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Bis{2-[(4-chlorophenyl)iminomethyl]-pyrrol-1-ido-κ^2N,N'}bis(dimethylamido-κN)titanium(IV) toluene monosolvate

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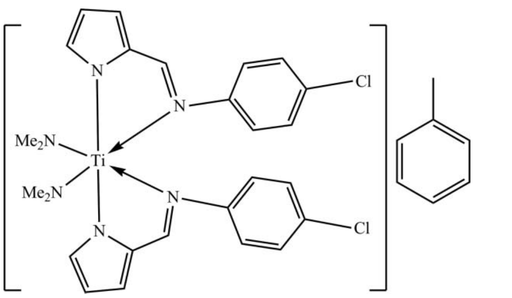
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.005 Å; R factor = 0.035; wR factor = 0.103; data-to-parameter ratio = 16.6.

The mononuclear title compound, $[Ti(C_{11}H_8ClN_2)_2(C_2H_6N)_2]\cdot C_7H_8$, was synthesized by the reaction of N-(4-chlorophenyl)-2-pyrrolylcarbaldimine with $Ti(C_2H_6N)_4$. The Ti^{IV} ion is situated on a twofold rotation axis and displays a distorted octahedral geometry defined by four N atoms from two 2-[(4-chlorophenyl)iminomethyl]pyrrol-1-ide ligands and two N atoms from two dimethylamine ligands. The Ti—$N_{pyrrole}$ bond length [2.1041 (19) Å] is longer than the Ti—$N_{dimethylamine}$ bond length [1.9013 (19) Å]; the imine N atom exhibits the longest Ti—N bond [2.3152 (17) Å]. The toluene solvent molecule is located on a twofold rotation axis running through the C atom of the methyl group. Consequently, the H atoms of the latter are rotationally disordered. The compound contains no markable hydrogen-bonding interactions.

Related literature

For the synthesis of N-(4-chlorophenyl)-2-pyrrolylcarbaldimine and its oxidovanadium(IV) complexes, see: Mozaffar *et al.* (2010). For the synthesis of titanium amido complexes and their applications in hydroamination reactions, see: Ramanathan *et al.* (2004); Cao *et al.* (2001); Bexrud *et al.* (2007); Tillack *et al.* (2005); Braunschweig & Breitling (2006); Zhao *et al.* (2012).



Experimental

Crystal data

$[Ti(C_{11}H_8ClN_2)_2(C_2H_6N)_2]\cdot C_7H_8$
M_r = 635.48
Orthorhombic, $P2_12_12$
a = 11.1952 (4) Å
b = 13.8545 (6) Å
c = 10.4651 (3) Å
V = 1623.18 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.46 mm^{-1}
T = 296 K
0.27 × 0.25 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.886, T_{max} = 0.914
7377 measured reflections
3172 independent reflections
2855 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.103
S = 1.04
3172 reflections
191 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.81 e Å^{-3}
Absolute structure: Flack (1983), 1338 Friedel pairs
Flack parameter: 0.00 (3)

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2614).

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Bis{2-[(4-chlorophenyl)iminomethyl]pyrrol-1-ido-κ^2N,N'}bis(dimethylamido-κN)titanium(IV) toluene monosolvate

Zhou Chen, Jian Wu, Yahong Li and Bin Hu

S1. Comment

The ligand *N*-(4-chlorophenyl)-2-pyrrolylcarbaldimine can be synthesized by the reaction of 4-chloroaniline and 2-pyrrolaldehyde. The ligand has been used in the synthesis of oxidovanadium(IV) complexes (Mozaffar *et al.*, 2010). Herein we report the synthesis and crystal structure of a titanium amido complex $[Ti(C_{11}H_8N_2Cl)_2(C_2H_6N)_2](C_6H_5CH_3)$, (I). Such titanium amido complexes were employed as catalysts in the hydroamination of alkynes (Ramanathan *et al.*, 2004; Cao *et al.*, 2001; Bexrud *et al.*, 2007; Tillack *et al.*, 2005; Braunschweig & Breitling, 2006; Zhao *et al.*, 2012).

The molecular structure of (I) is shown in Fig. 1. The Ti^{IV} ion has site symmetry 2 and displays a distorted octahedral geometry. It is coordinated by four N atoms from two symmetry-related bidentate *N*-(4-chlorophenyl)-2-pyrrolylcarbaldimine ligands and two nitrogen atoms from two dimethylamino ions. Two pyrrolyl N atoms from two coordinating *N*-(4-chlorophenyl)-2-pyrrolylcarbaldimine molecules occupying *trans* positions in the equatorial plane. The dihedral angle between the pyrrolcarbaldiimine and chlorophenyl moieties in the bidentate ligand is 44.90 (10)° . There is a solvate toluene molecule present that is also located on a twofold rotation axis. Since the methyl group of the solvate toluene lies on a special position of higher symmetry than the molecular can possess, the H atoms of this group are rotationally disordered.

The compound contains no remarkable hydrogen bonding interactions. In the crystal packing, the complexes form channels parallel to [001] where the solvent molecules are located.

S2. Experimental

To a solution of $Ti(NMe_2)_4$ (0.112 g, 0.5 mmol) in THF (2 ml) was added *N*-(4-chlorophenyl)-2-pyrrolylcarbaldimine (0.204 g, 1 mmol) in THF (3 ml). After stirring at room temperature overnight, volatiles were removed in vacuo, resulting in an orange solid (0.246 g, 91%). Single crystals of (I) were grown from a toluene/hexane (1:1) solution at 238 K.

S3. Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H = 0.93 Å for aromatic H atoms, 0.96 Å for CH_3 type H atoms and 0.98 Å for CH type H atoms, respectively. U_{iso}(H) values were set at 1.5Ueq(C) for methyl H atoms, and 1.2Ueq(C) for the rest of the H atoms. The methyl group of the solvent molecule lies on a twofold rotation axis; consequently, the H atoms of this methyl group are disordered and were refined with an occupancy of 0.5.

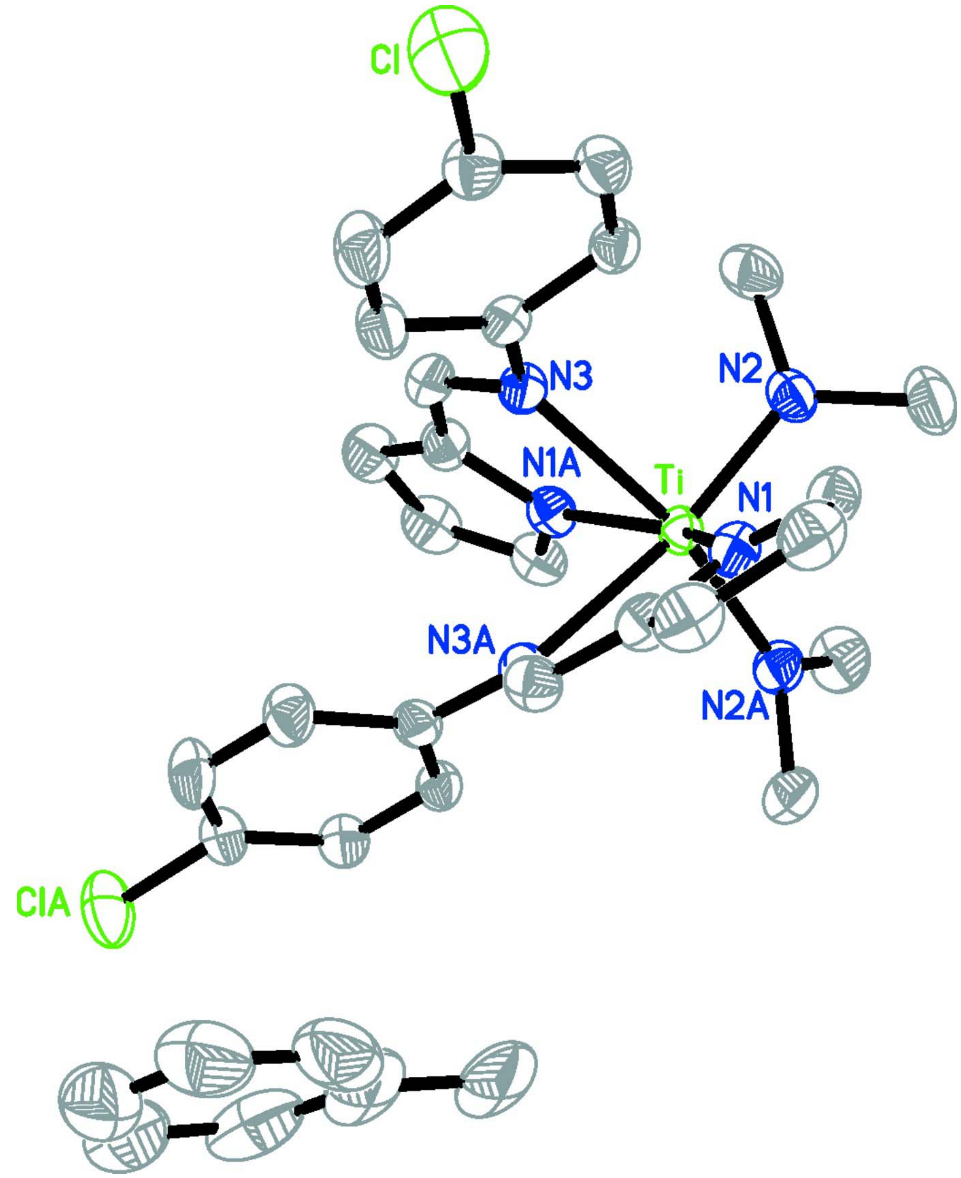

Figure 1

The molecular structure of (I), with atom labels and displacement ellipsoids at the 30% probability level. [Symmetry code: A) -*x* + 1, -*y*, *z*.]

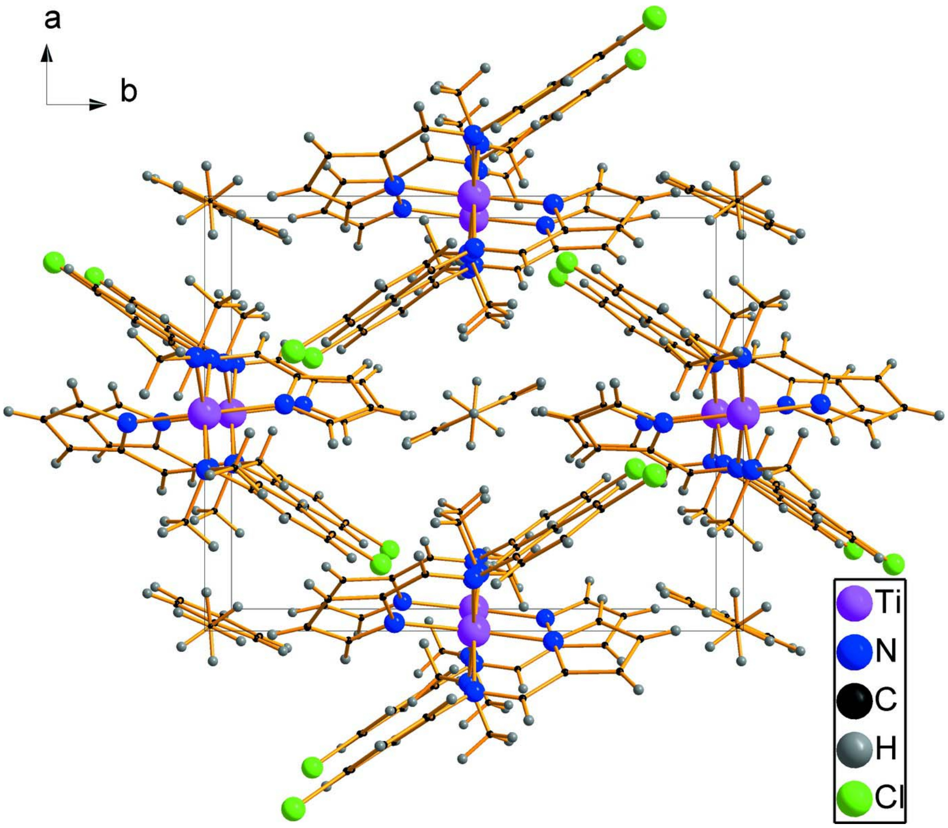

Figure 2

The packing diagram of the compound in a view down [001].

Bis{2-[(4-chlorophenyl)iminomethyl]pyrrol-1-ido- κ²N,N′}bis(dimethylamido-κN)titanium(IV) toluene monosolvate

Crystal data

$[Ti(C_{11}H_8ClN_2)_2(C_2H_6N)_2]\cdot C_7H_8$
$M_r = 635.48$
Orthorhombic, $P2_12_12$
Hall symbol: P 2 2ab
$a = 11.1952$ (4) Å
$b = 13.8545$ (6) Å
$c = 10.4651$ (3) Å
$V = 1623.18$ (10) Å^3
$Z = 2$
$F(000) = 664$
$D_x = 1.300$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3510 reflections
$\theta = 2.7$–$25.3°$
$\mu = 0.46$ mm^{-1}
$T = 296$ K
Block, red
0.27 × 0.25 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.886$, $T_{max} = 0.914$
7377 measured reflections
3172 independent reflections
2855 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.0°$
$h = -13 \rightarrow 13$
$k = -6 \rightarrow 17$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.103$
$S = 1.04$
3172 reflections
191 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2 + 0.167P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.81$ e Å^{-3}
Absolute structure: Flack (1983), 1338 Friedel pairs
Absolute structure parameter: 0.00 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Ti	0.5000	0.0000	−0.00125 (4)	0.03946 (15)	
N3	0.37242 (16)	−0.00104 (15)	0.17286 (15)	0.0444 (4)	
N1	0.52139 (16)	0.14665 (13)	0.04575 (18)	0.0468 (4)	
C7	0.32052 (19)	0.07660 (18)	0.2402 (2)	0.0438 (5)	
N2	0.37235 (18)	0.00986 (16)	−0.12037 (17)	0.0511 (4)	
C8	0.25902 (18)	0.14699 (16)	0.1737 (2)	0.0458 (5)	
H8	0.2554	0.1440	0.0850	0.055*	
C9	0.2030 (2)	0.22161 (18)	0.2368 (2)	0.0515 (5)	
H9	0.1606	0.2681	0.1915	0.062*	
C2	0.5137 (3)	0.30613 (18)	0.0851 (3)	0.0651 (7)	
H2	0.4953	0.3712	0.0762	0.078*	
C13	0.3605 (2)	−0.08821 (17)	0.2195 (2)	0.0506 (5)	
H13	0.3171	−0.0985	0.2940	0.061*	
C1	0.4781 (2)	0.23225 (17)	0.0050 (2)	0.0551 (6)	
H1	0.4307	0.2404	−0.0672	0.066*	
C12	0.3297 (2)	0.0845 (2)	0.3729 (2)	0.0594 (7)	
H12	0.3734	0.0392	0.4187	0.071*	
C11	0.2741 (3)	0.1593 (2)	0.4364 (2)	0.0673 (7)	
H11	0.2796	0.1642	0.5248	0.081*	
C3	0.5818 (3)	0.2653 (2)	0.1808 (3)	0.0642 (7)	
H3	0.6179	0.2972	0.2487	0.077*	
C10	0.2107 (2)	0.22629 (19)	0.3680 (2)	0.0549 (6)	
C5	0.2535 (2)	−0.0300 (2)	−0.1037 (3)	0.0651 (7)	

H5A	0.1973	0.0215	−0.0914	0.098*	
H5B	0.2526	−0.0716	−0.0304	0.098*	
H5C	0.2318	−0.0663	−0.1784	0.098*	
C4	0.5856 (2)	0.16622 (17)	0.1551 (2)	0.0505 (5)	
C14	1.0000	0.0000	0.3423 (7)	0.135 (2)	
C15	0.9586 (4)	0.0770 (4)	0.4130 (6)	0.1245 (18)	
H15	0.9309	0.1311	0.3696	0.149*	
C16	0.9561 (4)	0.0779 (4)	0.5446 (6)	0.1265 (17)	
H16	0.9251	0.1304	0.5888	0.152*	
C6	0.3784 (3)	0.0670 (2)	−0.2366 (3)	0.0746 (8)	
H6A	0.3631	0.0264	−0.3091	0.112*	
H6B	0.4565	0.0950	−0.2444	0.112*	
H6C	0.3196	0.1174	−0.2332	0.112*	
C17	1.0000	0.0000	0.6079 (7)	0.117 (2)	
H17	1.0000	0.0000	0.6968	0.141*	
Cl	0.13535 (9)	0.31837 (6)	0.44888 (7)	0.0879 (3)	
C18	1.0000	0.0000	0.2026 (6)	0.135 (2)	
H18A	0.9518	0.0524	0.1720	0.203*	0.50
H18B	0.9679	−0.0600	0.1720	0.203*	0.50
H18C	1.0803	0.0075	0.1720	0.203*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti	0.0425 (3)	0.0420 (3)	0.0339 (2)	0.0016 (2)	0.000	0.000
N3	0.0455 (9)	0.0466 (9)	0.0413 (8)	−0.0013 (10)	0.0007 (7)	0.0020 (9)
N1	0.0506 (10)	0.0436 (10)	0.0464 (9)	−0.0002 (8)	0.0061 (8)	0.0025 (8)
C7	0.0420 (10)	0.0498 (12)	0.0397 (10)	−0.0017 (10)	0.0044 (9)	0.0029 (9)
N2	0.0529 (10)	0.0574 (12)	0.0431 (8)	0.0072 (10)	−0.0077 (8)	0.0005 (9)
C8	0.0482 (12)	0.0519 (13)	0.0374 (10)	−0.0034 (10)	0.0014 (9)	0.0001 (9)
C9	0.0559 (13)	0.0489 (13)	0.0497 (13)	0.0044 (11)	−0.0017 (11)	0.0017 (10)
C2	0.0718 (17)	0.0404 (12)	0.0831 (17)	0.0009 (13)	0.0133 (15)	0.0038 (12)
C13	0.0515 (12)	0.0522 (14)	0.0482 (12)	−0.0038 (11)	0.0060 (10)	0.0076 (10)
C1	0.0579 (13)	0.0496 (13)	0.0579 (12)	0.0034 (10)	0.0104 (13)	0.0122 (11)
C12	0.0698 (15)	0.0671 (17)	0.0412 (12)	0.0118 (13)	−0.0048 (11)	0.0051 (12)
C11	0.091 (2)	0.0747 (18)	0.0364 (11)	0.0136 (16)	−0.0008 (12)	−0.0040 (12)
C3	0.0696 (16)	0.0471 (14)	0.0760 (17)	−0.0076 (12)	0.0056 (14)	−0.0090 (13)
C10	0.0634 (14)	0.0534 (14)	0.0480 (13)	0.0037 (12)	0.0050 (11)	−0.0074 (11)
C5	0.0571 (15)	0.0772 (18)	0.0611 (15)	0.0017 (13)	−0.0155 (12)	−0.0110 (12)
C4	0.0526 (12)	0.0466 (13)	0.0524 (12)	−0.0073 (11)	0.0042 (10)	−0.0051 (10)
C14	0.126 (3)	0.178 (5)	0.102 (3)	−0.114 (4)	0.000	0.000
C15	0.095 (3)	0.124 (4)	0.154 (5)	−0.039 (3)	−0.043 (3)	0.027 (3)
C16	0.094 (3)	0.144 (5)	0.141 (4)	−0.012 (3)	−0.015 (3)	−0.020 (4)
C6	0.087 (2)	0.084 (2)	0.0535 (14)	0.0153 (17)	−0.0109 (15)	0.0142 (14)
C17	0.094 (4)	0.153 (6)	0.104 (4)	0.016 (5)	0.000	0.000
Cl	0.1167 (7)	0.0798 (5)	0.0672 (4)	0.0314 (5)	0.0061 (4)	−0.0202 (4)
C18	0.126 (3)	0.178 (5)	0.102 (3)	−0.114 (4)	0.000	0.000

Geometric parameters (Å, º)

Ti—N2^{i}	1.9013 (19)	C12—H12	0.9300
Ti—N2	1.9013 (19)	C11—C10	1.370 (4)
Ti—N1	2.1041 (19)	C11—H11	0.9300
Ti—N1^{i}	2.1042 (19)	C3—C4	1.399 (4)
Ti—N3^{i}	2.3152 (17)	C3—H3	0.9300
Ti—N3	2.3152 (17)	C10—Cl	1.748 (3)
N3—C13	1.309 (3)	C5—H5A	0.9600
N3—C7	1.411 (3)	C5—H5B	0.9600
N1—C1	1.350 (3)	C5—H5C	0.9600
N1—C4	1.378 (3)	C4—C13^{i}	1.409 (3)
C7—C8	1.382 (3)	C14—C15	1.378 (6)
C7—C12	1.397 (3)	C14—C15^{ii}	1.378 (6)
N2—C5	1.452 (3)	C14—C18	1.462 (8)
N2—C6	1.453 (3)	C15—C16	1.377 (8)
C8—C9	1.378 (3)	C15—H15	0.9300
C8—H8	0.9300	C16—C17	1.359 (6)
C9—C10	1.376 (3)	C16—H16	0.9300
C9—H9	0.9300	C6—H6A	0.9600
C2—C3	1.379 (4)	C6—H6B	0.9600
C2—C1	1.382 (4)	C6—H6C	0.9600
C2—H2	0.9300	C17—C16^{ii}	1.359 (6)
C13—C4^{i}	1.409 (3)	C17—H17	0.9300
C13—H13	0.9300	C18—H18A	0.9600
C1—H1	0.9300	C18—H18B	0.9600
C12—C11	1.378 (4)	C18—H18C	0.9600
N2^{i}—Ti—N2	98.06 (12)	C7—C12—H12	119.8
N2^{i}—Ti—N1	97.88 (8)	C10—C11—C12	119.4 (2)
N2—Ti—N1	99.75 (8)	C10—C11—H11	120.3
N2^{i}—Ti—N1^{i}	99.76 (8)	C12—C11—H11	120.3
N2—Ti—N1^{i}	97.88 (8)	C2—C3—C4	106.3 (3)
N1—Ti—N1^{i}	152.96 (10)	C2—C3—H3	126.9
N2^{i}—Ti—N3^{i}	93.02 (7)	C4—C3—H3	126.9
N2—Ti—N3^{i}	168.31 (8)	C11—C10—C9	121.4 (2)
N1—Ti—N3^{i}	74.92 (8)	C11—C10—Cl	119.41 (19)
N1^{i}—Ti—N3^{i}	83.81 (7)	C9—C10—Cl	119.1 (2)
N2^{i}—Ti—N3	168.31 (8)	N2—C5—H5A	109.5
N2—Ti—N3	93.02 (7)	N2—C5—H5B	109.5
N1—Ti—N3	83.81 (7)	H5A—C5—H5B	109.5
N1^{i}—Ti—N3	74.92 (8)	N2—C5—H5C	109.5
N3^{i}—Ti—N3	76.19 (8)	H5A—C5—H5C	109.5
C13—N3—C7	118.36 (19)	H5B—C5—H5C	109.5
C13—N3—Ti	111.21 (16)	N1—C4—C3	109.6 (2)
C7—N3—Ti	129.97 (15)	N1—C4—C13^{i}	118.0 (2)
C1—N1—C4	106.1 (2)	C3—C4—C13^{i}	132.4 (2)
C1—N1—Ti	137.17 (17)	C15—C14—C15^{ii}	115.0 (7)

C4—N1—Ti	116.32 (15)	C15—C14—C18	122.5 (3)
C8—C7—C12	118.8 (2)	C15^{ii}—C14—C18	122.5 (3)
C8—C7—N3	119.42 (19)	C16—C15—C14	123.4 (6)
C12—C7—N3	121.8 (2)	C16—C15—H15	118.3
C5—N2—C6	110.5 (2)	C14—C15—H15	118.3
C5—N2—Ti	125.68 (17)	C17—C16—C15	118.2 (6)
C6—N2—Ti	123.6 (2)	C17—C16—H16	120.9
C9—C8—C7	121.0 (2)	C15—C16—H16	120.9
C9—C8—H8	119.5	N2—C6—H6A	109.5
C7—C8—H8	119.5	N2—C6—H6B	109.5
C10—C9—C8	119.0 (2)	H6A—C6—H6B	109.5
C10—C9—H9	120.5	N2—C6—H6C	109.5
C8—C9—H9	120.5	H6A—C6—H6C	109.5
C3—C2—C1	107.2 (2)	H6B—C6—H6C	109.5
C3—C2—H2	126.4	C16^{ii}—C17—C16	121.6 (7)
C1—C2—H2	126.4	C16^{ii}—C17—H17	119.2
N3—C13—C4^{i}	119.1 (2)	C16—C17—H17	119.2
N3—C13—H13	120.5	C14—C18—H18A	109.5
C4^{i}—C13—H13	120.5	C14—C18—H18B	109.5
N1—C1—C2	110.8 (2)	H18A—C18—H18B	109.5
N1—C1—H1	124.6	C14—C18—H18C	109.5
C2—C1—H1	124.6	H18A—C18—H18C	109.5
C11—C12—C7	120.3 (2)	H18B—C18—H18C	109.5
C11—C12—H12	119.8		

Symmetry codes: (i) −*x*+1, −*y*, *z*; (ii) −*x*+2, −*y*, *z*.