

Novel pyrazolate coordination modes and unusual Tl...Tl or Tl- π -(phenyl) interactions in the crystal structures of $[\{\text{Tl}_3(\text{Ph}_2\text{pz})_3\}_n]$, $[\{\text{Tl}_4(\text{Ph}_2\text{pz})_4\}_n]$, $[\{\text{Tl}_4(\text{Ph}_2\text{pz})_3(\text{OH})\}_2]$ and $[\{\text{Tl}_4(\text{MePhpz})_3(\text{OH})\}_n]$ (Ph₂pz = 3,5-diphenylpyrazolate; MePhpz = 3-methyl-5-phenylpyrazolate)

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$[\text{Tl}(\text{Ph}_2\text{pz})]$ (Ph₂pz = 3,5-diphenylpyrazolate) crystallises in two forms. The first from benzene has trinuclear molecules $[\text{Tl}_3(\text{Ph}_2\text{pz})_3]$ **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 Ph₂pz coordination are observed. Crystallisation of $[\text{Tl}(\text{Ph}_2\text{pz})]$ from 1,2-dimethoxyethane (dme) gives tetranuclear molecules $[\text{Tl}_4(\text{Ph}_2\text{pz})_4]$ **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 -Ph₂pz interaction. Crystallisation of $[\text{Tl}(\text{Ph}_2\text{pz})]$ or $[\text{Tl}(\text{MePhpz})]$ (MePhpz = 3-methyl-5-phenylpyrazolate) from dichloromethane afforded the partially hydrolysed tetranuclear cages $[\text{Tl}_4(\text{Ph}_2\text{pz})_3(\text{OH})]$ **3** or $[\text{Tl}_4(\text{MePhpz})_3(\text{OH})]$ **4**, which associate to give a dimer and a polymer respectively owing to Tl...Tl interactions, supported for the dimer by an intercalate distant Tl- π - η^5 -Ph₂pz 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

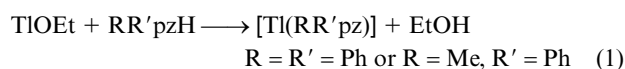
There has been a recent proliferation of new bonding modes for pyrazolate (pz) ligands.¹⁻⁶ In addition η^2 -binding^{7,8} has unexpectedly been extended from f-block⁷⁻¹¹ to d-block¹²⁻¹⁶ and main group¹⁷ elements. However, these developments do not necessarily exhaust the coordination versatility of these 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 $[\text{Tl}(\text{pypz})]_n$ [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 (Ph₂pz) 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...Tl²⁴⁻²⁹ Tl...arene³⁰⁻³⁶ 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 binding⁶ 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 trans-

metallation 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 $[\text{Tl}(\text{Ph}_2\text{pz})]$, and of the adventitious hydrolysis products of $[\text{Tl}(\text{Ph}_2\text{pz})]$ and $[\text{Tl}(\text{MePhpz})]$, viz. $[\text{Tl}_4(\text{RR}'\text{pz})_3(\text{OH})]$ (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 $[\text{Tl}(\text{Ph}_2\text{pz})]$ and $[\text{Tl}(\text{MePhpz})]$ were prepared by reaction (1).^{10,11}



Crystallisation of $[\text{Tl}(\text{Ph}_2\text{pz})]$ 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 $[\text{Tl}_4(\text{Ph}_2\text{pz})_3(\text{OH})]$ and $[\text{Tl}_4(\text{MePhpz})_3(\text{OH})]$, were obtained from attempts to crystallise $[\text{Tl}(\text{Ph}_2\text{pz})]$ and $[\text{Tl}(\text{MePhpz})]$ from CH₂Cl₂, when partial hydrolysis occurred (reaction (2)).



The infrared spectrum of $[\text{Tl}_4(\text{Ph}_2\text{pz})_3(\text{OH})]$ **3** has a weak but sharp absorption at 3517 cm⁻¹ attributable to $\nu(\text{OH})$.

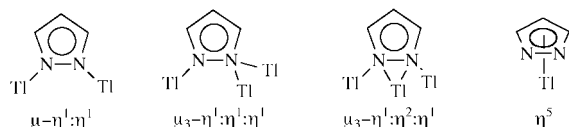


Fig. 1 The different pyrazolate bonding modes to thallium.

Structural studies

General. The results of low temperature single crystal X-ray studies of the two forms of $[\text{Ti}(\text{Ph}_2\text{pz})]$ and the two $[\text{Ti}_4(\text{RR}'\text{pz})_3(\text{OH})]$ complexes are consistent with assignment in terms of stoichiometry and connectivity as tri- and tetra-nuclear species:

- (a) $[\text{Ti}_3(\text{Ph}_2\text{pz})_3]$, **1**, from benzene
- (b) $[\text{Ti}_4(\text{Ph}_2\text{pz})_4]\cdot\text{dme}$, **2**·dme, from dme
- (c) $[\text{Ti}_4(\text{Ph}_2\text{pz})_3(\text{OH})]\cdot\text{CH}_2\text{Cl}_2$, **3**· CH_2Cl_2
- (d) $[\text{Ti}_4(\text{MePhpz})_3(\text{OH})]\cdot 0.5\text{CH}_2\text{Cl}_2$, **4**· $0.5\text{CH}_2\text{Cl}_2$

The structures demonstrate a diverse array of Ti–pyrazolate bonding modes, *viz.* $\mu\text{-}\eta^1:\eta^1$, $\mu_3\text{-}\eta^1:\eta^1:\eta^1$, $\mu_3\text{-}\eta^1:\eta^2:\eta^1$ and η^5 (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 $\mu_3\text{-}\eta^1:\eta^1:\eta^1$ is a new type of pyrazolate coordination. In addition significant $\text{Ti}\cdots\pi\text{-Ph}$ and $\text{Ti}\cdots\text{Ti}$ interactions are observed and give rise to associated structures (below). The overall features of the individual structures are considered first, and then Ti–N bond distances, bond angles and bonding are discussed for all structures.

(a) $[\text{Ti}_3(\text{Ph}_2\text{pz})_3]$, **1**. The molecular structure of **1** contains three different thallium centres, Ti(1), Ti(2) and Ti(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 $\text{Ti}\cdots\text{Ti}$ 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 $\text{Ti}\cdots\text{Ti}$ 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 $\mu_3\text{-}\eta^1:\eta^1:\eta^1$ arrangement, pz2 $\mu_3\text{-}\eta^1:\eta^2:\eta^1$ ligation, only once previously observed,¹ and pz3 the common $\mu\text{-}\eta^1:\eta^1$ 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 Ti_3 plane whilst pz3 lies more oblique to the Ti_3 plane and bridges Ti(1) and Ti(2). Four coordinate Ti(1) and three coordinate Ti(2) are linked to all three Ph_2pz ligands, whilst Ti(3) is ligated solely by pz1 and pz2.

With only two nitrogens coordinated to Ti(3), and in a cisoid arrangement ($\text{N}(12)\text{--Ti}(3)\text{--N}(22)$ 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 ($\text{C}(151)\text{--C}(156)$) of each trinuclear unit to the partly naked Ti(3) on an adjacent unit ($\text{Ti}\cdots\text{C}$ range 3.36(2)–3.60(2) Å). Accordingly each $[\text{Ti}_3(\text{Ph}_2\text{pz})_3]$ cage is considered linked to a neighbour by a $\text{Ti}(3)\text{--}(\pi\text{-}\eta^6\text{-Ph})$ interaction (Table 1), thereby forming a one-dimensional polymeric chain (**1**)_n. In addition to these contacts, there are four other intermolecular $\text{Ti}\cdots\text{C}$ distances of a similar magnitude (Table 1) but, unlike the $\text{Ti}(3)\cdots\eta^6\text{-Ph}$ interactions, these other contacts do not appear to have a significant influence on the overall arrangement of (**1**)_n. The $\text{Ti}\cdots\text{C}$ intermolecular separations

Table 1 Selected geometries (Å) for $[\text{Ti}_3(\text{Ph}_2\text{pz})_3]$ **1**

Strongly bonded interactions			
Ti(1)–N(11)	2.71(2)	Ti(2)–N(21)	2.74(2)
Ti(1)–N(21)	2.68(2)	Ti(2)–N(32)	2.69(2)
Ti(1)–N(22)	2.89(2)	Ti(3)–N(12)	2.68(2)
Ti(1)–N(31)	2.61(2)	Ti(3)–N(22)	2.63(2)
Ti(2)–N(12)	2.67(2)		
Interchange $\text{Ti}\cdots\text{C}$ interactions			
Ti(3) $\cdots\text{C}(151')$	3.59(2)	Ti(3) $\cdots\text{C}(156')$	3.60(2)
Ti(3) $\cdots\text{C}(152')$	3.46(2)	Ti(3) $\cdots\text{C}(331')$	3.45(2)
Ti(3) $\cdots\text{C}(153')$	3.39(3)	Ti(3) $\cdots\text{C}(336')$	3.53(2)
Ti(3) $\cdots\text{C}(154')$	3.36(2)	Ti(2) $\cdots\text{C}(153'')$	3.56(3)
Ti(3) $\cdots\text{C}(155')$	3.49(2)	Ti(2) $\cdots\text{C}(154'')$	3.40(2)
Transformations of the asymmetric unit: $'\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$. $''x - 1, y, z$.			

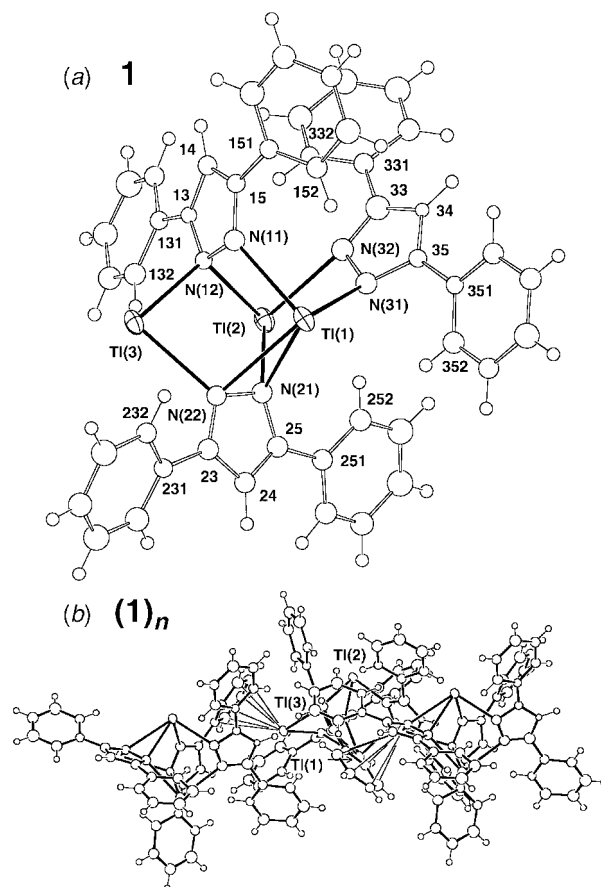


Fig. 2 (a) A projection of **1** oblique to the Ti_3 plane. 50% thermal envelopes are shown for the non-hydrogen atoms, here and in Fig. 3–5. Hydrogen atoms, where displayed, have arbitrary radii of 0.1 Å. (b) A projection of the extended molecular array of **1** formed by the $\text{Ti}(3)\cdots\eta^6\text{-Ph}\{\text{C}(151')\text{--C}(156')\}$ intermolecular interactions.

are similar to the range 3.34–3.74 Å recently associated with weakly attractive $\eta^6\text{-phenyl}\cdots\text{Ti}$ contacts in $[\text{Ti}_3\{(\text{Me}_3\text{SiN-CH}_2)_3\text{CPh}\}]$.³⁶ In (**1**)_n, $\langle\text{Ti}\cdots\text{C}\rangle$ (3.48 Å) is near the upper limit of the range (3.10–3.50 Å^{32–35}) for Ti–C bonds in complexes with discrete arenes $\eta^6\text{-bonded}$ to Ti^+ , but is much longer than the Ti–C bonds of thallium cyclopentadienides.³⁷ As $\langle\text{Ti}\cdots\text{C}\rangle$ of (**1**)_n is near to the sum (3.7 Å) of the van der Waals radii of Ti^+ ³⁸ and an arene ring,³⁹ the present $\text{Ti}\cdots\text{C}$ contacts are perhaps best viewed as supramolecular⁴⁰ interactions which fill the large gap in the Ti(3) coordination sphere.

(b) $[\text{Ti}_4(\text{Ph}_2\text{pz})_4]\cdot\text{dme}$, **2**·dme. The molecular structure of **2** (Fig. 3(a)) contains a tetrahedron of Ti atoms with non-bonding (see above) separations of 4.179(1)–4.599(1) Å, and with even longer distances ($\geq 5.265(1)$ Å) between Ti atoms of

[†] Note added at proof: this interpretation of $\text{Ti}\cdots\text{Ti}$ distances is consistent with a new report.⁵¹

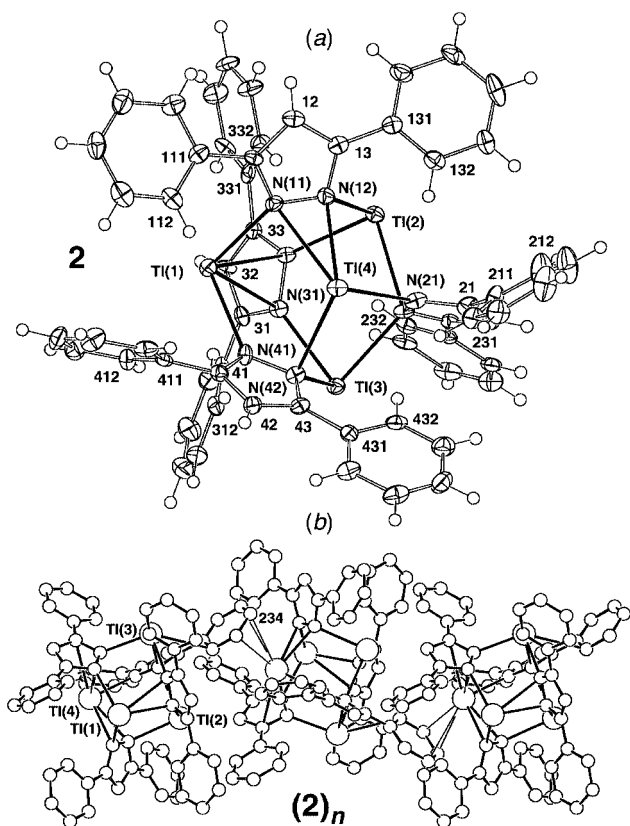


Fig. 3 (a) A projection of **2** showing the tetranuclear thallium cage. (b) A projection of the extended molecular array of **2** formed by the $\text{Ti}(4) \cdots \eta^3\text{-Ph}\{\text{C}(233')\cdots\text{C}(235')\}$ intermolecular interactions.

adjacent tetranuclear units. Binding of pyrazolate nitrogens gives four coordination for $\text{Ti}(1)$ and $\text{Ti}(4)$ and three coordination for the other Ti atoms. One bridging ligand caps each face of the Ti_4 tetrahedron.

Two pyrazolate ligands, pz1 and pz3, exhibit $\mu_3\text{-}\eta^1\text{:}\eta^2$: η^1 -coordination. The first binds η^2 to $\text{Ti}(4)$ and is η^1 -linked to $\text{Ti}(1)$ and $\text{Ti}(2)$, whilst the second is η^2 -bonded to $\text{Ti}(1)$ and η^1 to $\text{Ti}(2)$ and $\text{Ti}(3)$. By contrast, the other two, pz2 and pz4, bind in the new $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$ mode to $\text{Ti}(2,3,4)$ and $\text{Ti}(1,3,4)$ 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 Ti_4 tetrahedron, which has no $\text{Ti} \cdots \text{Ti}$ 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 $\text{Ti} \cdots \text{Ti}$ bonds (3.6468(4) Å) holding the Ti_4 cluster together.

In addition to nitrogen coordination there are a considerable number of intramolecular $\text{Ti} \cdots \text{C}$ contacts and three intermolecular $\text{Ti} \cdots \text{C}$ contacts at <3.60 Å, the upper limit chosen for weakly attractive $\text{Ti} \cdots \text{C}$ binding in **1**, and a value just within the sum (3.73 Å) of the van der Waals radii of Ti ³⁸ and an aromatic ring.³⁹ Because **2** has a larger surface area than **1**, intramolecular $\text{Ti} \cdots \text{Ph}$ contacts are more likely for **2** but it is less exposed for intermolecular interactions. Only the four coordinate $\text{Ti}(4)$ has supramolecular interactions <3.60 Å to an adjacent tetranuclear cage. Contacts (3.38(1)–3.48(1) Å) with adjacent carbons ($\text{C}(233)\cdots\text{C}(235)$) give rise to a $\text{Ti} \cdots \eta^3\text{-Ph}$ interaction, which links the Ti_4 units into a one-dimensional polymer ($2)_n$ (Fig. 3(b)). The remaining three $\text{Ti} \cdots \text{C}$ 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 $\text{Ti} \cdots \text{C}$ intramolecular contacts are between $\text{Ti}(1)$ and three pyrazolate carbons of ligand 3, providing an overall η^2 -interaction with this ligand. However given

Table 2 Selected geometries (Å) for $[\text{Ti}_4(\text{Ph}_2\text{pz})_4]_2$

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

^a Considered non-bonding.

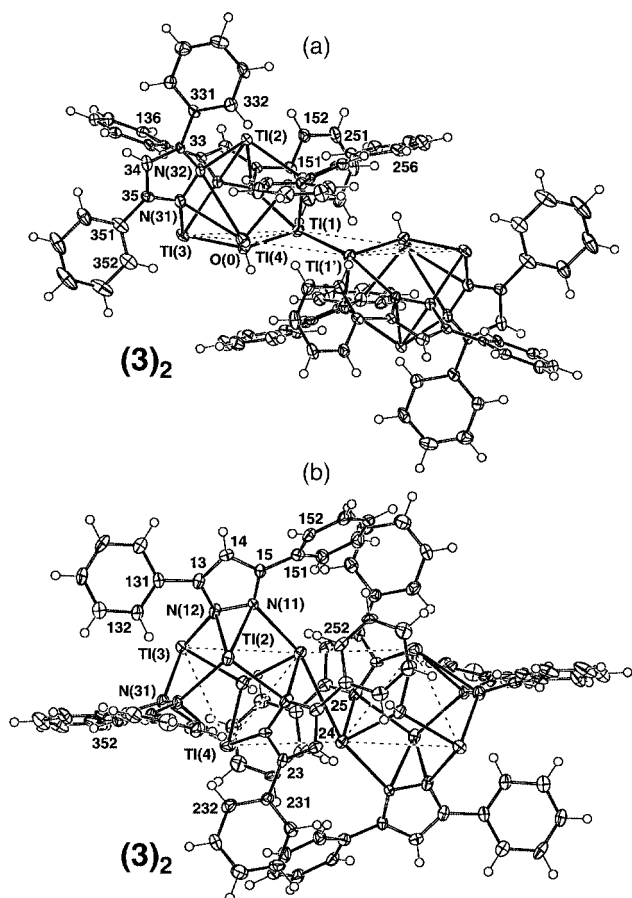
the difference between the $\text{Ti}\cdots\text{N}$ (2.794(8), 2.953(8) Å) and the $\text{Ti} \cdots \text{C}$ distances, it may be more accurate to describe the interaction as $\eta^2\text{-(N}_2\text{)}$ plus $\eta^3\text{-(C}_3\text{)}$. Within the 3.60 Å limit, no other $\text{Ti} \cdots \text{C}_3(\text{Ph}_2\text{pz})$ 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 Ti atoms by two such contacts (Table 2).

(c) $[\text{Ti}_4(\text{Ph}_2\text{pz})_3(\text{OH})]\cdot\text{CH}_2\text{Cl}_2$, **3**· CH_2Cl_2 . This complex is comprised of a pair of $[\text{Ti}_4(\text{Ph}_2\text{pz})_3(\text{OH})]$ tetranuclear cages which are linked by a bond between $\text{Ti}(1)$ and $\text{Ti}(1')$ (3.5317(6) Å) (Fig. 4(a)), and are related through an inversion centre located at the midpoint of $\text{Ti}(1) \cdots \text{Ti}(1')$. The $\text{Ti} \cdots \text{Ti}$ 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 Ti van der Waals radius.³⁸ Further it is *ca.* 0.1 Å shorter than the $\text{Ti} \cdots \text{Ti}$ bonds of the (unsupported) Ti_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 $\text{Ti} \cdots \text{Ti}$ bond to be formed. There is a tetrahedral array of the thallium atoms within the cages, and the pyrazolate supported $\text{Ti} \cdots \text{Ti}$ separations (3.9679(7)–4.4490(8) Å) are considered non-bonding. Six thallium atoms ($\text{Ti}(1,3,4), \text{Ti}(1',3',4')$) 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 $[\text{Ti}_4(\text{Ph}_2\text{pz})_3(\text{OH})]$ cage, oxygen lies on one side of the grid whereas all the Ph_2pz ligands and $\text{Ti}(2)$ lie on the other. Inclusion of the $\text{Ti} \cdots \text{Ti}$ bond leads to three four coordinate Ti atoms and one three coordinate ($\text{Ti}(3)$), by contrast with **2** which has two of each. Two very long $\text{Ti}\cdots\text{N}$ contacts (3.065(7), 3.130(7) Å) are considered pertinent (see later discussion). All thallium atoms except three coordinate $\text{Ti}(3)$ have at least one long (>2.9 Å) $\text{Ti}\cdots\text{N}$ bond and $\text{Ti}(4)$ has two. Two ligands, pz1 and pz3, are bonded $\mu_3\text{-}\eta^1\text{:}\eta^2$: η^1 and one $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$. The hydroxide near symmetrically bridges $\text{Ti}(1)$, $\text{Ti}(3)$ and $\text{Ti}(4)$, whilst $\text{Ti}(2)$ is ligated by all of pz1–3.

Within each cage, there are no structurally significant $\text{Ti} \cdots \text{C}$ contacts. However, there are interesting intermolecular contacts (Table 3). $\text{Ti}(1')$ is situated almost over the centre of the pz2 pyrazolate ring, and centrosymmetrically related $\text{Ti}(1)$ has a

Table 3 Selected geometries (Å) for [Ti₄(Ph₂pz)₃(OH)] **3**

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

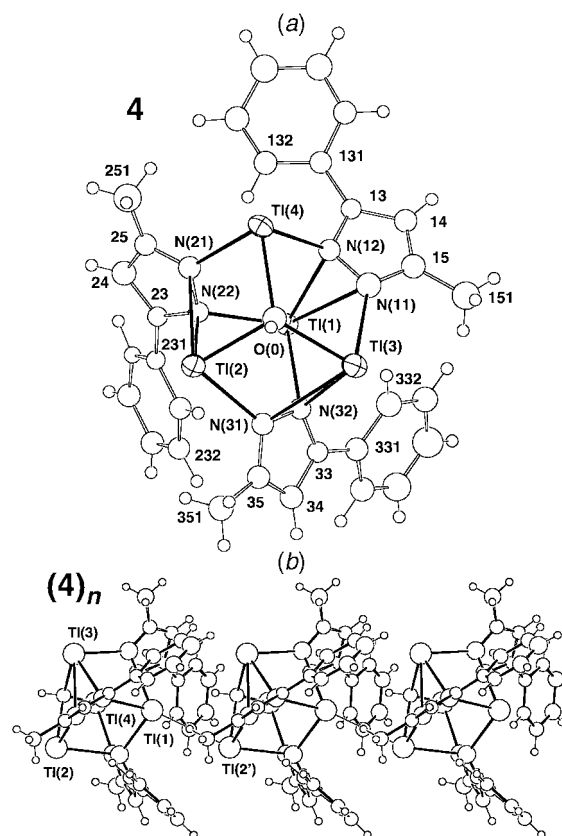
corresponding location. Two Ti...C separations are <3.60 Å, and can be considered weakly attracting; one is *ca.* 3.60 Å, whilst the Ti...N separations are longer (by >0.25 Å) than distances normally considered bonding. Thus at least a Ti–η²–pyrazolate supracage interaction can be proposed. However, the location of the Ti atom over the ring centre perhaps suggests that there may be a Ti–η⁵–Ph₂pz supracage interaction. Whether η⁵- or η²-, the two interage contacts are supportive of the Ti(1)...Ti(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) [Ti₄(MePhpz)₃(OH)]·0.5CH₂Cl₂, **4**·0.5CH₂Cl₂. 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 Ti(1) and Ti(2') (3.685(2) Å) giving an overall

Table 4 Selected geometries (Å) for [Ti₄(MePhpz)₃(OH)] **4**

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

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

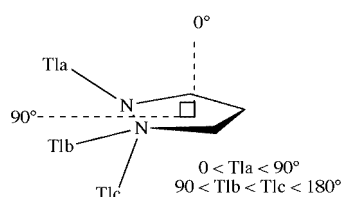
**Fig. 5** (a) A single tetranuclear unit **4** viewed (approximately) down the Ti(1) O(0) axis. (b) A projection of the extended molecular array of **4** formed by the interage Ti(1)...Ti(2') interaction.

polymeric structure (Fig. 5(b)). Although the Ti...Ti separation is longer than in (**3**)₂ it is still at the short end of the reported Ti...Ti interactions.^{24–29} All intracage Ti...Ti separations are longer (3.952(2)–4.410(2) Å) and are considered non-bonding. The cage has Ti(1) and O(0) lying above and below respectively the plane of Ti(2), Ti(3) and Ti(4), whilst the four thallium atoms have a tetrahedral arrangement. Both Ti(1) and Ti(2) are five-coordinate whilst Ti(3) and Ti(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 μ₃–η¹:η²:η¹ manner, and all are coordinated to Ti(1). The hydroxide oxygen is attached to Ti(2)–Ti(4) (Table 4). There are intracage Ti...C and one intermolecular Ti...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 Ti–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**

	Tl(1)	Tl(2)	Tl(3)	Tl(4)
1				
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 [Tl₃{Me₃SiNCH₂)}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)]₂⁴⁴ and 3.21 Å in a reinterpretation²³ 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 thallium³⁸ and nitrogen.³⁹ Each η^2 -R₂pz–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 -R₂pz–Ln or η^2 -R₂pz–U bonded complexes^{2,5,7,8,11} and are similar to those of [K(Ph₂pz)(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 -Ph₂pz coordination to potassium in [K(Ph₂pz)(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 -coordination¹² 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^t₂pz)₄],⁵ where one of the Bu^t₂pz 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 ($\leq 15^\circ$) 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 Ph₂pz 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

[Ti₃(Ph₂p_z)₃] 1 and [Ti₄(Ph₂p_z)₄] 2. The preparation and properties of [Ti(Ph₂p_z)] have been given.¹⁰ Single crystals of **1** and **2** were obtained from concentrated benzene and dme solutions respectively.

[Ti₄(Ph₂p_z)₃(OH)] 3. Single crystals of **3** were adventitiously obtained by crystallisation of [Ti(Ph₂p_z)] from dichloromethane. Infrared, (Nujol, ν/cm^{-1}): 3517w, 1598m, 1508w, 1254m, 1074w, 1054s, 1024m, 968m, 914w, 798w, 757vs, 735m, 698vs.

[Ti₄(MePhpz)₃(OH)] 4. Single crystals of **4** were grown from a concentrated dichloromethane solution of [Ti(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-K α radiation, λ 0.71073 Å), $N_{\text{t(otal)}}$ data being reduced to N independent absorption corrected ('empirical' correction ('SADABS')⁴⁸) unique (R_{int} quoted), using the proprietary software SMART/SAINT⁴⁹ (*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-K α radiation, λ = 0.71073 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** [Ti₃(Ph₂p_z)₃] \equiv C₄₅H₃₃N₆Ti₃, M = 1271.0. Monoclinic, space group $P2_1/n$ (C_{2h}^2 , no. 14, variant), a = 9.495(2), b = 15.506(3), c = 26.159(5) Å, β = 96.587(4)°, V 3826 Å³. D_{c} (Z = 4 trimers) 2.20₆ g cm⁻³; $F(000)$ = 2352. μ_{Mo} = 126 cm⁻¹; specimen: 0.25 × 0.15 × 0.18 mm; $T'_{\text{min,max}}$ 0.26, 0.62. $2\theta_{\text{max}}$ 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 Ti only.

(b) **2**·dme [Ti₄(Ph₂p_z)₄] \cdot dme \equiv C₆₄H₅₄N₈O₂Ti₄, M = 1784.63. Monoclinic, space group $P2_1/n$, a = 11.3668(3), b = 17.5657(2), c = 28.4648(7) Å, β = 93.373(1)°, V = 5674 Å³. D_{c} (Z = 4) = 2.08₉ g cm⁻³; $F(000)$ = 3336. μ_{Mo} = 114 cm⁻¹; specimen: 0.13 × 0.18 × 0.25 mm. $2\theta_{\text{max}}$ = 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)**₂·2CH₂Cl₂ [$\{$ Ti₄(Ph₂p_z)₃(OH)]₂·2CH₂Cl₂ \equiv C₉₂H₇₂Cl₄N₁₂O₂Ti₈, 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 Å³. D_{c} (Z = 2 centrosymmetric dimers of tetramers) = 2.38₇ g cm⁻³; $F(000)$ = 2880. μ_{Mo} = 148 cm⁻¹; specimen: 0.40 × 0.30 × 0.18 mm; $T'_{\text{min,max}}$ = 0.096, 0.432. $2\theta_{\text{max}}$ = 58°; N_{t} = 51172, N = 11124 (R_{int} = 0.082), N_{o} = 7654; R = 0.038, R_{w} = 0.042.

(d) **4**·0.5CH₂Cl₂ [Ti₄(MePhpz)₃(OH)]·0.5CH₂Cl₂ \equiv C_{30.5}H₂₉ClN₆O₂Ti₄, M = 1348.6. Monoclinic, space group $P2_1/n$, a = 7.331(1), b = 26.592(5), c = 18.044(3) Å, β = 97.516(3)°, V = 3487 Å³. D_{c} (Z = 4 tetramers) = 2.56₈ g cm⁻³; $F(000)$ = 2412. μ_{Mo} = 185 cm⁻¹; specimen: 0.12 × 0.08 × 0.03 mm; $T'_{\text{min,max}}$ = 0.34, 0.89. $2\theta_{\text{max}}$ = 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 Ti, 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.

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See <http://www.rsc.org/suppdata/doi/10.1039/A909048G> for crystallographic files in .cif format.

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