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Di-μ-chlorido-bis[dichlorido(*N*,*N*-diethylacetamidinato)(*N*,*N*-diethylacetamidine)titanium(IV)] acetonitrile disolvate

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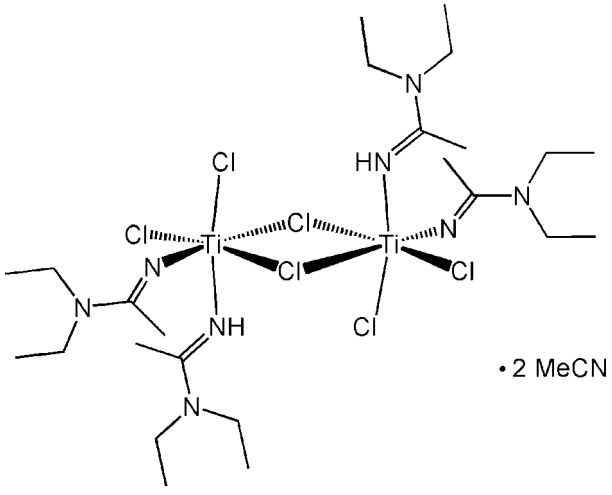
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.045; wR factor = 0.134; data-to-parameter ratio = 18.0.

In the centrosymmetric title compound $[Ti_2Cl_6(C_6H_{13}N_2)_2(C_6H_{14}N_2)_2]\cdot 2C_2H_3N$, an inversion center relates the two Ti atoms which display a distorted octahedral coordination geometry. There are two uncoordinated acetonitrile solvent molecules per molecule of title compound in the crystal structure.

Related literature

For the structure, see: Dunn *et al.* (1994); Guiducci *et al.* (2001); Lewkebandara *et al.* (1994); Nielson *et al.* (2001). For the reaction mechanism, see: Bradley & Ganorkar (1968); Chandra *et al.* (1970); Forsberg *et al.* (1987); Maresca *et al.* (1986); Rouschias & Wilkinson (1968).



Experimental

Crystal data

$[Ti_2Cl_6(C_6H_{13}N_2)_2(C_6H_{14}N_2)_2]\cdot 2C_2H_3N$
M_r = 845.36
Triclinic, $P\overline{1}$
a = 9.6217 (6) Å
b = 11.1812 (7) Å
c = 11.2298 (8) Å
α = 95.680 (1)°
β = 105.192 (1)°
γ = 106.938 (1)°
V = 1095.03 (12) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.76 mm^{-1}
T = 298 (2) K
0.30 × 0.15 × 0.15 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003*a*)
T_{min} = 0.870, T_{max} = 0.890
8928 measured reflections
3871 independent reflections
2999 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.134
S = 1.02
3871 reflections
215 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2003*b*); 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: LX2036).

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supplementary materials

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Di-μ-chlorido-bis[dichlorido(*N*,*N*-diethylacetamidinato)(*N*,*N*-diethylacetamidine)titanium(IV)] acetonitrile disolvate

N. A. Straessler, M. T. Caudle and T. L. Groy

Comment

The structure of title compound, (I) was solved as part of an investigation into the effects of nitriles on *N*,*N*-dialkylamido titanium(IV) complexes. Compound (I) is a dimeric molecule in which two symmetrically equivalent titanium atoms are each coordinated by one anionic diethylacetamidino group (N1), one neutral diethylacetamidine ligand (N3), two terminal chlorides (Cl2 and Cl3), and two equivalent bridging chlorides (Cl1). This gives a pseudo–octahedral configuration about each titanium center. The acetamidine and acetamidino ligands are oriented in *cis* coordination positions.

The Ti_2Cl_2 unit of (I) is distorted such that the Ti1—Cl1 bond that is *trans* to the diethylacetamidino ligand is significantly longer than the Ti—Cl1 bond that is *trans* to Cl3 (2.7002 (8) Å *versus*. 2.4557 (8) Å). This is consistent with the greater sigma-electron donating ability of the acetamidino ligand relative to the Cl^-. The Ti—Cl1—Ti bond angle is 102.96 (3)°, similar to that of other dichloro-bridged Ti^{4+} compounds (Nielson *et al.*, 2001). The terminal titanium–chloride bond lengths (Ti—Cl2 = 2.3882 (8) Å and Ti—Cl3 = 2.3511 (9) Å) are shorter than the bridging Ti—Cl1 bonds, and are within the normal range for such linkages.

In general, the ligands in (I) bend away from the diethylacetamidino group resulting in bond angles greater than the ideal 90° for octahedral complexes {N1—Ti—Cl3 = 101.24 (9)°, N1—Ti—Cl1 = 95.57 (9)°, N1—Ti—Cl2 = 95.51 (8)°, N1—Ti—N3 = 94.42 (10)°}. This can be attributed to electrostatic repulsion caused by substantial pi–electron donation from the diethylacetamidino nitrogen to the empty 3 d orbitals on Ti^{4+}. The approximately linear Ti—N1—C1 bond angle (165.7 (2)°) and the short Ti—N1 bond length (1.751 (2) Å) indicate significant Ti—N1 multiple–bond character analogous to those observed in titanium(IV) imides (Guiducci *et al.*, 2001; Lewkebandara *et al.*, 1994; Dunn *et al.*, 1994). The Ti—N3 acetamidine bond length is 2.130 (2) Å, which is 0.379 Å longer than the Ti—N1 acetamidino bond length at 1.751 (2) Å, clearly supporting multiple–bond character in the Ti—N1 bond.

Formation of metal–amidine complexes has been shown to occur by two different mechanisms: (1) acetonitrile insertion into metal–amide bonds (Bradley & Ganorkar, 1968; Chandra *et al.*, 1970); (2) nucleophilic attack by free amine on co-ordinated nitriles in the presence of metal ions (Forsberg *et al.*, 1987; Rouschias & Wilkinson, 1968; Maresca *et al.*, 1986). However, secondary amines such as diethylamine do not react with nitriles in the absence of metal ions. The addition of $TiCl_4$ to acetonitrile results in a yellow solvate formed by coordination of CH_3CN to the titanium atom. We speculate that (I) then most likely forms *via* mechanism 2 because the metal-nitrogen linkage to the nitrile is established before addition of diethylamine. Furthermore, direct insertion of CH_3CN has been reported to only occur slowly (Bradley & Ganorkar, 1968), whereas we observe reaction of diethylamine with the $TiCl_4$–acetonitrile solvate to occur immediately.

Experimental

While stirring under an atmosphere of nitrogen, 2 ml (18.24 mmol) of $TiCl_4$ were added to approximately 50 ml of anhydrous acetonitrile in a Schlenk flask. To the resulting bright yellow solution was added 5.66 ml (54.71 mmol) of diethylamine. The exothermic reaction turned dark orange and white solid began to precipitate immediately. After twelve hours of stirring, solid white diethylammonium chloride was removed by filtration under nitrogen, and the filtrate was concentrated by intermittent evaporation with a stream of nitrogen over a period of four days. Removal of almost half of the solvent yielded X-ray quality crystals of **I**.

Refinement

Hydrogen atoms were positioned geometrically and allowed to ride on their bonding partners with C—H distances = 0.96Å and U_{iso}(H) = 1.5U_{eq}(C) for the methyl H atoms, C—H distances = 0.97Å and U_{iso}(H) = 1.2U_{eq}(C) for the methylene H atoms, and N—H distance = 0.86Å and U_{iso}(H) = 1.2U_{eq}(N) for the amino hydrogen.

Figures

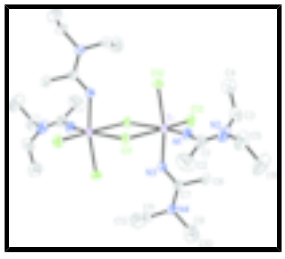

Fig. 1. Thermal ellipsoid plot of centrosymmetric title compund shown at the 30% probability level. Solvent molecules and hydrogen atoms omitted for clarity. Only unique atoms are labeled.

Di-μ-chlorido-bis[dichlorido(*N*,*N*-diethylacetamidinato)(N,*N*- diethylacetamidine)titanium(IV)] acetonitrile disolvate

Crystal data

$[Ti_2Cl_6(C_6H_{13}N_2)_2(C_6H_{14}N_2)_2]\cdot 2C_2H_3N$	$Z = 1$
$M_r = 845.36$	$F_{000} = 444$
Triclinic, $P\overline{1}$	$D_x = 1.282$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 9.6217$ (6) Å	Cell parameters from 5597 reflections
$b = 11.1812$ (7) Å	$\theta = 4.7–55.0°$
$c = 11.2298$ (8) Å	$\mu = 0.76$ mm^{-1}
$\alpha = 95.680$ (1)°	$T = 298$ (2) K
$\beta = 105.192$ (1)°	Block, orange
$\gamma = 106.938$ (1)°	0.30 × 0.15 × 0.15 mm
$V = 1095.03$ (12) Å^3	

Data collection

Bruker SMART APEX diffractometer	3871 independent reflections
Radiation source: fine-focus sealed tube	2999 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.045$
$T = 298(2)$ K	$\theta_{max} = 25.0^{o}$
ω scan	$\theta_{min} = 1.9^{o}$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003a)	$h = -11 \rightarrow 11$
$T_{min} = 0.870$, $T_{max} = 0.890$	$k = -13 \rightarrow 13$
8928 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H-atom parameters constrained
$wR(F^2) = 0.134$	$w = 1/[\sigma^2(F_o^2) + (0.0851P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
3871 reflections	$\Delta\rho_{max} = 0.82$ e Å^{-3}
215 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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}
Ti	0.68333 (5)	0.53749 (4)	0.65286 (4)	0.04665 (18)
Cl1	0.62466 (7)	0.54169 (6)	0.42723 (6)	0.0509 (2)
Cl2	0.65097 (9)	0.31620 (6)	0.60603 (8)	0.0697 (3)
Cl3	0.66161 (11)	0.52732 (8)	0.85562 (7)	0.0787 (3)
N1	0.8818 (3)	0.5903 (2)	0.6847 (2)	0.0596 (6)

C1	1.0294 (5)	0.6394 (3)	0.6804 (3)	0.0803 (10)
C2	1.0542 (5)	0.7145 (5)	0.5730 (5)	0.135 (2)
H2A	1.1219	0.6877	0.5358	0.203*
H2B	1.0979	0.8041	0.6073	0.203*
H2C	0.9579	0.6978	0.5101	0.203*
N2	1.1381 (3)	0.6309 (3)	0.7609 (3)	0.0836 (9)
C3	1.1039 (5)	0.5546 (4)	0.8621 (4)	0.0909 (12)
H3A	1.1916	0.5854	0.9371	0.109*
H3B	1.0184	0.5697	0.8837	0.109*
C4	1.0682 (6)	0.4183 (5)	0.8236 (5)	0.136 (2)
H4A	1.0827	0.3799	0.8967	0.204*
H4B	1.1345	0.4034	0.7774	0.204*
H4C	0.9641	0.3815	0.7714	0.204*
C5	1.2977 (4)	0.6763 (4)	0.7612 (4)	0.0981 (14)
H5A	1.3002	0.6815	0.6760	0.118*
H5B	1.3466	0.6153	0.7897	0.118*
C6	1.3848 (5)	0.8030 (5)	0.8434 (5)	0.132 (2)
H6A	1.4855	0.8319	0.8353	0.198*
H6B	1.3917	0.7964	0.9292	0.198*
H6C	1.3334	0.8626	0.8189	0.198*
N3	0.6676 (3)	0.72414 (19)	0.66808 (19)	0.0484 (5)
H3C	0.5873	0.7282	0.6148	0.058*
C7	0.7531 (3)	0.8339 (2)	0.7406 (2)	0.0480 (6)
C8	0.8672 (3)	0.8363 (3)	0.8616 (3)	0.0621 (8)
H8A	0.8564	0.7507	0.8738	0.093*
H8B	0.8499	0.8823	0.9300	0.093*
H8C	0.9684	0.8776	0.8584	0.093*
N4	0.7431 (3)	0.9462 (2)	0.7128 (2)	0.0579 (6)
C9	0.8370 (4)	1.0706 (3)	0.7955 (3)	0.0731 (9)
H9A	0.8673	1.1323	0.7443	0.088*
H9B	0.9289	1.0624	0.8501	0.088*
C10	0.7545 (5)	1.1182 (4)	0.8737 (4)	0.1025 (14)
H10A	0.8175	1.2011	0.9222	0.154*
H10B	0.7312	1.0608	0.9293	0.154*
H10C	0.6615	1.1237	0.8203	0.154*
C11	0.6473 (4)	0.9544 (3)	0.5929 (3)	0.0742 (10)
H11A	0.6273	1.0346	0.6006	0.089*
H11B	0.5503	0.8862	0.5705	0.089*
C12	0.7191 (6)	0.9456 (5)	0.4896 (4)	0.1124 (16)
H12A	0.6590	0.9637	0.4153	0.169*
H12B	0.7236	0.8612	0.4721	0.169*
H12C	0.8204	1.0061	0.5157	0.169*
N5	0.7942 (7)	0.9547 (5)	0.1738 (6)	0.175 (2)
C13	0.7192 (6)	0.8570 (5)	0.1685 (5)	0.1060 (14)
C14	0.6195 (7)	0.7345 (5)	0.1617 (6)	0.1335 (18)
H14A	0.5241	0.7402	0.1683	0.200*
H14B	0.6639	0.6977	0.2293	0.200*
H14C	0.6025	0.6819	0.0828	0.200*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti	0.0470 (3)	0.0384 (3)	0.0445 (3)	0.0127 (2)	−0.0004 (2)	0.0059 (2)
Cl1	0.0511 (4)	0.0509 (4)	0.0447 (4)	0.0153 (3)	0.0081 (3)	0.0041 (3)
Cl2	0.0661 (5)	0.0421 (4)	0.0841 (6)	0.0206 (4)	−0.0059 (4)	0.0067 (4)
Cl3	0.0915 (6)	0.0739 (5)	0.0456 (4)	0.0040 (5)	0.0037 (4)	0.0171 (4)
N1	0.0457 (14)	0.0528 (14)	0.0677 (15)	0.0153 (11)	0.0003 (11)	0.0041 (11)
C1	0.076 (2)	0.073 (2)	0.081 (2)	0.032 (2)	0.008 (2)	−0.0126 (18)
C2	0.079 (3)	0.152 (5)	0.187 (5)	0.022 (3)	0.055 (3)	0.099 (4)
N2	0.0541 (17)	0.082 (2)	0.097 (2)	0.0180 (15)	0.0127 (16)	−0.0198 (17)
C3	0.083 (3)	0.103 (3)	0.084 (3)	0.041 (2)	0.006 (2)	0.027 (2)
C4	0.126 (4)	0.097 (4)	0.134 (4)	0.023 (3)	−0.022 (3)	0.010 (3)
C5	0.051 (2)	0.118 (3)	0.113 (3)	0.027 (2)	0.022 (2)	−0.027 (3)
C6	0.058 (2)	0.137 (4)	0.159 (5)	−0.001 (3)	0.030 (3)	−0.046 (4)
N3	0.0502 (13)	0.0409 (12)	0.0443 (12)	0.0163 (10)	−0.0014 (9)	0.0029 (9)
C7	0.0476 (15)	0.0463 (15)	0.0444 (14)	0.0132 (12)	0.0093 (12)	0.0026 (11)
C8	0.0627 (19)	0.0536 (17)	0.0512 (17)	0.0114 (15)	−0.0018 (13)	0.0011 (13)
N4	0.0654 (16)	0.0363 (12)	0.0557 (14)	0.0118 (11)	0.0013 (11)	−0.0024 (10)
C9	0.083 (2)	0.0399 (16)	0.072 (2)	0.0089 (16)	0.0028 (17)	−0.0060 (14)
C10	0.134 (4)	0.077 (3)	0.090 (3)	0.044 (3)	0.022 (3)	−0.013 (2)
C11	0.093 (2)	0.0432 (16)	0.070 (2)	0.0233 (16)	−0.0030 (18)	0.0061 (14)
C12	0.150 (4)	0.106 (3)	0.071 (3)	0.026 (3)	0.029 (3)	0.032 (2)
N5	0.170 (5)	0.122 (4)	0.249 (6)	0.012 (3)	0.132 (5)	0.038 (4)
C13	0.102 (3)	0.101 (3)	0.132 (4)	0.028 (3)	0.069 (3)	0.031 (3)
C14	0.144 (5)	0.101 (4)	0.162 (5)	0.029 (3)	0.065 (4)	0.041 (3)

Geometric parameters (Å, °)

Ti—N1	1.751 (2)	N3—C7	1.307 (3)
Ti—N3	2.130 (2)	N3—H3C	0.8600
Ti—Cl3	2.3511 (9)	C7—N4	1.348 (3)
Ti—Cl2	2.3882 (8)	C7—C8	1.498 (4)
Ti—Cl1	2.4557 (8)	C8—H8A	0.9600
Ti—Cl1^{i}	2.7002 (8)	C8—H8B	0.9600
Cl1—Ti^{i}	2.7002 (8)	C8—H8C	0.9600
N1—C1	1.381 (4)	N4—C11	1.447 (4)
C1—N2	1.225 (4)	N4—C9	1.478 (3)
C1—C2	1.566 (6)	C9—C10	1.484 (5)
C2—H2A	0.9600	C9—H9A	0.9700
C2—H2B	0.9600	C9—H9B	0.9700
C2—H2C	0.9600	C10—H10A	0.9600
N2—C5	1.469 (4)	C10—H10B	0.9600
N2—C3	1.534 (5)	C10—H10C	0.9600
C3—C4	1.454 (6)	C11—C12	1.506 (5)
C3—H3A	0.9700	C11—H11A	0.9700
C3—H3B	0.9700	C11—H11B	0.9700

C4—H4A	0.9600	C12—H12A	0.9600
C4—H4B	0.9600	C12—H12B	0.9600
C4—H4C	0.9600	C12—H12C	0.9600
C5—C6	1.485 (6)	N5—C13	1.106 (6)
C5—H5A	0.9700	C13—C14	1.406 (7)
C5—H5B	0.9700	C14—H14A	0.9600
C6—H6A	0.9600	C14—H14B	0.9600
C6—H6B	0.9600	C14—H14C	0.9600
C6—H6C	0.9600		
N1—Ti—N3	94.42 (10)	C5—C6—H6C	109.5
N1—Ti—Cl3	101.24 (9)	H6A—C6—H6C	109.5
N3—Ti—Cl3	90.72 (6)	H6B—C6—H6C	109.5
N1—Ti—Cl2	95.51 (8)	C7—N3—Ti	134.05 (18)
N3—Ti—Cl2	168.45 (6)	C7—N3—H3C	113.0
Cl3—Ti—Cl2	93.10 (3)	Ti—N3—H3C	113.0
N1—Ti—Cl1	95.57 (9)	N3—C7—N4	123.2 (2)
N3—Ti—Cl1	84.04 (6)	N3—C7—C8	119.0 (2)
Cl3—Ti—Cl1	162.74 (4)	N4—C7—C8	117.8 (2)
Cl2—Ti—Cl1	89.15 (3)	C7—C8—H8A	109.5
N1—Ti—Cl1^{i}	172.61 (9)	C7—C8—H8B	109.5
N3—Ti—Cl1^{i}	84.93 (6)	H8A—C8—H8B	109.5
Cl3—Ti—Cl1^{i}	86.13 (3)	C7—C8—H8C	109.5
Cl2—Ti—Cl1^{i}	84.46 (3)	H8A—C8—H8C	109.5
Cl1—Ti—Cl1^{i}	77.04 (3)	H8B—C8—H8C	109.5
Ti—Cl1—Ti^{i}	102.96 (3)	C7—N4—C11	121.7 (2)
C1—N1—Ti	165.7 (2)	C7—N4—C9	123.6 (2)
N2—C1—N1	121.7 (4)	C11—N4—C9	114.5 (2)
N2—C1—C2	120.8 (4)	N4—C9—C10	112.4 (3)
N1—C1—C2	117.4 (3)	N4—C9—H9A	109.1
C1—C2—H2A	109.5	C10—C9—H9A	109.1
C1—C2—H2B	109.5	N4—C9—H9B	109.1
H2A—C2—H2B	109.5	C10—C9—H9B	109.1
C1—C2—H2C	109.5	H9A—C9—H9B	107.9
H2A—C2—H2C	109.5	C9—C10—H10A	109.5
H2B—C2—H2C	109.5	C9—C10—H10B	109.5
C1—N2—C5	125.3 (4)	H10A—C10—H10B	109.5
C1—N2—C3	117.5 (3)	C9—C10—H10C	109.5
C5—N2—C3	116.9 (3)	H10A—C10—H10C	109.5
C4—C3—N2	113.5 (4)	H10B—C10—H10C	109.5
C4—C3—H3A	108.9	N4—C11—C12	112.4 (3)
N2—C3—H3A	108.9	N4—C11—H11A	109.1
C4—C3—H3B	108.9	C12—C11—H11A	109.1
N2—C3—H3B	108.9	N4—C11—H11B	109.1
H3A—C3—H3B	107.7	C12—C11—H11B	109.1
C3—C4—H4A	109.5	H11A—C11—H11B	107.9
C3—C4—H4B	109.5	C11—C12—H12A	109.5
H4A—C4—H4B	109.5	C11—C12—H12B	109.5

C3—C4—H4C	109.5	H12A—C12—H12B	109.5
H4A—C4—H4C	109.5	C11—C12—H12C	109.5
H4B—C4—H4C	109.5	H12A—C12—H12C	109.5
N2—C5—C6	112.4 (3)	H12B—C12—H12C	109.5
N2—C5—H5A	109.1	N5—C13—C14	178.0 (6)
C6—C5—H5A	109.1	C13—C14—H14A	109.5
N2—C5—H5B	109.1	C13—C14—H14B	109.5
C6—C5—H5B	109.1	H14A—C14—H14B	109.5
H5A—C5—H5B	107.9	C13—C14—H14C	109.5
C5—C6—H6A	109.5	H14A—C14—H14C	109.5
C5—C6—H6B	109.5	H14B—C14—H14C	109.5
H6A—C6—H6B	109.5		

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

Fig. 1