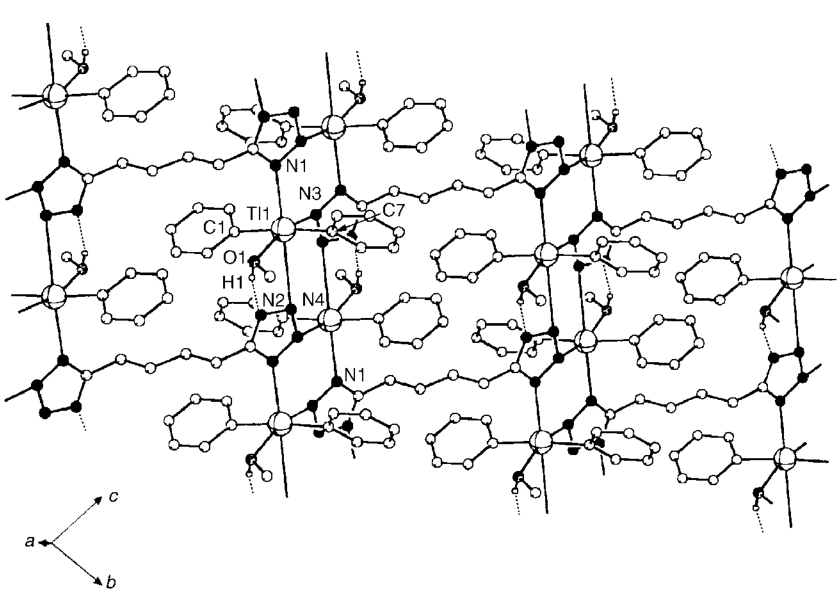


Fig. 5 The lattice structure of compound **11** viewed approximately perpendicular to the *bc* plane.

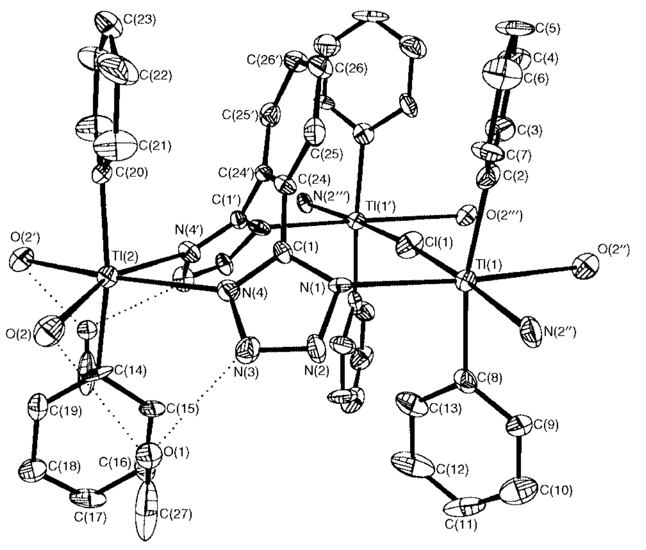


Fig. 6 The structure of compound **12** showing the atomic labelling used in the text. Thermal ellipsoids are at the 30% probability level. Selected metric data: Tl(1)–C(2) 2.12(2), Tl(1)–C(8) 2.11(2), Tl(1)–N(1) 2.60(1), Tl(1)–N(2″) 2.87(1), Tl(1)–O(2′) 2.95(1), Tl(1)–Cl(1) 2.777(1), Tl(2)–C(14) 2.08(2), Tl(2)–C(20) 2.10(2), Tl(2)–N(4) 2.61(1) and Tl(2)–O(2) 2.95(1) Å; C(2)–Tl(1)–C(8) 168.0(6), C(8)–Tl(1)–N(1) 94.2(5), C(2)–Tl(1)–N(1) 94.9(5), C(2)–Tl(1)–O(2″) 84.5(5), C(2)–Tl(1)–N(2″) 86.8(5), C(2)–Tl(1)–Cl(1) 94.6(5), C(8)–Tl(1)–Cl(1) 93.7(5), C(8)–Tl(1)–N(2″) 85.5(5), C(8)–Tl(1)–O(2″) 87.9(5), N(1)–Tl(1)–N(2″) 89.7(3), N(1)–Tl(1)–O(2″) 169.7(3), N(1)–Tl(1)–Cl(1) 86.7(3), Cl(1)–Tl(1)–N(2″) 176.2(3), Cl(1)–Tl(1)–O(2″) 83.1(2), C(14)–Tl(2)–C(20) 171.4(8), C(14)–Tl(2)–O(2) 82.7(4), C(20)–Tl(2)–O(2) 93.0(4), C(14)–Tl(2)–N(4) 95.4(6), C(20)–Tl(2)–N(4) 91.5(5), N(4′)–Tl(2)–N(4) 73.4(6), N(4)–Tl(2)–O(2′) 156.5(3), N(4)–Tl(2)–O(2) 83.4(4)°, O(2′)–Tl(2)–O(2) 119.4(4) and Tl(1′)–Cl(1)–Tl(1) 174.8(3)°. Primed atoms are generated by the mirror plane containing Tl(2) and Cl(1) and bisecting C(24)–C(24′), C(26)–C(26′); O(2″) is related to O(2) by $1 + x, y, z$ and N(2″) to N(2) by $-x, -y, -z$ while O(2″), N(2″) are related to the corresponding O(2‴), N(2‴) by the mirror plane which contains Cl(1).

requires additional stabilisation by the hydrogen bonding between N(2) and the methanol attached to Tl(1) [H(1) ··· N(2) 2.02(3) Å], which is comparable in strength to that in **7a** [H(1A) ··· N(4) 1.9(2) Å]. Considerable distortion of the co-ordination sphere about thallium is required to accommodate this hydrogen bond and it is particularly manifest in the acute N(4″)–Tl(1)–O(1) [70.2(3)°]. The ribbons of alternating six-membered rings are further connected by –(CH$_2$)$_4$– bridges to form sheets. The overall structure is in contrast to that of the related tin compound 1,6-(Bu$_3$SnN$_4$C)$_2$(CH$_2$)$_6$, which adopts a bi-layer structure.[22] Including hydrogen bonds each tetrazole is terdentate and exhibits an N^1 + N^2 + N^3 + N^4 mode of co-ordination, the first example of co-ordination saturation of a tetrazole.

Compound 12. X-Ray quality crystals of 1,2-bis[1-(diphenylthallyl)tetrazol-5-yl]benzene–diphenylthallium chloride–methanol–water (1/1/2/2) were grown slowly from a methanolic solution at room temperature. The asymmetric unit of compound **12** (Fig. 6) contains both 1,2-[Ph$_2$Tl(N$_4$C)]$_2$C$_6$H$_4$ and a co-ordinated Ph$_2$TlCl, which we assume was generated serendipitously by contamination of the Ph$_2$TlOH used in the synthesis with its precursor, Ph$_2$TlCl. Two water molecules and two molecules of the crystallisation solvent, methanol, complete the structure. The asymmetric unit consists of half this collective, the other half of the assembly being produced by a mirror plane containing Tl(2) and Cl(1) and bisecting C(24)–C(24′), C(26)–C(26′). The mirror plane also contains the phenyl ring C(14)–C(19) and it bisects the phenyl ring based on C(20)–C(23). There are two types of distorted octahedral thallium centres in the asymmetric unit, one of *trans*-C$_2$TlO$_2$N$_2$ stereochemistry [Tl(2)] and the other *trans*-C$_2$TlN$_2$OCl [Tl(1)]. In both cases, the phenyl groups are in axial positions [C(14)–Tl(2)–C(20) 171.4(8); C(2)–Tl(1)–C(8) 168.0(6)°]. The equatorial positions of Tl(1) are occupied by two *cis*-tetrazolic nitrogens, a bridging chlorine atom and an oxygen of a neighbouring water. The four equatorial bond angles show noticeable deviations from the ideal [N(1)–Tl(1)–Cl(1) 86.7(3), N(1)–Tl(1)–N(2″) 89.7(3), N(2″)–Tl(1)–O(2″) 100.5(3), Cl(1)–Tl(1)–O(2″) 83.1(3)°]. The Tl(1)–N(2″) bond [2.87(1) Å] is longer than Tl(1)–N(1) [2.60(1) Å], which is more in keeping with the covalent Tl–N bond lengths of **7a** [Tl(1)–N(1) 2.512(9) Å] and **11** [Tl(1)–N(1) 2.535(9) Å]. Again, as with **7a** and **11**, the preference for thallium binding in **12** is the more hindered N^1 position. The Tl(1)–O(2″) bond of 2.95(1) Å is only marginally longer than the Tl–O bond lengths of the H$_2$O:→Tl bond in (Me$_3$SiCH$_2$)$_2$TlN(SO$_2$Me)$_2$·H$_2$O [Tl–O 2.799(3), 2.813(3) Å][23] and is close to the Tl–O bond lengths resulting from a dative Me(H)O:→Tl co-ordination in **11** [2.970(8) Å] but longer than the analogous bond in **7a** [2.691(7) Å]. The bridging chlorine, which arises from the co-ordinated Ph$_2$TlCl, is equidistant from two thallium centres [Tl(1)–Cl(1) 2.777(1) Å]. The co-ordinated Ph$_2$TlCl is thus indistinguishable from the second thallium of the parent 1,2-(Ph$_2$TlN$_4$C)$_2$C$_6$H$_4$ fragment. The Tl–Cl bond is intermediate in length between reported terminal [*e.g.* TlCl$_3$·3C$_5$H$_5$N 2.520(6), 2.498(4) Å][24] and bridging Tl–Cl bond lengths [*e.g.* {(*p*-HC$_6$F$_4$)$_2$Tl(Cl)(OPPh$_3$)}$_2$: 2.936(3) Å].[25] The equatorial positions of Tl(2) are occupied by two *cis*-tetrazolic nitrogens and the oxygens of two water molecules. The four equatorial bond angles here show major deviations from 90° [O(2)–Tl(2)–N(4) 83.4(4), N(4)–Tl(2)–N(4′) 73.4(6), N(4′)–Tl(2)–O(2′) 83.4(4), O(2′)–Tl(2)–O(2) 119.4(4)°]. The Tl–N bond lengths [Tl(2)–N(4) 2.61(1) Å] are identical to the Tl(1)–N(1) bond length [2.60(1) Å] and again the preference for N^1 co-ordination is noteworthy. The Tl(2)–O(2) bond length of 2.95(1) Å is, fortuitously, exactly the same as Tl(1)–O(2′) and the same comments apply as made above.

With respect to the thallium centres, Tl(2) is co-ordinated to two N^1 atoms which is unusual as it involves the two most sterically sensitive pairs of nitrogen sites. N^1 + N^1 co-ordination is relatively rare but has been observed in 6-diphenylstannyl-2,3,4,5-tetrazabicyclo[3,4]nona-1,3-diene (though here the incorporation of tin into a bicyclic species is partly responsible)[1] and 1,2-(Et$_3$SnN$_4$C)$_2$C$_6$H$_4$.[2] Tl(1) is co-ordinated to tetrazole N^1 and N^2 sites which is also the case in compound **7a**. In all the structures reported here, however, it is the universal choice of N^1 as the primary binding site for thallium which serves to distinguish this series from the triorganotin analogues we have previously studied. Since the covalent radius of thallium is greater than that of tin this observation is at first sight surprising, however it seems reasonable to suggest that the *trans*-C$_2$Tl stereochemistry provides a more open metal centre than do the three hydrocarbon groups bonded equatorially to tin in a *trans*-N$_2$SnC$_3$ arrangement.

The supramolecular structure of compound **12** consists of polymeric sheets of molecules parallel to the *ab* plane (Fig. 7). The water molecules act as bridges between the thallium centres along the *a* direction. O(2) bonds to Tl(2) and also to Tl(1) of a lattice neighbour. The sheet is propagated in the *b* direction by Tl(1) bonding to N(2) generated by the symmetry operator $-x, -y, -z$. Methanol, as a guest in the lattice, cements these sheets by hydrogen bonding through O(1) to the tetrazolic nitrogen N(3) and O(2) of the water [N(3) ··· O(1) 2.77(2); O(1) ··· O(2) 2.82(2) Å]. The hydrogen bond between the tetrazolic nitrogen and the methanol oxygen is similar in length to the one seen in **11** [O(1)–N(2) 2.81(1) Å]. The sum total of all these interactions renders the oxygens of the water molecules four-co-ordinate and each tetrazole terdentate, the second example after **11** of N^1 + N^2 + N^3 + N^4 co-ordination.

The most striking feature of this lattice arrangement is the presence once again of the six-membered Tl$_2$N$_4$ ring in its mesh of interactions, which has previously been noted in compounds

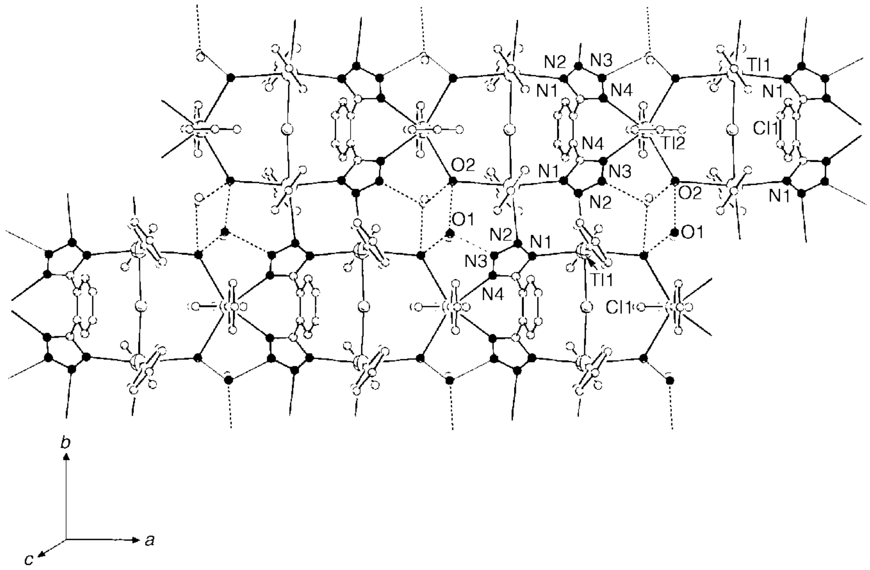


Fig. 7 The lattice structure of compound **12** viewed perpendicular to the *ab* plane.

7a and **11**. The formation of this ring, which involves only Tl(1) and not Tl(2), is brought about by the intermolecular bond formation between Tl(1) and N(2″) generated by the symmetry operator $-x$, $-y$, $-z$. As in **7a** and **11**, this ring is also a chair with a fold angle of 47.1° and the two thallium atoms displaced 1.41(3) Å above and below the plane of the four nitrogens. The Tl_2N_4 rings present in each of the compounds in the series have a wide diversity of fold angles [**7a** 8.5; **11** 9.8, 30.4; **12** 47.1°] and are thus extremely flexible in comparison with cyclohexane (fold angle *ca.* 55°).

Conclusion

Diorganothallium tetrazoles can be synthesized and differ structurally from their triorganotin counterparts. For thallium there is a pronounced preference for N^1 binding and the formation of lattices which incorporate very flexible Tl_2N_4 rings. Terdentate tetrazoles have been identified for the first time and highlight the structural versatility of this heterocycle in supramolecular chemistry.

Experimental

Spectra were recorded on the following instruments: JEOL GX270 (^{1}H, ^{13}C NMR) and Perkin-Elmer 599B (IR). For all compounds, infrared spectra were recorded as Nujol mulls on KBr plates or as KBr discs, and all NMR data on saturated solutions in $(CD_3)_2SO$ unless indicated otherwise.

Diphenylthallium azide and diphenylthallium hydroxide were prepared by the methods of Srivastava and Bajpai[26] and Casas *et al.*,[27] respectively. Tetrazoles were prepared by a cycloaddition between the appropriate nitrile and Bu_3SnN_3 followed by reaction with HCl.[28] All the other chemicals were purchased commercially and used without further purification. **CAUTION**: owing to their potentially explosive nature, all preparations and subsequent reactions with azides were conducted under an inert atmosphere behind a rigid safety screen.

Syntheses

Dithallium(I) 5,5′-methylenebis(tetrazolate) 1. A solution of thallium(I) ethoxide (0.44 g, 1.77 mmol) in absolute ethanol (15 cm^3) was added dropwise to a solution of bis(tetrazol-5-yl)methane (0.13 g, 0.86 mmol) in absolute ethanol (20 cm^3). A white precipitate was formed immediately, which was collected by filtration, washed with methanol and dried *in vacuo*. Yield 0.30 g, 63%, mp 290 °C (decomp.) [Found (Calc. for $C_3H_2N_8Tl_2$): C 6.5 (6.4); H 0.32 (0.36); N 20.1 (20.0)%]. ^{1}H NMR [D_2O solution]: δ 4.38 (s, 2H, CH_2). IR (cm^{-1}, KBr disk): 2966, 2947, 2905, 2874, 1483, 1469, 1454, 1379, 1271, 1182, 1118, 1113, 1099, 1089, 1049, 1018, 767 and 665.

Also prepared by the same methodology were the following compounds.

Dithallium(I) 5,5′-tetramethylenebis(tetrazolate) 2. White powder (75%), mp 242 °C [Found (Calc. for $C_3H_4N_4Tl$): C 12.1 (12.0); H 1.28 (1.34); N 18.5 (19.0)%]. ^{1}H NMR [D_2O solution]: δ 1.55 (m, 4H, $CH_2CH_2CH_2CH_2$) and 2.71 (m, 4H, $CH_2CH_2CH_2CH_2$). ^{13}C NMR [D_2O solution]: δ 23.4 ($CH_2CH_2CH_2CH_2$) and 27.1 ($CH_2CH_2CH_2CH_2$). IR (cm^{-1}, Nujol): 3405, 2955, 2855, 2726, 1734, 1601, 1460, 1377, 1310, 1146, 1127 and 1061.

Dithallium(I) 5,5′-*m*-phenylenebis(tetrazolate) dihydrate 3. White powder. Yield 70%, mp 300 °C (decomp.) [Found (Calc. for $C_4H_4N_4OTl$): C 14.5 (14.6); H 1.21 (1.23); N 16.5 (17.3)%]. ^{1}H NMR [D_2O solution]: δ 8.44 (t, 1H, *2*-C_6H_4), 7.95 (dd, 2H, *4,6*-C_6H_4; ^3J 7.6, ^4J 1.8 Hz) and 7.53 (t, 1H, *5*-C_6H_4). ^{13}C NMR [D_2O solution]: δ 163.5 (CN_4), 131.2 (*2*-C_6H_4), 130.4 (*1,3*-C_6H_4), 128.8 (*4,6*-C_6H_4) and 125.9 (*5*-C_6H_4). IR (cm^{-1}, KBr disk): 3352, 2959, 1653, 1427, 1375, 1331, 1194, 1128, 1082, 1028, 900, 804, 767, 744, 690 and 426.

Dithallium(I) 5,5′-*p*-phenylenebis(tetrazolate) 4. White powder. Yield 71%, mp 235 °C (decomp.) [Found (Calc. for $C_4H_2N_4Tl$): C 15.8 (15.4); H 0.62 (0.65); N 17.7 (18.3)%]. ^{1}H NMR: δ 7.98 (s, 4H, *2,3,5,6*-C_6H_4). ^{13}C NMR: δ 160.5 (CN_4), 131.0 (*1,4*-C_6H_4), 130.7 (*2,6*-C_6H_4) and 127.5 (*3,5*-C_6H_4). IR (cm^{-1}, Nujol): 2926, 2855, 1464, 1426, 1377, 1335, 1267, 1194, 1105, 1060, 1026, 851, 741, 725, 532, 482 and 422.

Trithallium(I) benzene-1,3,5-tris(tetrazolate) dihydrate 5. White powder (97%), mp 241 °C (decomp.). The product is not soluble in commonly available solvents [Found (Calc. for $C_9H_7N_{12}O_2Tl_3$): C 11.5 (11.7); H 0.64 (0.76), N 16.6 (18.0)%]. IR (cm^{-1}, KBr disk): 3414, 1616, 1414, 1190, 1128, 1032, 889, 787, 748, 682, 621 and 449.

Dithallium(I) 5,5′-azobis(tetrazolate) monohydrate 6 and bis[(1,4,7,10,13,16-tetraoxacyclooctadecane)thallium(I)] 5,5′-azobis(tetrazolate) 6a. Thallium(I) sulfate (0.80 g, 1.59 mmol) was dissolved in water (20 cm^3) and added dropwise to disodium 5,5′-azobis(tetrazolate)[12] in water (25 cm^3) at 95 °C. The solution was filtered hot and on cooling crystals of $[Tl]_2[C_2N_{10}]\cdot H_2O$ **6** formed [Found (Calc. for $C_2H_2N_{10}OTl_2$): C 5.08

(4.07); H 0.51 (0.34), N 23.6 (24.5)%]. This material (0.11 g, 0.19 mmol) was dissolved in hot ethanol (2 cm^3) along with 18-crown-6 (0.10 g, 0.39 mmol). Crystals of $[Tl(18\text{-crown-}6)^+]_2[C_2N_{10}^{2-}]$ **6a** deposited on cooling [Found (Calc. for $C_{13}H_{24}N_5O_6Tl$): C 27.9 (28.3); H 4.51 (4.40), N 12.5 (12.7)%]. IR (cm^{-1}, KBr disk): 3500, 2800, 1600, 1410, 1320, 1300, 1220 and 1200.

1-Diphenylthallyl-5-phenyltetrazole 7 and 1-diphenylthallyl-5-phenyltetrazole methanolate 7a. *Method 1.* Diphenylthallium azide (0.42 g, 1.3 mmol) was added to an excess of benzonitrile (20 cm^3) and the mixture stirred at 150 °C for 10 hours under N_2. The initial suspension became a clear solution and then after two hours turned yellow. On cooling to room temperature after 10 hours a white solid was obtained. The solid was collected by filtration, washed with hexanes and recrystallised from hot methanol to yield the anhydrous product as a white powder (**7**) mixed with some crystals of a methanol solvate (**7a**). Compound **7**: mp 244 °C (decomp.) [Found (Calc. for $C_{19}H_{15}N_4Tl$): C 45.1 (45.3); H 2.92 (3.01); N 11.0 (11.1)%]. ^{1}H NMR (100 °C): δ 8.24–7.21 (m, 15H, phenyl protons). ^{13}C NMR (100 °C): δ 161.0 (CN_4); 137.5, 135.5, 133.4, 132.3, 132.1, 130.0, 129.6, 128.5, 127.3, 126.0, 119.0 and 111.4 (phenyl carbons). IR (cm^{-1}, KBr disk): 3414, 3065, 1637, 1616, 1576, 1479, 1458, 1442, 1433, 1385, 1359, 1142, 1074, 1018, 1008, 997, 725, 688, 619 and 447. Compound **7a**: Found (Calc. for $C_{20}H_{19}N_4OTl$): C 43.8 (44.8); H 2.96 (3.58); N 10.8 (10.5)%].

Method 2. A solution of 5-phenyltetrazole (0.05 g, 0.35 mmol) in methanol (50 cm^3) was added dropwise to a well stirred solution of diphenylthallium hydroxide (0.13 g, 0.35 mmol) in hot methanol (200 cm^3). The resultant clear solution was refluxed for 3 hours. Hot filtration afforded a clear solution, which on cooling gave compound **7a** as a white solid (0.14 g, 80%), mp 206 °C (decomp.) [Found: C 44.4; H 2.96; N 10.9%]. ^{1}H NMR (80 °C): δ 8.39–7.20 (m, phenyl protons) and 3.24 (s, 3H, CH_3OH). ^{13}C NMR (80 °C): δ 160.6 (CN_4), 137.6, 134.6, 132.2, 130.5, 127.9, 126.7 and 125.7 (phenyl carbons). IR (cm^{-1}, KBr disk): 3408, 3042, 1616, 1576, 1479, 1458, 1442, 1431, 1385, 1359, 1261, 1142, 1099, 1074, 1022, 1008, 997, 729, 690 and 449.

The following compounds were also prepared by the same method as for **7** (Method 2).

1,3-Bis[1-(diphenylthallyl)tetrazol-5-yl]benzene dihydrate 8. From 1,3-bis(tetrazol-5-yl)benzene (0.03 g, 0.15 mmol) in methanol (80 cm^3) with diphenylthallium hydroxide (0.11 g, 0.29 mmol) in hot methanol (220 cm^3). White powder (0.12 g, 85%), mp 228 °C (decomp.) [Found (Calc. for $C_{16}H_{14}N_4OTl$): C 40.0 (39.8); H 2.70 (2.90); N 11.5 (11.6)%]. ^{1}H NMR (80 °C): δ 8.70–7.20 (m, phenyl protons). ^{13}C NMR (80 °C): δ 160.9 (CN_4), 134.8, 132.8, 132.3, 130.3, 127.9, 126.0, 124.4 and 123.7 (phenyl carbons). IR (cm^{-1}, KBr disk): 3414, 1637, 1616, 1574, 1516, 1479, 1433, 1385, 1309, 1261, 1217, 1136, 1018, 997, 804, 767, 742, 727, 690 and 619.

Bis[1-(diphenylthallyl)tetrazol-5-yl]methane dihydrate 9. From bis(tetrazol-5-yl)methane (0.02 g, 0.14 mmol) in methanol (40 cm^3) with diphenylthallium hydroxide (0.10 g, 0.27 mmol) in hot methanol (200 cm^3). White powder (0.06 g, 47%), mp 225 °C (decomp.) [Found (Calc. for $C_{27}H_{26}N_8O_2Tl_2$): C 36.7 (35.9); H 2.47 (2.88); N 11.8 (12.4)%]. ^{1}H NMR: δ 8.19–7.26 (10H, m, phenyl protons) and 4.20 (s, 2H, CH_2). ^{13}C NMR: δ 157.6 (CN_4); 138.1, 135.2, 128.4 (phenyl carbons) and 20.5 (CH_2). IR (cm^{-1}, KBr disk): 3047, 1952, 1576, 1481, 1471, 1433, 1383, 1300, 1192, 1130, 1091, 1057, 1030, 1020, 997, 760, 727, 692, 461 and 451.

1,2-Bis[1-(diphenylthallyl)tetrazol-5-yl]ethane dihydrate 10. From 1,2-bis(tetrazol-5-yl)ethane (0.03 g, 0.16 mmol) in methanol (70 cm^3) and diphenylthallium hydroxide (0.11 g, 0.29 mmol) in hot methanol (170 cm^3). Brown crystals (0.06 g, 35%) [Found (Calc. for $C_{14}H_{14}N_4OTl$): C 36.2 (36.7); H 3.33 (3.05); N 11.1 (12.2)%].^{1}H NMR (100 °C): δ 8.54–7.30 (phenyl protons) and 2.50 (s, 4H, CH_2CH_2). ^{13}C NMR (100 °C): δ 138.1, 134.9, 130.6, 129.4, 128.4, 128.0, 127.5, 125.9 (phenyl carbons), 22.6 (CH_2), 25.8 (CH_2). IR (cm^{-1}, KBr disk): 3410, 1618, 1574, 1479, 1433, 1408, 1329, 1203, 1143, 1070, 1018, 997, 729 and 688.

1,4-Bis[1-(diphenylthallyl)tetrazol-5-yl]butane dimethanolate 11. From 1,4-bis(tetrazol-5-yl)butane (0.02 g, 0.11 mmol) in methanol (20 cm^3) and diphenylthallium hydroxide (0.08 g, 0.21 mmol) in hot methanol (200 cm^3). Brown crystals (0.04 g, 41%), mp 192 °C (decomp.) [Found (Calc. for $C_{16}H_{18}N_4OTl$): C 38.9 (39.5); H 3.36 (3.70); N 11.4 (11.5)%]. ^{1}H NMR (100 °C): δ 8.30–7.26 (phenyl protons), 2.50 (m, 4H, $CH_2CH_2CH_2CH_2$), 1.62 (m, 4H, $CH_2CH_2CH_2CH_2$) and 3.19 (s, 3H, CH_3OH). ^{13}C NMR (100 °C): δ 137.7, 134.4, 130.5, 127.8, 125.8 (phenyl carbons), 26.4 ($CH_2CH_2CH_2CH_2$) and 22.9 ($CH_2CH_2CH_2CH_2$). IR (cm^{-1}, KBr disk): 3412, 3049, 2924, 1637, 1616, 1576, 1479, 1450, 1433, 1394, 1315, 1203, 1143, 1126, 1066, 1020, 997, 727, 690 and 449.

1,2-Bis-[1-(diphenylthallyl)tetrazol-5-yl]benzene–diphenylthallium chloride–water–methanol (1/1/2/2) 12. From 1,2-bis(tetrazol-5-yl)benzene (0.01 g, 0.06 mmol) in methanol (20 cm^3) and diphenylthallium hydroxide (0.04 g, *ca.* 0.12 mmol) contaminated with Ph_2TlCl in hot methanol (200 cm^3). Brown crystals (0.04 g), mp 34 °C (decomp.) [Found (Calc. for $C_{46}H_{46}ClN_8O_4Tl_3$): C 38.1 (38.8); H 3.11 (3.24); N 8.0 (7.9)%]. ^{1}H NMR: δ 7.20–7.42 (m, 34H, phenyl protons) and 3.39 (s, 6H, CH_3OH). ^{13}C NMR: δ 160.5 (CN_4); 138.1, 135.3, 131.0, 129.9, 128.2, 127.8 and 126.3 (phenyl carbons). IR (cm^{-1}, KBr disk): 3412, 3045, 1637, 1616, 1479, 1431, 1385, 1350, 1261, 1118, 1022, 999, 952, 910, 802, 754, 725, 690, 486 and 447.

1,4-Bis[1-(diphenylthallyl)tetrazol-5-yl]–diphenylthallium chloride–water (1/0.5/2) 13. From 1,4-bis(tetrazol-5-yl)benzene (0.03 g, 0.14 mmol) in methanol (90 cm^3) and diphenylthallium hydroxide (0.10 g, *ca.* 0.27 mmol) contaminated with Ph_2TlCl in hot methanol (150 cm^3). White powder (0.09 g), mp 218 °C (decomp.) [Found (Calc. for $C_{38}H_{33}ClN_8O_2Tl_{2.5}$): C 39.0 (39.3); H 2.99 (2.87); N 10.4 (9.6)%]. ^{1}H NMR (80 °C): δ 8.50–7.00 (m, 24H, phenyl protons). ^{13}C NMR (80 °C): δ 160.7 (CN_4); 137.6, 134.6, 131.0, 130.5, 128.7 and 125.6 (phenyl carbons). IR (cm^{-1}, KBr disk): 3414, 1637, 1618, 1574, 1477, 1433, 1385, 1338, 1265, 1151, 1136, 1103, 1020, 1006, 997, 744, 727, 690, 482 and 453.

X-Ray crystallography

Crystal and experimental data are summarised in Table 1.

Compound 6a. A crystal of approximate dimensions 0.5 × 0.45 × 0.45 mm was used for data collection. In the final least squares cycles all atoms were allowed to vibrate anisotropically.

Compound 7a. A crystal of approximate dimensions 0.5 × 0.4 × 0.4 mm was used. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant except in the case of the methanolic proton, H(1A) [attached to O(1)] which was located (although the esds on the fractional coordinates are large) and refined at a distance of 0.98(2) Å from the parent atom.

Compound 11. A crystal of approximate dimensions 0.2 × 0.1 × 0.1 mm was used. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant.

Table 1 Crystal and experimental data

	6a	**7a**	**11**	**12**
Empirical formula	$C_{26}H_{48}N_{10}O_{12}Tl_2$	$C_{20}H_{19}N_4OTl$	$C_{16}H_{18}N_4OTl$	$C_{46}H_{46}ClN_8O_4Tl_3$
Formula weight	1101.5	535.8	486.7	1423.5
T/K	293(2)	170(2)	170(2)	293(2)
Space group	$P2_1/n$	$P\bar{1}$(no. 2)	$P\bar{1}$(no. 2)	$P2_1/m$
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
a/Å	11.922(2)	8.413(3)	7.596(2)	11.041(2)
b/Å	8.500(1)	9.509(3)	9.862(2)	17.520(5)
c/Å	19.517(3)	12.148(5)	11.388(1)	12.406(2)
α/°		81.02(3)	108.88(2)	
β/°	104.41(1)	78.17(3)	97.69(3)	105.21(2)
γ/°		85.76(3)	92.10(1)	
V/Å^3	1915.6	938.6(6)	797.0(3)	2315.7(9)
Z	2	2	2	2
μ/mm^{-1}	8.469	8.619	10.139	10.521
Reflections collected	2853	3946	3191	3987
Independent reflections	1710	2298	2234	3751
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0761, 0.1972	0.0342, 0.0978	0.0394, 0.1061	0.0563, 0.1320
(all data)	0.0772, 0.2024	0.0433, 0.1311	0.0420, 0.1065	0.1001, 0.1590

The thermal parameters of atoms in the phenyl ring containing C(1) were constrained as were those of atoms in the tetrazole ring.

Compound 12. A crystal of approximate dimensions 0.3 × 0.3 × 0.2 mm was used. Data were corrected for a mean 30% decay of the crystal in the X-ray beam. In the final least squares cycles all atoms were allowed to vibrate anisotropically except for O(1), where anisotropic refinement resulted in unsatisfactory thermal parameters. Hydrogen atoms were included at calculated positions where relevant, except for the methanolic hydrogen [attached to O(1)] and the two water hydrogens [attached to O(2)] which could not be located, even by examining a difference electron density map based on low Bragg angle data.

CCDC reference number 186/1865.

See http://www.rsc.org/suppdata/dt/a9/a910235n/ for crystallographic files in .cif format.

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