DALTON
FULL PAPER

Novel pyrazolate coordination modes and unusual Tl···Tl or Tl-π-(phenyl) interactions in the crystal structures of $[\{Tl_3(Ph_2pz)_3\}_n]$, $[\{Tl_4(Ph_2pz)_4\}_n]$, $[\{Tl_4(Ph_2pz)_3(OH)\}_2]$ and $[\{Tl_4(MePhpz)_3(OH)\}_n]$ (Ph_2pz = 3,5-diphenylpyrazolate; MePhpz = 3-methyl-5-phenylpyrazolate)

Glen B. Deacon,*[a] Ewan E. Delbridge,[a] Craig M. Forsyth,[a] Brian W. Skelton[b] and Allan H. White[b]

[a] *Department of Chemistry, Monash University, Vic. 3800, Australia*
[b] *Department of Chemistry, The University of Western Australia, Nedlands, W.A. 6907, Australia*

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$[Tl(Ph_2pz)]$ (Ph_2pz = 3,5-diphenylpyrazolate) crystallises in two forms. The first from benzene has trinuclear molecules $[Tl_3(Ph_2pz)_3]$ **1** linked by intermolecular Tl–π-η^6-Ph contacts. Within **1** the three thallium atoms are different, having coordination numbers of two (but also with the Tl···η^6-Ph contact), three and four, whilst μ-η^1:η^1, μ_3-η^1:η^2:η^1 and (the new) μ_3-η^1:η^1:η^1 modes of Ph_2pz coordination are observed. Crystallisation of $[Tl(Ph_2pz)]$ from 1,2-dimethoxyethane (dme) gives tetranuclear molecules $[Tl_4(Ph_2pz)_4]$ **2** solvated by dme. Three or four coordinate Tl atoms are observed with μ_3-η^1:η^2:η^1 and μ_3-η^1:η^1:η^1-pyrazolate coordination. In addition there is an intermolecular Tl–π-η^3-Ph interaction linking the tetranuclear molecules into a polymer, and sundry intramolecular Tl···C contacts, the most important of which is an unsymmetrical Tl–π-η^5-Ph_2pz interaction. Crystallisation of $[Tl(Ph_2pz)]$ or [Tl(MePhpz)] (MePhpz = 3-methyl-5-phenylpyrazolate) from dichloromethane afforded the partially hydrolysed tetranuclear cages $[Tl_4(Ph_2pz)_3(OH)]$ **3** or $[Tl_4(MePhpz)_3(OH)]$ **4**, which associate to give a dimer and a polymer respectively owing to Tl···Tl interactions, supported for the dimer by an intercage distant Tl–π-η^5-Ph_2pz contact. Complex **3** features three and four coordinate Tl atoms and μ_3-η^1:η^2:η^1 and μ_3-η^1:η^1:η^1-pyrazolate binding, whilst **4** has three, four and five coordinate thallium atoms and solely μ_3-η^1:η^2:η^1-pyrazolate ligands.

Introduction

There has been a recent proliferation of new bonding modes for pyrazolate (pz) ligands.[1–6] In addition η^2-binding[7,8] has unexpectedly been extended from f-block[7–11] to d-block[12–16] and main group[17] elements. However, these developments do not necessarily exhaust the coordination versatility of these ligands. Thallium(I) pyrazolates are of particular structural interest since the low charge limits the nitrogen donor atoms available per thallium, opening the way for novel binding modes. In the sole reported structure of a thallium(I) pyrazolate,[18] $[Tl(pypz)]_n$ [pypz = 3-(2′-pyridyl)pyrazolate] the ligand has the common[9,19–22] μ-η^1:η^1 ligation of the pyrazolate ring to two thallium atoms to give an overall polymeric structure. In addition each thallium has a pyridine nitrogen coordinated giving overall three coordination. Ferrocenyltris(3-*tert*-butylpyrazolyl)boratothallium(I) has a related structure.[23] Coordination of 3,5-disubstituted pyrazolate ligands such as 3,5-diphenylpyrazolate (Ph_2pz) and 3-methyl-5-phenylpyrazolate (MePhpz) to thallium should give quite different structures, since there are no auxiliary lone pairs on the ligand substituents to support μ-η^1:η^1 coordination and the substituents may cause steric constraints. Thus, thallium may seek coordination saturation by less usual means such as weak Tl···Tl[24–29] Tl···arene[30–36] interactions, both of which have recently been observed *together* in a thallium(I) amide.[36] The observation of the first examples of η^5-pyrazolate binding[6] suggests that thallium could also adopt the μ-η^5:η^5-coordination mode, which is well established in thallium(I) cyclopentadienides,[37] as an alternative to N-bonding. We have recently reported syntheses of several new thallium(I) pyrazolate complexes for use as reagents in the preparation of lanthanoid(II) pyrazolates by redox transmetallation reactions,[10,11] but could not obtain crystals suitable for X-ray study. Further investigation has overcome this problem and we report the crystal structures of two forms of $[Tl(Ph_2pz)]$, and of the adventitious hydrolysis products of $[Tl(Ph_2pz)]$ and [Tl(MePhpz)], *viz.* $[Tl_4(RR'pz)_3(OH)]$ (R = R′ = Ph; R = Me, R′ = Ph). These fulfil the expectation of structural versatility including observation of a new pyrazolate coordination mode.

Results and discussion

Source of crystals

Both $[Tl(Ph_2pz)]$ and [Tl(MePhpz)] were prepared by reaction (1).[10,11]

$$TlOEt + RR'pzH \longrightarrow [Tl(RR'pz)] + EtOH \quad (R = R' = Ph \text{ or } R = Me, R' = Ph) \quad (1)$$

Crystallisation of $[Tl(Ph_2pz)]$ from benzene and 1,2-dimethoxyethane (dme) yielded two different forms of the compound, each suitable for X-ray study. In addition, a few single crystals of $[Tl_4(Ph_2pz)_3(OH)]$ and $[Tl_4(MePhpz)_3(OH)]$, were obtained from attempts to crystallise $[Tl(Ph_2pz)]$ and [Tl(MePhpz)] from CH_2Cl_2, when partial hydrolysis occurred (reaction (2)).

$$4[Tl(RR'pz)] + H_2O \longrightarrow [Tl_4(RR'pz)_3(OH)] + RR'pzH \quad (2)$$

The infrared spectrum of $[Tl_4(Ph_2pz)_3(OH)]$ **3** has a weak but sharp absorption at 3517 cm^{-1} attributable to ν(OH).

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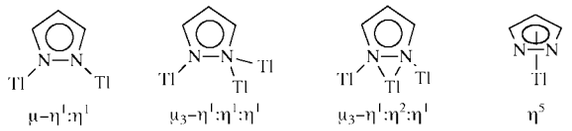


Fig. 1 The different pyrazolate bonding modes to thallium.

Structural studies

General. The results of low temperature single crystal X-ray studies of the two forms of $[Tl(Ph_2pz)]$ and the two $[Tl_4(RR'pz)_3(OH)]$ complexes are consistent with assignment in terms of stoichiometry and connectivity as tri- and tetranuclear species:

(*a*) $[Tl_3(Ph_2pz)_3]$, **1**, from benzene
(*b*) $[Tl_4(Ph_2pz)_4]\cdot$dme, **2**·dme, from dme
(*c*) $[Tl_4(Ph_2pz)_3(OH)]\cdot CH_2Cl_2$, $\mathbf{3}\cdot CH_2Cl_2$
(*d*) $[Tl_4(MePhpz)_3(OH)]\cdot 0.5CH_2Cl_2$, $\mathbf{4}\cdot 0.5CH_2Cl_2$

The structures demonstrate a diverse array of Tl–pyrazolate bonding modes, *viz.* μ-η¹:η¹, μ₃-η¹:η¹:η¹, μ₃-η¹:η²:η¹ and η⁵ (Fig. 1). Although the first mode is well known, especially for d-block elements,[9,19–22] the third has previously been observed only once, *viz*. in coordination to potassium,[1] the last has only recently been reported *viz.* in bonding to ruthenium,[6] whilst μ₃-η¹:η¹:η¹ is a new type of pyrazolate coordination. In addition significant Tl···π-Ph and Tl···Tl interactions are observed and give rise to associated structures (below). The overall features of the individual structures are considered first, and then Tl–N bond distances, bond angles and bonding are discussed for all structures.

(*a*) $[Tl_3(Ph_2pz)_3]$, 1. The molecular structure of **1** contains three different thallium centres, Tl(1), Tl(2) and Tl(3), which lie in an approximate equilateral triangle with separations of 4.023(2), 4.109(2) and 4.487(1) Å, and are coordinated by 4, 3 and 2 nitrogen atoms respectively (Fig. 2(*a*)). The Tl···Tl separations (4.023(2), 4.109(2), 4.487(1) Å) exceed the sum of two van der Waals radii of thallium (3.94 Å)[38] and hence are considered non-bonding. Proposals of weak Tl···Tl bonds at distances of 3.49–4.06 Å[24–29] have been reported, but we consider that interactions at values beyond two van der Waals radii are highly problematical.†

Each pyrazolate ligand adopts a different bridging mode with pz1 having the new μ₃-η¹:η¹:η¹ arrangement, pz2 μ₃-η¹:η²:η¹ ligation, only once previously observed,[1] and pz3 the common μ-η¹:η¹ mode. Two ligands, pz1 and pz2, interact with all three thallium centres (Fig. 2(*a*)). The planes of two ligands, pz1 and pz2, lie normal to the Tl_3 plane whilst pz3 lies more oblique to the Tl_3 plane and bridges Tl(1) and Tl(2). Four coordinate Tl(1) and three coordinate Tl(2) are linked to all three Ph_2pz ligands, whilst Tl(3) is ligated solely by pz1 and pz2.

With only two nitrogens coordinated to Tl(3), and in a cisoid arrangement (N(12)–Tl(3)–N(22) 81.5(5)°), there is a substantial gap in the coordination sphere (Fig. 2(*a*)). From the extended molecular array (Fig. 2(*b*)), there is a close approach of a phenyl group (C(151)–C(156)) of each trinuclear unit to the partly naked Tl(3) on an adjacent unit (Tl···C range 3.36(2)–3.60(2) Å). Accordingly each $[Tl_3(Ph_2pz)_3]$ cage is considered linked to a neighbour by a Tl(3)–(π-η⁶-Ph) interaction (Table 1), thereby forming a one-dimensional polymeric chain $(\mathbf{1})_n$. In addition to these contacts, there are four other intermolecular Tl···C distances of a similar magnitude (Table 1) but, unlike the Tl(3)···η⁶-Ph interactions, these other contacts do not appear to have a significant influence on the overall arrangement of $(\mathbf{1})_n$. The Tl···C intermolecular separations

† Note added at proof: this interpretation of Tl···Tl distances is consistent with a new report.[51]

Table 1 Selected geometries (Å) for $[Tl_3(Ph_2pz)_3]$ **1**

Strongly bonded interactions			
Tl(1)–N(11)	2.71(2)	Tl(2)–N(21)	2.74(2)
Tl(1)–N(21)	2.68(2)	Tl(2)–N(32)	2.69(2)
Tl(1)–N(22)	2.89(2)	Tl(3)–N(12)	2.68(2)
Tl(1)–N(31)	2.61(2)	Tl(3)–N(22)	2.63(2)
Tl(2)–N(12)	2.67(2)		
Intercage Tl···C interactions			
Tl(3)···C(151′)	3.59(2)	Tl(3)···C(156′)	3.60(2)
Tl(3)···C(152′)	3.46(2)	Tl(3)···C(331′)	3.45(2)
Tl(3)···C(153′)	3.39(3)	Tl(3)···C(336′)	3.53(2)
Tl(3)···C(154′)	3.36(2)	Tl(2)···C(153″)	3.56(3)
Tl(3)···C(155′)	3.49(2)	Tl(2)···C(154″)	3.40(2)

Transformations of the asymmetric unit: $'\ \frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$. $''\ x-1, y, z$.

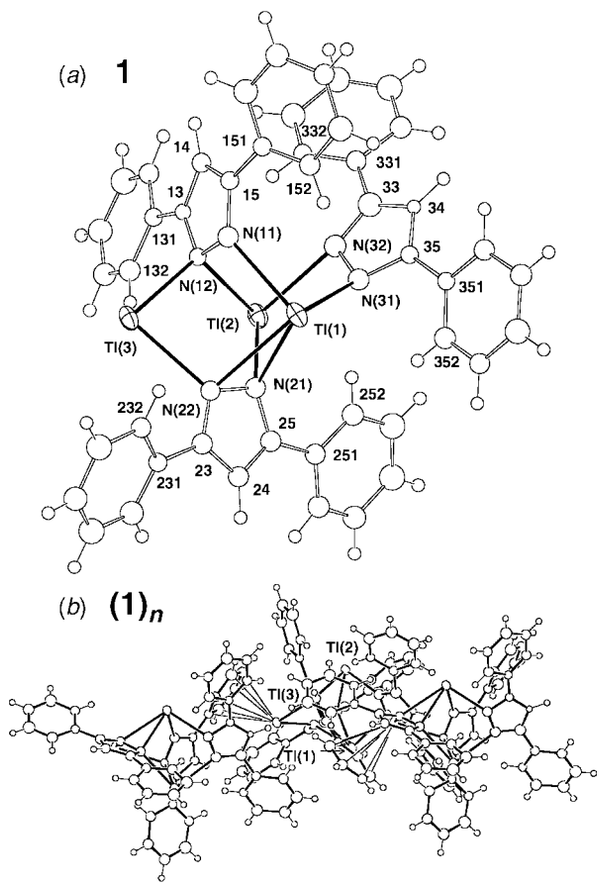


Fig. 2 (*a*) A projection of **1** oblique to the Tl_3 plane. 50% thermal envelopes are shown for the non-hydrogen atoms, here and in Fig. 3–5. Hydrogen atoms, where displayed, have arbitrary radii of 0.1 Å. (*b*) A projection of the extended molecular array of **1** formed by the Tl(3)···η⁶-Ph{C(151′)–C(156′)} intercage interactions.

are similar to the range 3.34–3.74 Å recently associated with weakly attractive η⁶-phenyl···Tl contacts in $[Tl_3\{(Me_3SiNCH_2)_3CPh\}]$.[36] In $(\mathbf{1})_n$, ⟨Tl···C⟩ (3.48 Å) is near the upper limit of the range (3.10–3.50 Å[32–35]) for Tl–C bonds in complexes with discrete arenes η⁶-bonded to Tl^+, but is much longer than the Tl–C bonds of thallium cyclopentadienides.[37] As ⟨Tl···C⟩ of $(\mathbf{1})_n$ is near to the sum (3.7 Å) of the van der Waals radii of Tl^+ [38] and an arene ring,[39] the present Tl···C contacts are perhaps best viewed as supramolecular[40] interactions which fill the large gap in the Tl(3) coordination sphere.

(*b*) $[Tl_4(Ph_2pz)_4]\cdot$dme, 2·dme. The molecular structure of **2** (Fig. 3(*a*)) contains a tetrahedron of Tl atoms with non-bonding (see above) separations of 4.179(1)–4.599(1) Å, and with even longer distances (≥5.265(1) Å) between Tl atoms of

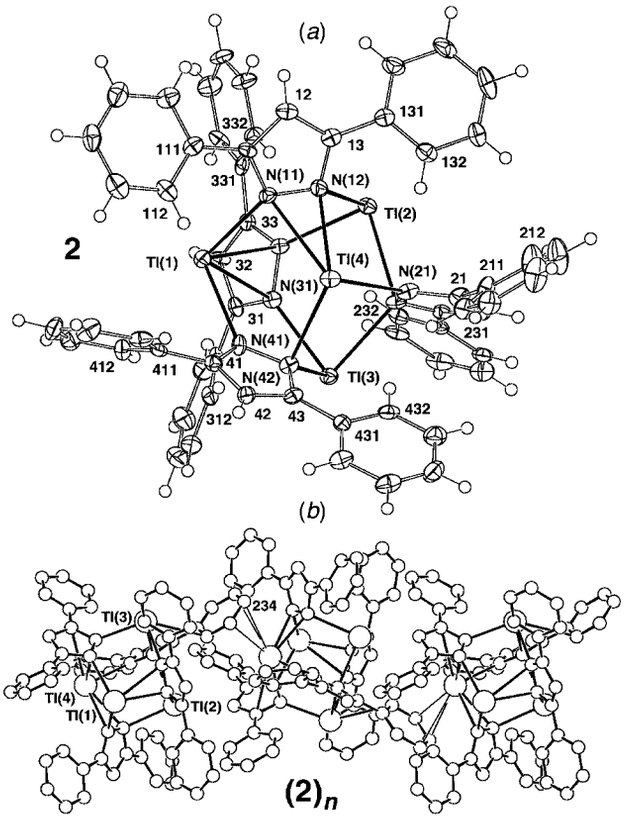


Fig. 3 (*a*) A projection of **2** showing the tetranuclear thallium cage. (*b*) A projection of the extended molecular array of **2** formed by the Tl(4)···η^3-Ph{C(233′)–C(235′)} intercage interactions.

adjacent tetranuclear units. Binding of pyrazolate nitrogens gives four coordination for Tl(1) and Tl(4) and three coordination for the other Tl atoms. One bridging ligand caps each face of the Tl_4 tetrahedron.

Two pyrazolate ligands, pz1 and pz3, exhibit μ_3-η^1:η^2:η^1-coordination. The first binds η^2 to Tl(4) and is η^1-linked to Tl(1) and Tl(2), whilst the second is η^2-bonded to Tl(1) and η^1 to Tl(2) and Tl(3). By contrast, the other two, pz2 and pz4, bind in the new μ_3-η^1:η^1:η^1 mode to Tl(2,3,4) and Tl(1,3,4) respectively. Pairs of thallium atoms with the same coordination number have different coordination environments owing to the dispositions of the bridging ligands (Fig. 3(*a*)). The present Tl_4 tetrahedron, which has no Tl···Tl bonding and is supported entirely by bridging ligands, contrasts that in thallium(I) hydridotris(3-cyclopropylpyrazol-1-yl)borate,[27] which has only unsupported weak Tl···Tl bonds (3.6468(4) Å) holding the Tl_4 cluster together.

In addition to nitrogen coordination there are a considerable number of intramolecular Tl···C contacts and three intermolecular Tl···C contacts at <3.60 Å, the upper limit chosen for weakly attractive Tl···C binding in **1**, and a value just within the sum (3.73 Å) of the van der Waals radii of Tl[38] and an aromatic ring.[39] Because **2** has a larger surface area than **1**, intramolecular Tl···Ph contacts are more likely for **2** but it is less exposed for intermolecular interactions. Only the four coordinate Tl(4) has supramolecular interactions <3.60 Å to an adjacent tetranuclear cage. Contacts (3.38(1)–3.48(1) Å) with adjacent carbons (C(233)–C(235)) give rise to a Tl···η^3-Ph interaction, which links the Tl_4 units into a one-dimensional polymer $(\mathbf{2})_n$ (Fig. 3(*b*)). The remaining three Tl···C distances to this phenyl group (3.65(1)–3.77(1) Å) are significantly longer and we prefer to view them as essentially non-interacting, though we note another worker has used a 3.74 Å upper limit.[36] The most intriguing Tl···C intramolecular contacts are between Tl(1) and three pyrazolate carbons of ligand 3, providing an overall η^5-interaction with this ligand. However given the difference between the Tl–N (2.794(8), 2.953(8) Å) and the Tl···C distances, it may be more accurate to describe the interaction as η^2-(N_2) plus η^3-(C_3). Within the 3.60 Å limit, no other Tl···C_3(Ph_2pz) interaction is observed. In the main, the intramolecular contacts comprise an *ipso* C of a pyrazolate and an *ortho* C of the attached phenyl, sometimes together with the *ipso* phenyl carbon. Some Ph_2pz *ipso* carbons bridge two Tl atoms by two such contacts (Table 2).

Table 2 Selected geometries (Å) for $[Tl_4(Ph_2pz)_4]$ **2**

Strongly bonded interactions			
Tl(1)–N(11)	2.706(9)	Tl(3)–N(22)	2.682(9)
Tl(1)–N(31)	2.953(8)	Tl(3)–N(31)	2.597(9)
Tl(1)–N(32)	2.794(8)	Tl(3)–N(42)	2.542(8)
Tl(1)–N(41)	2.628(9)	Tl(4)–N(11)	2.932(9)
Tl(2)–N(12)	2.718(9)	Tl(4)–N(12)	2.757(9)
Tl(2)–N(22)	2.696(8)	Tl(4)–N(21)	2.632(9)
Tl(2)–N(32)	2.563(9)	Tl(4)–N(42)	2.878(9)
Intercage Tl···C interactions			
Tl(1)···C(11)	3.53(1)	Tl(2)···C(23)	3.35(1)
Tl(1)···C(112)	3.43(1)	Tl(2)···C(33)	3.49(1)
Tl(1)···C(31)	3.40(1)	Tl(2)···C(332)	3.46(1)
Tl(1)···C(33)	3.21(1)	Tl(3)···C(23)	3.34(1)
Tl(1)···C(41)	3.45(1)	Tl(3)···C(231)	3.40(1)
Tl(1)···C(411)	3.51(1)	Tl(3)···C(232)	3.20(1)
Tl(1)···C(412)	3.39(1)	Tl(3)···C(31)	3.49(1)
Tl(1)···C(32)	3.58(1)	Tl(3)···C(312)	3.31(1)
Tl(2)···C(13)	3.31(1)	Tl(3)···C(43)	3.56(1)
Tl(2)···C(131)	3.40(1)	Tl(4)···C(43)	3.18(1)
Tl(2)···C(132)	3.32(1)		
Intercage Tl···C distances			
Tl(4)···C(231′)[a]	3.77(1)	Tl(4)···C(234′)	3.38(1)
Tl(4)···C(232′)[a]	3.65(1)	Tl(4)···C(235′)	3.46(1)
Tl(4)···C(233′)	3.48(1)	Tl(4)···C(236′)[a]	3.65(1)

[a] Considered non-bonding.

(*c*) $[Tl_4(Ph_2pz)_3(OH)]\cdot CH_2Cl_2$, $3\cdot CH_2Cl_2$. This complex is comprised of a pair of $[Tl_4(Ph_2pz)_3(OH)]$ tetranuclear cages which are linked by a bond between Tl(1) and Tl(1′) (3.5317(6) Å) (Fig. 4(*a*)), and are related through an inversion centre located at the midpoint of Tl(1)···Tl(1′). The Tl···Tl separation is at the low end of those reported previously as weakly bonding (3.49–4.06 Å[24–29]) and is well within twice the Tl van der Waals radius.[38] Further it is *ca.* 0.1 Å shorter than the Tl···Tl bonds of the (unsupported) Tl_4 tetrahedron of thallium(I) hydridotris(3-cyclopropylpyrazol-1-yl)borate.[27] Thus, it must be considered a very significant interaction. Replacement of a Ph_2pz ligand of **2** by the much smaller hydroxide exposes a thallium centre sufficiently for a Tl···Tl bond to be formed. There is a tetrahedral array of the thallium atoms within the cages, and the pyrazolate supported Tl···Tl separations (3.9679(7)–4.4490(8) Å) are considered non-bonding. Six thallium atoms (Tl(1,3,4),Tl(1′,3′,4′)) in the dimer are arranged in a planar polytriangular grid (Fig. 4(*b*)). The structural view of **3** in Fig. 4(*a*) shows that, in each $[Tl_4(Ph_2pz)_3(OH)]$ cage, oxygen lies on one side of the grid whereas all the Ph_2pz ligands and Tl(2) lie on the other. Inclusion of the Tl···Tl bond leads to three four coordinate Tl atoms and one three coordinate (Tl(3)), by contrast with **2** which has two of each. Two very long Tl–N contacts (3.065(7), 3.130(7) Å) are considered pertinent (see later discussion). All thallium atoms except three coordinate Tl(3) have at least one long (>2.9 Å) Tl–N bond and Tl(4) has two. Two ligands, pz1 and pz3, are bonded μ_3-η^1:η^2:η^1 and one μ_3-η^1:η^1:η^1. The hydroxide near symmetrically bridges Tl(1), Tl(3) and Tl(4), whilst Tl(2) is ligated by all of pz1–3.

Within each cage, there are no structurally significant Tl···C contacts. However, there are interesting intercage contacts (Table 3). Tl(1′) is situated almost over the centre of the pz2 pyrazolate ring, and centrosymmetrically related Tl(1) has a

Table 3 Selected geometries (Å) for $[Tl_4(Ph_2pz)_3(OH)]$ **3**

Strongly bonded interactions			
Tl(1)–N(11)	2.613(6)	Tl(3)–O(0)	2.485(6)
Tl(1)–N(21)	2.933(7)	Tl(3)–N(12)	2.606(7)
Tl(1)–O(0)	2.432(6)	Tl(3)–N(31)	2.648(7)
Tl(2)–N(11)	3.065(7)	Tl(4)–O(0)	2.432(6)
Tl(2)–N(12)	2.737(7)	Tl(4)–N(22)	2.591(7)
Tl(2)–N(21)	2.722(7)	Tl(4)–N(31)	2.905(7)
Tl(2)–N(32)	2.642(7)	Tl(4)–N(32)	3.130(7)
Intercage Tl · · · C(N) and Tl · · · Tl interactions			
Tl(1′) · · · N(21)	3.390(7)	Tl(1′) · · · C(24)	3.562(8)
Tl(1′) · · · N(22)	3.511(7)	Tl(1′) · · · C(25)	3.411(8)
Tl(1′) · · · C(23)	3.606(8)	Tl(1) · · · Tl(1′)	3.5317(6)

Transformation of the asymmetric unit: ′ $1 - x, -y, 1 - z$.

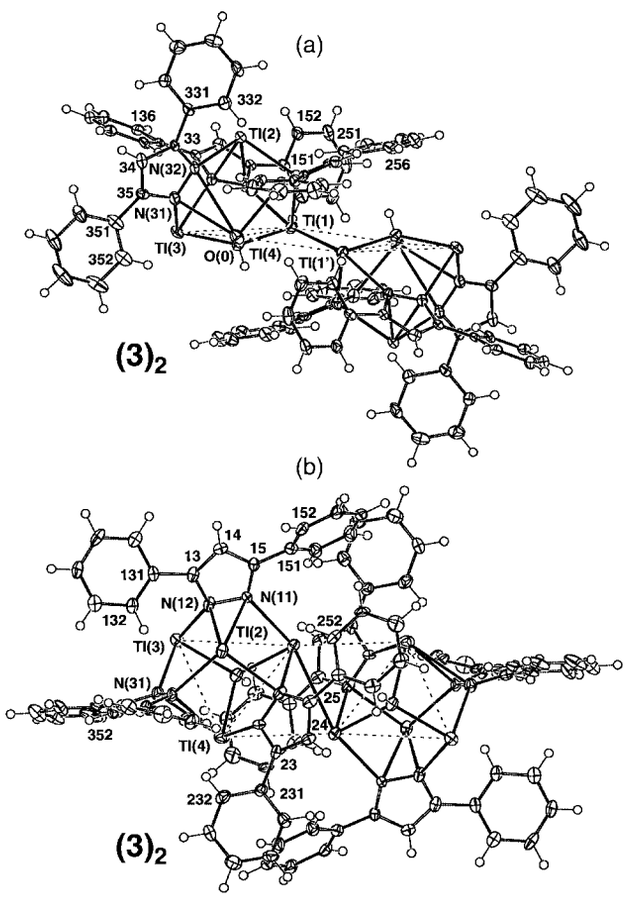


Fig. 4 (*a*) A projection of the centrosymmetric dimer of **3**. (*b*) A projection of **3** illustrating the polytriangular grid of Tl(1, 2, 3, 1′, 2′, 3′).

corresponding location. Two Tl · · · C separations are <3.60 Å, and can be considered weakly attracting; one is *ca.* 3.60 Å, whilst the Tl · · · N separations are longer (by >0.25 Å) than distances normally considered bonding. Thus at least a Tl–η^2-pyrazolate supracage interaction can be proposed. However, the location of the Tl atom over the ring centre perhaps suggests that there may be a Tl–η^5-Ph_2pz supracage interaction. Whether η^5- or η^2-, the two intercage contacts are supportive of the Tl(1) · · · Tl(1′) linkage. The dichloromethane of solvation is well behaved in refinement with the chloride atoms contacting phenyl hydrogen atoms, and one of the hydrogens contacting a distant thallium.

(*d*) $[Tl_4(MePhpz)_3(OH)]\cdot 0.5CH_2Cl_2$, $4\cdot 0.5CH_2Cl_2$. The molecular structure of **4** (Fig. 5(*a*)) is found to be a tetranuclear cage which is linked to adjacent cages by metal · · · metal interactions between Tl(1) and Tl(2′) (3.685(2) Å) giving an overall

Table 4 Selected geometries (Å) for $[Tl_4(MePhpz)_3(OH)]$ **4**

Tl(1)–N(11)	3.01(2)	Tl(3)–N(11)	2.65(2)
Tl(1)–N(12)	2.76(2)	Tl(3)–N(31)	3.00(2)
Tl(1)–N(22)	2.56(2)	Tl(3)–N(32)	2.72(2)
Tl(1)–N(32)	2.63(2)	Tl(3)–O(0)	2.42(2)
Tl(2)–N(21)	2.97(2)	Tl(4)–N(21)	2.63(2)
Tl(2)–N(31)	2.58(2)	Tl(4)–N(12)	2.63(2)
Tl(2)–N(22)	2.73(2)	Tl(4)–O(0)	2.46(2)
Tl(2)–O(0)	2.46(2)	Tl(1) · · · Tl(2′)	3.685(2)

Transformation of the asymmetric unit: ′ $x + 1, y, z$.

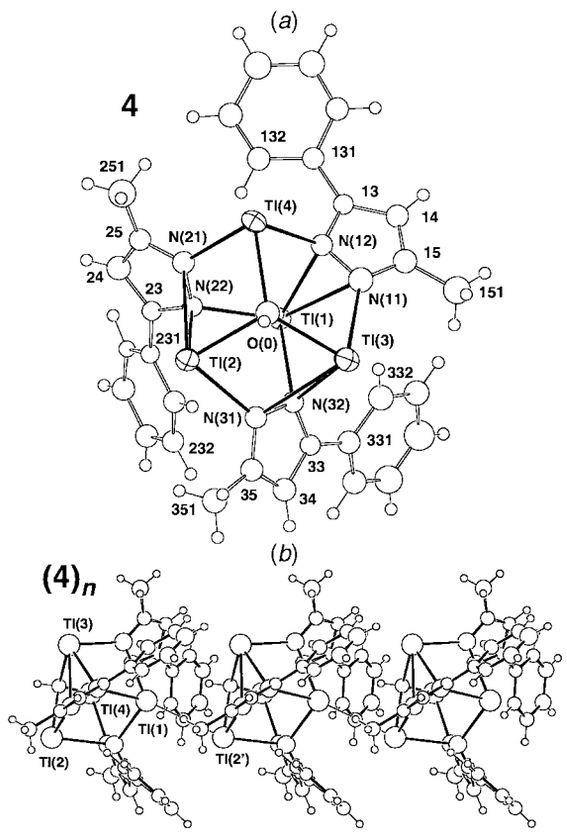


Fig. 5 (*a*) A single tetranuclear unit **4** viewed (approximately) down the Tl(1) O(0) axis. (*b*) A projection of the extended molecular array of **4** formed by the intercage Tl(1) · · · Tl(2′) interaction.

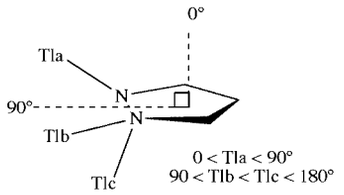
polymeric structure (Fig. 5(*b*)). Although the Tl · · · Tl separation is longer than in $(\mathbf{3})_2$ it is still at the short end of the reported Tl · · · Tl interactions.[24–29] All intracage Tl · · · Tl separations are longer (3.952(2)–4.410(2) Å) and are considered non-bonding. The cage has Tl(1) and O(0) lying above and below respectively the plane of Tl(2), Tl(3) and Tl(4), whilst the four thallium atoms have a tetrahedral arrangement. Both Tl(1) and Tl(2) are five-coordinate whilst Tl(3) and Tl(4) are four and three-coordinate respectively. Observation of a higher coordination number for some thallium atoms in **4** than in **1**–**3** is consistent with less bulky pyrazolate ligands in **4**.

All pyrazolate ligands are bonded in a μ_3-η^1:η^2:η^1 manner, and all are coordinated to Tl(1). The hydroxide oxygen is attached to Tl(2)–Tl(4) (Table 4). There are intracage Tl · · · C and one intermolecular Tl · · · C contacts within 3.6 Å, but none appear structurally significant. One interaction with a pyrazolate *ipso* carbon and the *ortho* carbon of the attached phenyl is similar to ones shown by **2**.

Thallium and nitrogen environments

The spread of proposed Tl–N bond lengths in **1**–**4** is large (Tables 1–4) (**1** 2.61(2)–2.89(2); **2** 2.542(8)–2.953(8); **3** 2.591(7)–3.130(7); **4** 2.56(2)–3.01(2) Å) with the bulk of distances at

Table 5 Angles (θ/°) between Tl–N bonds and the normal to the pyrazolate ring plane in **1**–**4**



90° is indicative of σ-bonding: 0 and 180° are indicative of π-bonding

1	Tl(1)	Tl(2)	Tl(3)	Tl(4)
pz1	N(11) 109.6	N(12) 146.5	N(12) 37.3	—
pz2	N(21) 140.6, N(22) 136.3	N(21) 56.7	N(22) 66.1	—
pz3	N(31) 128.7	N(32) 75.0	—	—
2				
pz1	N(11) 62.3	N(12) 47.6	—	N(11) 42.8, N(12) 133.5
pz2	—	N(22) 23.2	N(22) 13.9	N(21) 156.9
pz3	N(31) 159.8, N(32) 171.6 C(31) 144.2, C(32) 140.6 C(33) 149.3	N(32) 75.0	N(31) 104.7	—
pz4	N(41) 69.2	—	N(42) 155.6	N(42) 78.3
3				
pz1	N(11) 86.5	N(11) 28.5, N(12) 11.8	N(12) 60.8	—
pz2	N(21) 53.0 N(21)[a] 70.7, N(22)[a] 66.5, C(23)[a] 45.7, C(24)[a] 33.0, C(25)[a] 52.5	N(21) 38.9	—	N(22) 62.0
pz3	—	N(32) 63.6	N(31) 57.9	N(31) 39.2, N(32) 43.7
4				
pz1	N(11) 31.3, N(12) 22.3	—	N(11) 98.8	N(12) 54.7
pz2	N(22) 135.1	N(21) 28.9, N(22) 149.8	—	N(21) 79.8
pz3	N(32) 124.9	N(31) 104.1	N(31) 39.4, N(32) 32.6	—

[a] These values refer to Tl(1′).

2.50–2.80 Å and a more limited number at 2.85–3.15 Å (Tables 1–4). There is abundant precedent for the former values, *e.g.* Tl–N distances range between 2.507(7) and 2.762(8) Å in thallium(I) 3-(2′-pyridyl)pyrazolate,[18] between 2.43(2) and 2.75(2) Å in $[Tl_3\{Me_3SiNCH_2)_3CPh\}]$,[36] and between 2.638(5) and 2.780(5) Å in thallium(I) ferrocenyltris(pyrazol-1-yl)borate.[41] Weaker Tl–N interactions have also been reported in the range 2.80–3.21 Å, *viz*. at 2.937(4)–3.165(4) Å in thallium(I) dihydridobis(3-(2′-pyridyl)pyrazol-1-yl)borate,[42] at 2.876(4) Å in thallium(I) methyltris(3,5-dimethylpyrazol-1-yl)borate,[43] near 3.00 Å in $[\{Tl(PhNNNPh)\}_2]$[44] and 3.21 Å in a reinterpretation[23] of the structure of the above ferrocenylborate. In any case the range 2.88–3.15 Å is well within the sum (3.47 Å) of the van der Waals radii of thallium[38] and nitrogen.[39] Each η^2-R_2pz–Tl unit has one long (>2.88 Å) Tl–N bond with the second substantially shorter (by 0.16–0.33 Å), and usually <2.80 Å (sole exception Tl(4)–N(31) of **3**). Similar substantial differences in M–N bond lengths for η^2-bonded pyrazolates have also been observed on coordination to potassium,[1] and this mode of binding has been termed "slipped η^2" by Winter.[13] The N–Tl–N bite angles (26.9(2)–29.0(5)°) are small compared with those of, for example, η^2-R_2pz–Ln or η^2-R_2pz–U bonded complexes[2,5,7,8,11] and are similar to those of $[\{K(Ph_2pz)(thf)\}_6]$.[1] Within the limited precision of their determinations, N–N bond distances show no correlation with the type of pyrazolate coordination.

Most pyrazolate nitrogens in **1**–**4** have two thallium atoms attached, despite the presence of only one lone pair per nitrogen. Likewise two metal atoms per nitrogen are a feature of μ_3-η^1:η^2:η^1-Ph_2pz coordination to potassium in $[\{K(Ph_2pz)(thf)\}_6]$,[1] whilst two lanthanoid atoms are attached to each nitrogen in μ-η^2:η^2-bonded lanthanoid pyrazolates.[2,3] Structures with two metals attached to a single pyridine nitrogen are also known.[45–47] This can be accommodated with a range of bonding options besides a three centre 2e bond involving the nitrogen lone pair. It has been shown that pyrazolate molecular orbitals can be described which provide electron density between the nitrogens for η^2-coordination[12] whilst not precluding lone pair electron density for the more usual η^1-attachment.[1] Moreover, the use of π-electron density in binding can be envisaged and has been observed in $[KEr(Bu^t_2pz)_4]$,[5] where one of the Bu^t_2pz ligands η^2-bonded to erbium is also π-η^3(CNN)-bonded to potassium. Predominantly π-bonded thallium atoms should have Tl–N bonds normal to the pyrazolate plane and σ-bonded should have Tl–N coplanar with the pyrazolate ring. In Table 5, angles (θ) between Tl–N and the *normal* to the pyrazolate plane are listed. Values close to 0 and 180° are considered indicative of π-bonding and ones near 90° denote σ-bonding. However, very few angles, only 10 out of 46 for **1**–**4** (Table 5), lie near (≤ 15°) the limits 0, 180 and 90°. Seven of these are near 90°, and only three near 180 or 0°. Only one pyrazolate ligand in all structures *viz*. the μ_3-η^1:η^2:η^1-bonded pz3 of **2** has more than one θ angle near 0, 90 or 180°. Attachment of both Tl(2) and Tl(3) is near the σ requirement whilst the η^2-attachment to Tl(1) has values 9 and 20° from the π value (Fig. 3(*a*)). The exceptional conformity of this ligand to a simple bond model highlights the divergence of the rest. Thus, the paucity of angles (θ) near the 0, 180 or 90° limits (Table 5) and the lack of correlation between bond distances or coordination mode and θ angles suggests highly ionic bonding where steric factors involving the moderately bulky Ph_2pz ligands are more important than thallium(I) stereochemical preferences. This enables the attachment of two thalliums to many of the nitrogen donors in different arrangements, thereby giving rise to μ_3-η^1:η^1:η^1 and μ_3-η^1:η^2:η^1 pyrazolate coordination and consequent cage formation.

Experimental

All manipulations of products were under an inert atmosphere. IR spectra of Nujol mulls between NaCl plates were obtained with a Perkin-Elmer 1600 FTIR spectrometer.

Preparations

$[Tl_3(Ph_2pz)_3]$ 1 and $[Tl_4(Ph_2pz)_4]$ 2. The preparation and properties of $[Tl(Ph_2pz)]$ have been given.[10] Single crystals of **1** and **2** were obtained from concentrated benzene and dme solutions respectively.

$[Tl_4(Ph_2pz)_3(OH)]$ 3. Single crystals of **3** were adventitiously obtained by crystallisation of $[Tl(Ph_2pz)]$ from dichloromethane. Infrared, (Nujol, ν/cm^{-1}): 3517w, 1598m, 1508w, 1254m, 1074w, 1054s, 1024m, 968m, 914w, 798w, 757vs, 735m, 698vs.

$[Tl_4(MePhpz)_3(OH)]$ 4. Single crystals of **4** were grown from a concentrated dichloromethane solution of [Tl(MePhpz)], the preparation of which has been reported.[11]

Structure determinations

Initially a number of the specimens were examined with 'four-circle' instrumentation and those diffracting inauspiciously were put aside. Subsequently they were resurrected successfully using new CCD diffractometer facilities and solved and refined to the level herein. For **1**, **3**, and **4** spheres of data were measured at *ca*. 153 K using a Bruker AXS CCD area-detector instrument (monochromatic Mo-Kα radiation, λ 0.7107$_3$ Å), $N_{t(total)}$ data being reduced to N independent absorption corrected ('empirical' correction ('SADABS')[48]) unique (R_{int} quoted), using the proprietary software SMART/SAINT[49] (*etc*.), N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinement (anisotropic thermal parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ constrained estimates (hydroxyl hydrogen observed in difference map for **3** only)). For **2** a hemisphere of data was collected at 123(1) K using an Enraf-Nonius CCD area-detector instrument (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) yielding N_t data after integration using the DENZO SMN software package.[50] A total of N unique reflections (N_o ($I > 2\sigma(I)$) 'observed') were used in least squares refinement (anisotropic U for non-hydrogen atoms, $(x, y, z, U_{iso})_H$ constrained) after structure solution and expansion by Patterson and Fourier techniques.

Crystal/refinement data. (*a*) **1** $[Tl_3(Ph_2pz)_3] \equiv C_{45}H_{33}N_6Tl_3$, $M = 1271.0$. Monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14, variant), $a = 9.495(2)$, $b = 15.506(3)$, $c = 26.159(5)$ Å, $\beta = 96.587(4)°$, V 3826 Å^3. D_c ($Z = 4$ trimers) 2.20$_6$ g cm^{-3}; $F(000) = 2352$. $\mu_{Mo} = 126$ cm^{-1}; specimen: $0.25 \times 0.15 \times 0.18$ mm; 'T'$_{min,max}$ 0.26, 0.62. $2\theta_{max}$ 50°. $N_t = 42807$, $N = 6654$ (R_{int} = 0.072), N_o = 4072; $R = 0.064$, $R_w = 0.071$.

Variata. Weak and limited data, obtained on a marginal specimen, would support meaningful anisotropic thermal parameter refinement for Tl only.

(*b*) **2**·dme $[Tl_4(Ph_2pz)_4]$·dme$\equiv C_{64}H_{54}N_8O_2Tl_4$, $M = 1784.63$. Monoclinic, space group $P2_1/n$, $a = 11.3668(3)$, $b = 17.5657(2)$, $c = 28.4648(7)$ Å, $\beta = 93.373(1)°$, $V = 5674$ Å^3. D_c ($Z = 4$) = 2.08$_9$ g cm^{-3}; $F(000) = 3336$. $\mu_{Mo} = 114$ cm^{-1}; specimen: $0.13 \times 0.18 \times 0.25$ mm. $2\theta_{max} = 56.6°$; $N_t = 34735$, N 12968 (R_{int} 0.075), N_o 9643; R 0.055, R_w 0.133.

Variata. The dme of crystallisation was modelled as disordered with O(2), C(61), C(62) and C(63) each refined in two sites with populations set at 0.5.

(*c*) **(3)**$_2$·2CH_2Cl_2 $[\{Tl_4(Ph_2pz)_3(OH)\}_2]$·2$CH_2Cl_2 \equiv C_{92}H_{72}Cl_4N_{12}O_2Tl_8$, $M = 3154.6$. Monoclinic, space group $P2_1/c$, (C_{2h}^5, no. 14), $a = 13.851(2)$, $b = 21.533(4)$, $c = 14.721(3)$ Å, β 92.160(3)°, $V = 4388$ Å^3. D_c ($Z = 2$ centrosymmetric dimers of tetramers) = 2.38$_7$ g cm^{-3}; $F(000) = 2880$. $\mu_{Mo} = 148$ cm^{-1}; specimen: $0.40 \times 0.30 \times 0.18$ mm; 'T'$_{min,max} = 0.096$, 0.432. $2\theta_{max} = 58°$; $N_t = 51172$, $N = 11124$ ($R_{int} = 0.082$), $N_o = 7654$; $R = 0.038$, $R_w = 0.042$.

(*d*) **4**·0.5CH_2Cl_2 $[Tl_4(MePhpz)_3(OH)]$·0.5$CH_2Cl_2 \equiv C_{30.5}H_{29}ClN_6OTl_4$, $M = 1348.6$. Monoclinic, space group $P2_1/n$, $a = 7.331(1)$, $b = 26.592(5)$, $c = 18.044(3)$ Å, $\beta = 97.516(3)°$, $V = 3487$ Å^3. D_c ($Z = 4$ tetramers) = 2.56$_8$ g cm^{-3}; $F(000) = 2412$. $\mu_{Mo} = 185$ cm^{-1}; specimen: $0.12 \times 0.08 \times 0.03$ mm; 'T'$_{min,max}$ = 0.34, 0.89. $2\theta_{max} = 50°$; $N_t = 40698$, $N = 6010$ ($R_{int} = 0.089$), $N_o = 4469$; $R = 0.067$, $R_w = 0.087$.

Variata. Limited data, obtained on a marginal specimen, would support anisotropic thermal parameter refinement for Tl, Cl only. Difference map residues, in the context of the history of the sample, were modelled as dichloromethane, disordered about a symmetry element, component site occupancies set at 0.5 after trial refinement.

CCDC reference number 186/1818.

See http://www.rsc.org/suppdata/dt/a9/a909048g/ for crystallographic files in .cif format.

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