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Di-μ-chloro-bis[(*N*-*tert*-butylimido)chlorobis(pyridine-κN)titanium(IV)] perdeuterobenzene disolvate

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The title compound, $[Ti_2(C_4H_9N)_2Cl_2(C_5H_5N)_4]\cdot 2C_6D_6$, possesses a dinuclear structure featuring two six-coordinate pseudo-octahedral titanium(IV) centres with bridging Cl atoms. The complex is located on a crystallographic inversion centre.

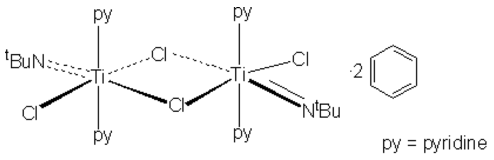
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.030
wR factor = 0.036
Data-to-parameter ratio = 15.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Over the last 15 years, the chemistry of titanium–imido complexes has received considerable attention (Wigley, 1994). It has been shown that these complexes can be utilized in a wide variety of stoichiometric and sometimes catalytic coupling reactions with unsaturated substrates (Gade & Mountford, 2001, and references therein). A general entry point to new titanium–imido chemistry is gained *via* the readily prepared synthons $[Ti(NR)Cl_2(py)_3]$ (R = ^{t}Bu or aryl) (Mountford, 1997). During the course of our studies, we reported that prolonged exposure of $[Ti(N^tBu)Cl_2(py)_3]$ to vacuum results in the loss of the *trans* pyridine ligand (Blake *et al.*, 1997). We report here the solid-state structure of $[Ti_2(\mu\text{-}Cl)_2(N^tBu)_2Cl_2(py)_4]$ crystallized as its perdeuterobenzene disolvate, (I).



(I)

Molecules of (I) adopt a dinuclear structure in the solid state, possessing crystallographically imposed C_i molecular symmetry. The solid-state structure is entirely consistent with the previously reported solution ^{1}H and ^{13}C NMR data (Blake *et al.*, 1997). The two pseudo-octahedral six-coordinate titanium(IV) centres are bridged by two Cl atoms. The bridging Cl—Ti bond lengths [Ti1—Cl2 = 2.4600 (4) Å and Ti1—Cl2A = 2.7438 (4) Å] are longer than the terminal Ti—Cl bond length [Ti1—Cl1 = 2.3898 (4) Å]. The bridging Cl—Ti bond distance of the Cl atom *trans* to the imido group is considerably longer than the bridging Ti—Cl bond distance of the Cl atom *cis* to the imido group [difference between Ti1—Cl2 and Ti1—Cl2^i = 0.2838 (6) Å; symmetry code as in Table 1]. This is a reflection of the strong *trans* influence exercised by the imido group. The near linearity of the Ti═N^{t}Bu linkage [Ti1═N1—C1 = 170.9 (2)°] is consistent with the imido ligand acting as a four-electron donor to the titanium centre (Wigley, 1994).

The structure of (I) is closely related to that of the corresponding titanium–imido species $[Ti_2(\mu\text{-}Cl)_2(N\text{-}2\text{-}PhC_6H_4)_2Cl_2(py)_4]$ and $[Ti_2(\mu\text{-}Cl)_2(N\text{-}2\text{-}t\text{Bu}C_6H_4)_2Cl_2(py)_4]$, synthe-

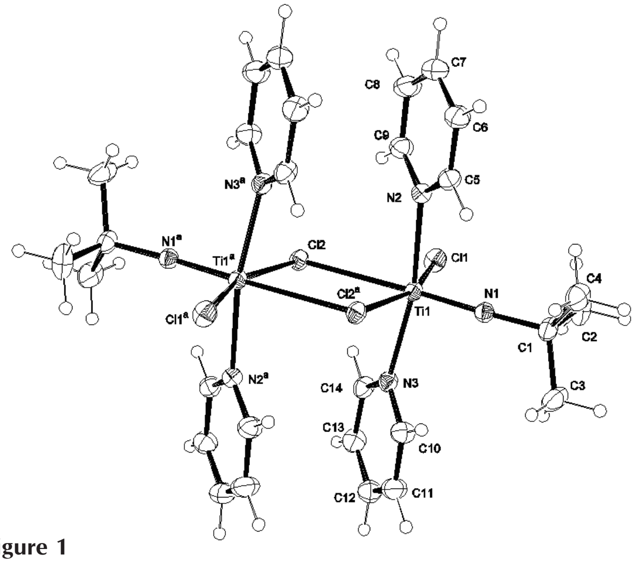


Figure 1
View of the molecular structure of (I). The displacement parameters are drawn at the 20% probability level and H atoms have been omitted for clarity. The solvent of crystallization has been omitted and the minor orientation of the disordered *tert*-butyl group is not shown. Atoms carrying the suffix *A* are related to their counterparts by the symmetry code (1 − *x*, 1 − *y*, 1 − *z*).

sized by Nielson and co-workers (Nielson *et al.*, 2001), and the bond lengths and angles around $Ti_2(\mu\text{-Cl})_2$ are similar in all three compounds.

Experimental

The title compound was prepared according to the previously described procedure (Blake *et al.*, 1997) and authenticated by comparison of its solution ^{1}H NMR spectrum with that previously reported. Crystallization from C_6D_6 afforded crystals of (I) as air-sensitive yellow blocks.

Crystal data

$[Ti_2(C_4H_9N)_2Cl_2(C_5H_5N)_4]\cdot 2C_6D_6$
$M_r = 864.58$
Triclinic, $P\overline{1}$
$a = 8.0662$ (2) Å
$b = 11.0937$ (2) Å
$c = 12.7589$ (3) Å
$\alpha = 101.6259$ (9)°
$\beta = 90.1675$ (10)°
$\gamma = 103.4005$ (11)°
$V = 1086.37$ (4) Å^3
$Z = 1$
$D_x = 1.321$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 18502 reflections
$\theta = 5$–28°
$\mu = 0.65$ mm^{-1}
$T = 150$ K
Prism, pale orange
0.30 × 0.12 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.82$, $T_{max} = 0.95$
18502 measured reflections
4933 independent reflections
3925 reflections with $I > 0$
$R_{int} = 0.028$
$\theta_{max} = 27.4°$
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F
$R = 0.030$
$wR = 0.037$
$S = 1.03$
3925 reflections
252 parameters
H-atom parameters constrained
Weighting scheme: see text
$(\Delta/\sigma)_{max} = 0.019$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ti1—Cl1	2.3898 (4)	C5—C6	1.384 (2)
Ti1—Cl2	2.7438 (4)	C6—C7	1.380 (3)
Ti1—Cl2^i	2.4600 (4)	C7—C8	1.381 (3)
Ti1—N1	1.6921 (12)	C8—C9	1.386 (2)
Ti1—N2	2.2355 (12)	N3—C10	1.345 (2)
Ti1—N3	2.2316 (12)	N3—C14	1.3416 (19)
N1—C1	1.442 (4)	C10—C11	1.384 (2)
N1—C51	1.435 (19)	C11—C12	1.383 (3)
C1—C2	1.533 (5)	C12—C13	1.374 (3)
C1—C3	1.523 (4)	C13—C14	1.387 (2)
C1—C4	1.531 (5)	C15—C16	1.379 (3)
C51—C52	1.532 (15)	C15—C20	1.386 (3)
C51—C53	1.544 (14)	C16—C17	1.384 (3)
C51—C54	1.549 (14)	C17—C18	1.387 (3)
N2—C5	1.3387 (19)	C18—C19	1.384 (3)
N2—C9	1.343 (2)	C19—C20	1.381 (3)
Cl1—Ti1—Cl2	84.062 (14)	N1—C51—C54	109.4 (10)
Cl1—Ti1—Cl2^i	161.860 (17)	C52—C51—C53	110.3 (10)
Cl2—Ti1—Cl2^i	77.891 (13)	C52—C51—C54	109.9 (10)
Cl1—Ti1—N1	99.89 (4)	C53—C51—C54	110.1 (10)
Cl2—Ti1—N1	176.05 (4)	Ti1—N2—C5	118.15 (10)
Cl2^i—Ti1—N1	98.15 (4)	Ti1—N2—C9	124.02 (11)
Cl1—Ti1—N2	88.47 (3)	C5—N2—C9	117.82 (13)
Cl2—Ti1—N2	84.25 (3)	N2—C5—C6	123.11 (14)
Cl2^i—Ti1—N2	87.92 (3)	C5—C6—C7	118.72 (15)
N1—Ti1—N2	95.69 (5)	C6—C7—C8	118.77 (15)
Cl1—Ti1—N3	90.60 (3)	C7—C8—C9	119.22 (16)
Cl2—Ti1—N3	84.89 (3)	N2—C9—C8	122.36 (16)
Cl2^i—Ti1—N3	89.63 (3)	Ti1—N3—C10	120.12 (10)
N1—Ti1—N3	95.13 (5)	Ti1—N3—C14	122.11 (10)
N2—Ti1—N3	169.14 (4)	C10—N3—C14	117.52 (13)
Ti1—Cl2—Ti1^i	102.109 (13)	N3—C10—C11	122.96 (15)
Ti1—N1—C1	170.9 (2)	C10—C11—C12	118.93 (16)
Ti1—N1—C51	177.3 (6)	C11—C12—C13	118.57 (15)
N1—C1—C2	107.1 (3)	C12—C13—C14	119.46 (15)
N1—C1—C3	110.4 (3)	N3—C14—C13	122.53 (15)
C2—C1—C3	109.5 (3)	C16—C15—C20	119.88 (17)
N1—C1—C4	110.5 (3)	C15—C16—C17	120.09 (17)
C2—C1—C4	109.7 (3)	C16—C17—C18	120.11 (17)
C3—C1—C4	109.6 (3)	C17—C18—C19	119.68 (18)
N1—C51—C52	107.5 (10)	C18—C19—C20	120.12 (17)
N1—C51—C53	109.7 (10)	C15—C20—C19	120.12 (16)

Symmetry code: (i) 1 − *x*, 1 − *y*, 1 − *z*.

All H atoms were positioned geometrically after each cycle of refinement. A three-term Chebychev polynomial weighting scheme was applied: $w = \{1 - [\Delta F/2\sigma(F)]^2\}^2/[1.08T_0(x) + 0.471T_1(x) + 0.742T_2(x)]$, where $x = F_{calc}/F_{max}$ (Prince, 1983; Watkin, 1994).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO*; data reduction: *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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