

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

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

Zhou Chen,<sup>a</sup> Jian Wu,<sup>b</sup> Yahong Li<sup>a,b\*</sup> and Bin Hu<sup>a</sup>

<sup>a</sup>Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, People's Republic of China, and <sup>b</sup>Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China  
Correspondence e-mail: liyahong@suda.edu.cn

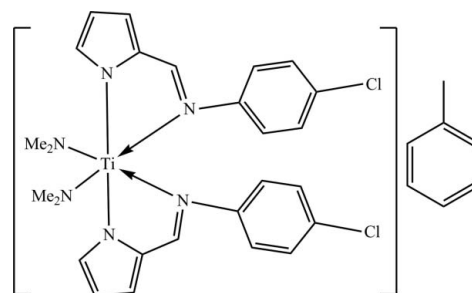
Received 28 March 2012; accepted 5 April 2012

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(C-C) = 0.005$  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-pyrrolylcarbalimine 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-pyrrolylcarbalimine 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

$[Ti(C_{11}H_8ClN_2)_2(C_2H_6N)_2] \cdot C_7H_8$   $V = 1623.18$  (10) Å<sup>3</sup>  
 $M_r = 635.48$   $Z = 2$   
 Orthorhombic,  $P2_12_12_1$  Mo  $K\alpha$  radiation  
 $a = 11.1952$  (4) Å  $\mu = 0.46$  mm<sup>-1</sup>  
 $b = 13.8545$  (6) Å  $T = 296$  K  
 $c = 10.4651$  (3) Å  $0.27 \times 0.25 \times 0.20$  mm

#### Data collection

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

#### Refinement

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

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.

The authors appreciate financial support from the Hundreds of Talents Program (2005012) of the CAS, the Natural Science Foundation of China (20872105), the Qinglan Project of Jiangsu Province (Bu109805) and the Open Project of the Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education of Lanzhou University (LZUMMM2010003).

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

### References

- Bexrud, J. A., Li, C. & Schafer, L. L. (2007). *Organometallics*, **26**, 6366–6372.  
 Braunschweig, H. & Breitling, F. M. (2006). *Coord. Chem. Rev.* **250**, 2691–2720.  
 Bruker (2005). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Cao, C., Ciszewski, J. T. & Odom, A. L. (2001). *Organometallics*, **20**, 5011–5013.

- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Mozaffar, A., Mohammad Hadi, G., Susan, T., Khosro, M. & Fatemeh, M. (2010). *J. Chem. Sci.* **122**, 539–548.
- Ramanathan, B., Keith, A. J., Armstrong, D. & Odom, A. L. (2004). *Org. Lett.* **6**, 2957–2960.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tillack, A., Khedkar, V., Jiao, H. & Beller, M. (2005). *Eur. J. Org. Chem.* pp. 5001–5012.
- Zhao, Y., Lin, M., Chen, Z., Pei, H., Li, Y., Chen, Y., Wang, X., Li, L., Cao, Y., Zhang, Y. & Li, W. (2012). *RSC Adv.* **2**, 144–150.

## supplementary materials

*Acta Cryst.* (2012). E68, m596–m597 [doi:10.1107/S1600536812014961]

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

Zhou Chen, Jian Wu, Yahong Li and Bin Hu

### 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<sub>11</sub>H<sub>8</sub>N<sub>2</sub>Cl)<sub>2</sub>(C<sub>2</sub>H<sub>6</sub>N)<sub>2</sub>](C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), (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<sup>IV</sup> 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 pyrrolcarbaldimine 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.

### Experimental

To a solution of Ti(NMe<sub>2</sub>)<sub>4</sub> (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.

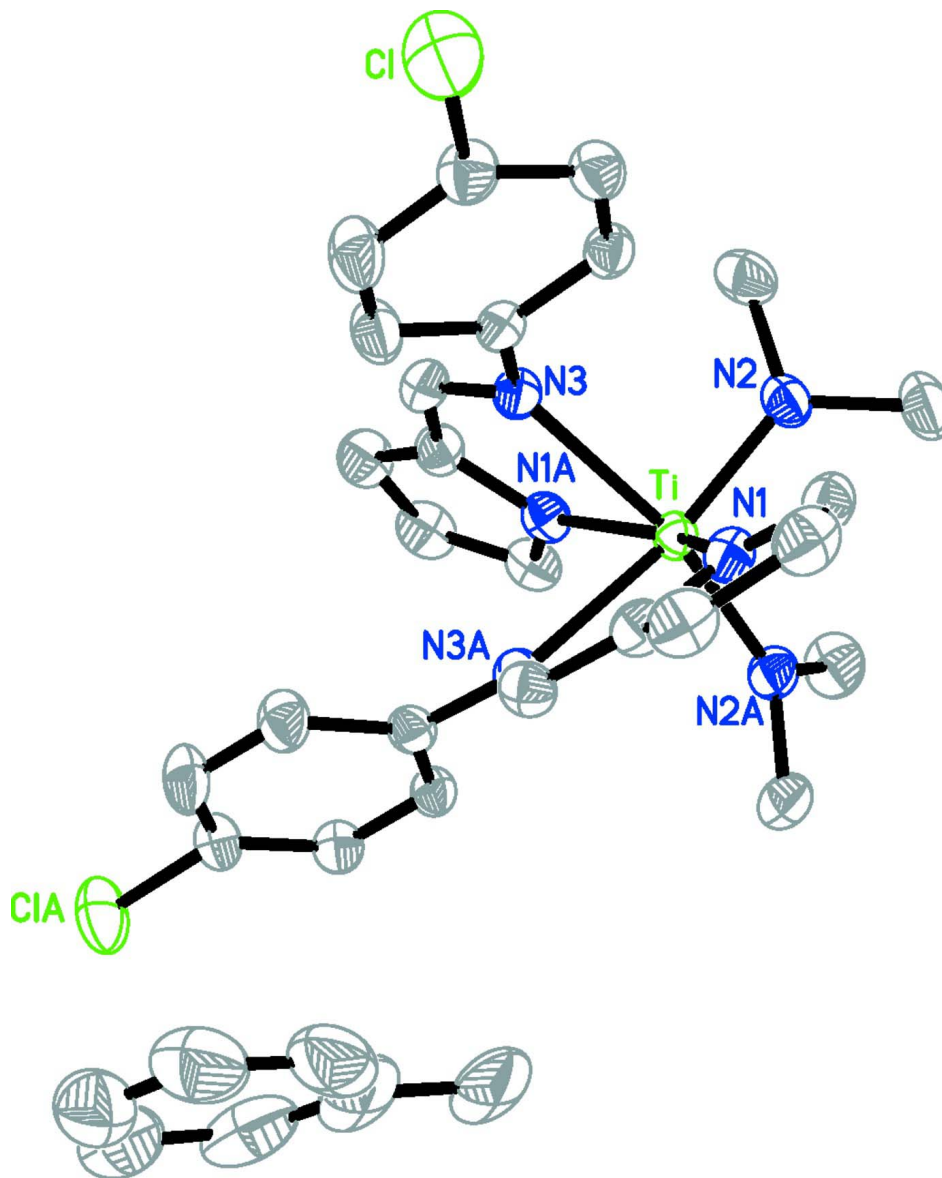
### Refinement

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<sub>3</sub> type H atoms and 0.98 Å for CH type H atoms, respectively. *U*<sub>iso</sub>(H) values were set at 1.5U<sub>eq</sub>(C) for methyl H atoms, and 1.2U<sub>eq</sub>(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.

### Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINTE* (Bruker, 2005); data reduction: *SAINTE* (Bruker, 2005); 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* (Sheldrick, 2008).



**Figure 1**

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

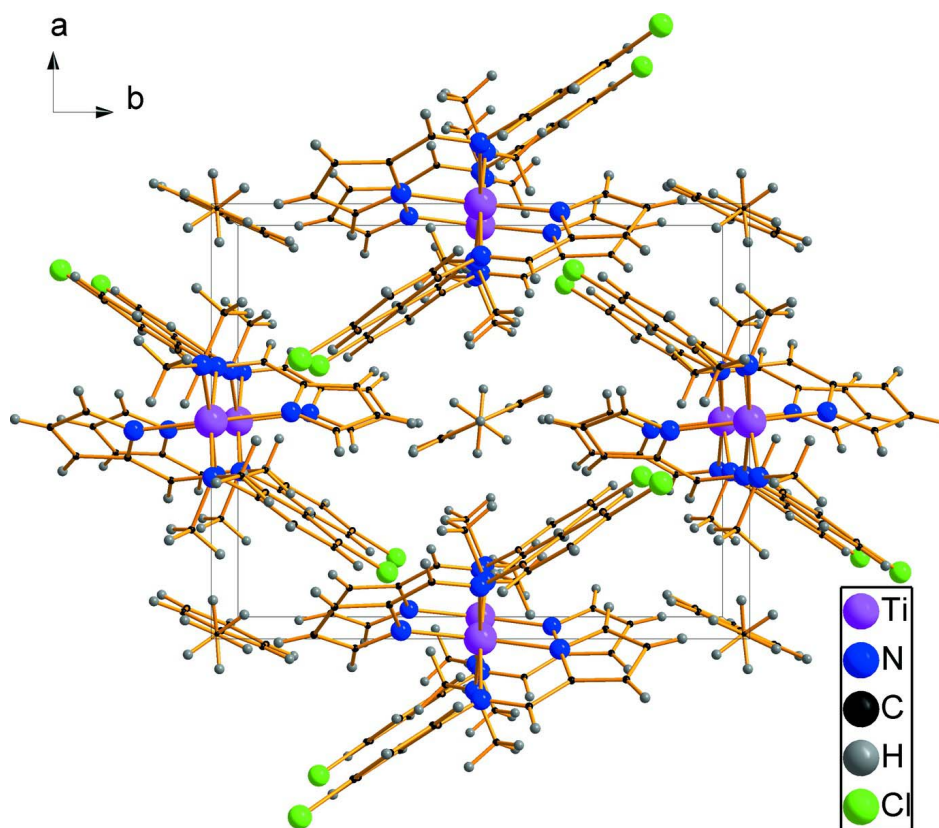


Figure 2

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

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

*Crystal data*

$[\text{Ti}(\text{C}_{11}\text{H}_8\text{ClN}_2)_2(\text{C}_2\text{H}_6\text{N})_2] \cdot \text{C}_7\text{H}_8$

$M_r = 635.48$

Orthorhombic,  $P2_12_12$

Hall symbol:  $P\ 2\ 2ab$

$a = 11.1952\ (4)\ \text{\AA}$

$b = 13.8545\ (6)\ \text{\AA}$

$c = 10.4651\ (3)\ \text{\AA}$

$V = 1623.18\ (10)\ \text{\AA}^3$

$Z = 2$

$F(000) = 664$

$D_x = 1.300\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3510 reflections

$\theta = 2.7\text{--}25.3^\circ$

$\mu = 0.46\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, red

$0.27 \times 0.25 \times 0.20\ \text{mm}$

*Data collection*

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  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  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 2.0^\circ$

$h = -13 \rightarrow 13$

$k = -6 \rightarrow 17$

$l = -12 \rightarrow 12$

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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.81 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack (1983), 1338 Friedel  
 pairs  
 Flack 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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	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*	
C1	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 ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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
C1	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, °)

Ti—N2 <sup>i</sup>	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 <sup>i</sup>	2.1042 (19)	C3—C4	1.399 (4)
Ti—N3 <sup>i</sup>	2.3152 (17)	C3—H3	0.9300
Ti—N3	2.3152 (17)	C10—C1	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 <sup>i</sup>	1.409 (3)
C7—C8	1.382 (3)	C14—C15	1.378 (6)
C7—C12	1.397 (3)	C14—C15 <sup>ii</sup>	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 <sup>ii</sup>	1.359 (6)
C13—C4 <sup>i</sup>	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 <sup>i</sup> —Ti—N2	98.06 (12)	C7—C12—H12	119.8
N2 <sup>i</sup> —Ti—N1	97.88 (8)	C10—C11—C12	119.4 (2)
N2—Ti—N1	99.75 (8)	C10—C11—H11	120.3
N2 <sup>i</sup> —Ti—N1 <sup>i</sup>	99.76 (8)	C12—C11—H11	120.3
N2—Ti—N1 <sup>i</sup>	97.88 (8)	C2—C3—C4	106.3 (3)
N1—Ti—N1 <sup>i</sup>	152.96 (10)	C2—C3—H3	126.9
N2 <sup>i</sup> —Ti—N3 <sup>i</sup>	93.02 (7)	C4—C3—H3	126.9
N2—Ti—N3 <sup>i</sup>	168.31 (8)	C11—C10—C9	121.4 (2)
N1—Ti—N3 <sup>i</sup>	74.92 (8)	C11—C10—C1	119.41 (19)
N1 <sup>i</sup> —Ti—N3 <sup>i</sup>	83.81 (7)	C9—C10—C1	119.1 (2)
N2 <sup>i</sup> —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 <sup>i</sup> —Ti—N3	74.92 (8)	N2—C5—H5C	109.5
N3 <sup>i</sup> —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 <sup>i</sup>	118.0 (2)
C1—N1—C4	106.1 (2)	C3—C4—C13 <sup>i</sup>	132.4 (2)
C1—N1—Ti	137.17 (17)	C15—C14—C15 <sup>ii</sup>	115.0 (7)
C4—N1—Ti	116.32 (15)	C15—C14—C18	122.5 (3)
C8—C7—C12	118.8 (2)	C15 <sup>ii</sup> —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 <sup>i</sup> —C17—C16	121.6 (7)
C1—C2—H2	126.4	C16 <sup>i</sup> —C17—H17	119.2
N3—C13—C4 <sup>i</sup>	119.1 (2)	C16—C17—H17	119.2
N3—C13—H13	120.5	C14—C18—H18A	109.5
C4 <sup>i</sup> —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)  $-x+2, -y, z$ .