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Di-μ-chlorido-bis{bis[*N*,*N*-bis(trimethylsilyl)amido]-titanium(III)}

Coralie C. Quadri, Karl W. Törnroos and Erwan Le Roux*

Department of Chemistry, University of Bergen, Allégaten 41, N-5007 Bergen, Norway. *Correspondence e-mail: Erwan.LeRoux@uib.no

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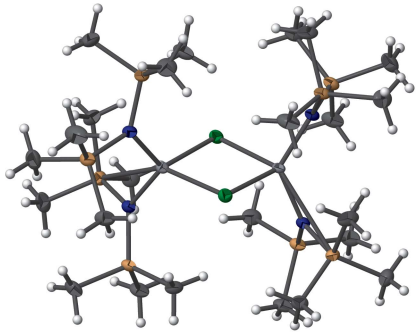
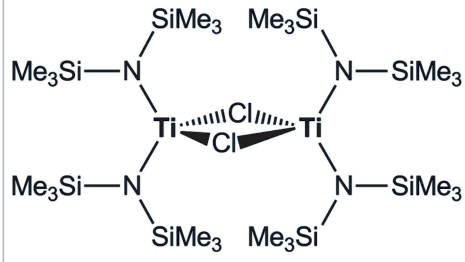
Structural data: full structural data are available from iucrdata.iucr.org

The molecular structure of the title compound, $[Ti_2Cl_2(C_6H_{18}NSi_2)_4]$. shows a binuclear motif of Ti^{III} atoms, formulated as $[Ti(\mu\text{-}Cl)(N(SiMe_3)_2)_2]_2$, with two μ-Cl atoms bridging two $((Me_3Si)_2N)_2Ti$ moieties. The coordination environment of both central Ti^{III} atoms is distorted tetrahedral, with a nearly planar four-membered Ti_2Cl_2 core [Ti—Cl—Ti—Cl = 2.796 (15)°].

3D view



Chemical scheme



Structure description

Group 4 metal silylamide chlorides are versatile starting materials for many inorganic and organometallic compounds, and have been widely used as catalysts (Lappert *et al.*, 1980,2009) and as precursors in chemical vapor deposition (CVD) (Just & Rees, 2000; Carmalt *et al.*, 2005) and atomic layer deposition (ALD) of microelectronic films (Fix *et al.*, 1990,1991; Winter *et al.*, 1994). The use of halide ligands has been established to enhance the volatility of the group 4 silylamide precursors for CVD/ALD processes (Vaartstra *et al.*, 2006). Although analogous compounds such as $[Ti(Cl)_{4-x}(N(SiMe_3)_2)_x]$ (with x = 4, 3, 2 and 1) of titanium(IV) (Alcock *et al.*, 1976; Planalp *et al.*, 1983; Airoldi & Bradley, 1975; Airoldi *et al.*, 1980), $[Ti(N(SiMe_3)_2)_3]$ (Bradley & Copperthwaite, 1971; Alyea *et al.*, 1972; Bradley *et al.*, 1978; Minhas *et al.*, 1992) and $[Ti(Cl)_2(N(SiMe_3)_2)(THF)_2]$ (Putzer *et al.*, 1996) of titanium(III) have been synthesized, there is so far no other report of titanium(III) silylamide chloride compounds.

The title compound crystallizes as a chloride-bridged dimer $[Ti(\mu\text{-}Cl)(N(SiMe_3)_2)_2]_2$ with two four-coordinate titanium(III) atoms. It is isostructural with the molecular compounds $[M(\mu\text{-}Cl)(N(SiMe_3)_2)_2]_2$ with M = Yb (Niemeyer, 2002) and In (Yamashita *et al.*, 2014). The titanium(III) atoms occupy a pseudo-tetrahedral environment with two bonded $\{(Me_3Si)_2N\}$ moieties and two bridging chloride atoms bonded to each titanium(III) atom resulting in the formation of a characteristic edge-sharing ditetrahedral configuration (Fig. 1). The four-membered Ti_2Cl_2 core is nearly planar [torsion

Table 1
Selected geometric parameters (Å, °).

Ti1—N1	1.9371 (13)	Ti2—N3	1.9459 (13)
Ti1—N4	1.9379 (14)	Ti2—N2	1.9534 (13)
Ti1—Cl1	2.4226 (5)	Ti2—Cl2	2.4094 (5)
Ti1—Cl2	2.4227 (5)	Ti2—Cl1	2.4190 (5)
N1—Ti1—N4	118.42 (6)	N3—Ti2—Cl2	114.38 (4)
N1—Ti1—Cl1	121.02 (4)	N2—Ti2—Cl2	102.71 (4)
N4—Ti1—Cl1	102.91 (4)	N3—Ti2—Cl1	103.24 (4)
N1—Ti1—Cl2	100.57 (4)	N2—Ti2—Cl1	115.13 (4)
N4—Ti1—Cl2	123.75 (4)	Cl2—Ti2—Cl1	87.938 (16)
Cl1—Ti1—Cl2	87.550 (16)	Ti2—Cl1—Ti1	92.070 (16)
N3—Ti2—N2	126.91 (6)	Ti2—Cl2—Ti1	92.306 (16)

angle Ti1—Cl1—Ti2—Cl2 = 2.796 (15)°] with the four nitrogen atoms in a trigonal–planar coordination geometry [deviation from the $N_{(silylamide)}$-centroid (Si—Ti—Si) ring ranges from 0.077 to 0.116 Å], suggesting a possible π-overlap between the N lone pair and the vacant Ti orbitals. The Ti—Cl bond lengths (Table 1) are shorter than those observed in the Ti^{III},Ti^{III}-chloride bridged dimers $[Ti(\mu\text{-}Cl)(\eta\text{-}C_5H_5)_2]_2$ (Jungst *et al.*, 1977), $[Ti(\mu\text{-}Cl)(\eta\text{-}C_5H_4Me)_2]_2$ (Bradley & Copperthwaite, 1971; Alyea *et al.*, 1972; Bradley *et al.*, 1978; Minhas *et al.*, 1992), $[Ti(\mu\text{-}Cl)\{(\eta^5\text{-}C_5H_4NSiMe_3)_2Fe\}]_2^{2+}$ (Shafir & Arnold, 2001), $[Ti(\mu\text{-}Cl)\{(Me_3SiNCH_2CH_2)_2\text{-}NSiMe_3\}]_2$ (Love *et al.*, 1999) ranging from 2.566 (2)–2.4414 (10) Å. This is most probably the result of a better rearrangement between the less-bulky silylamide ligands bonded to each titanium(III) atom with torsion angles, N3—Ti1—Ti2—N1 and N2—Ti1—Ti2—N4, of −24.05 (7) and −26.50 (8)°, respectively, which deviates from perfect alignment following the non-crystallographic plane perpendicular to the four-membered Ti_2Cl_2 plane and through the pseudo-C_2 axis Ti1—Ti2. The Ti—N bond lengths (Table 1) are similar to those found in other Ti^{III} silylamide complexes ($d_{avg} \simeq 1.94$ Å) (Alcock *et al.*, 1976; Planalp *et al.*, 1983; Airoldi & Bradley, 1975; Airoldi *et al.*, 1980).

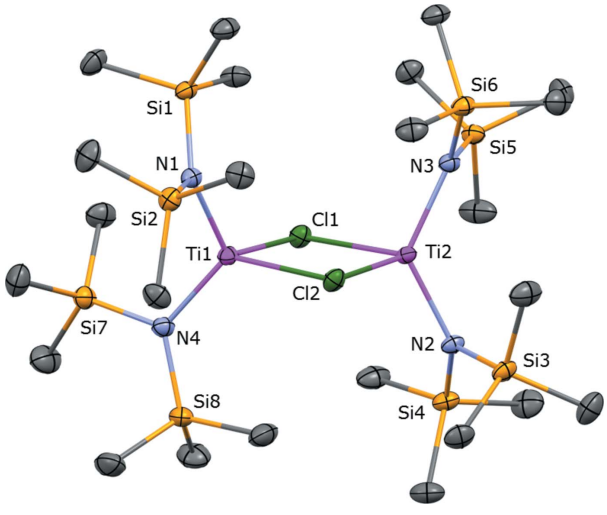


Figure 1
The molecular structure of the title compound with anisotropic displacement parameters set at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ti_2Cl_2(C_6H_{18}NSi_2)_4]$
M_r	808.27
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	103
a, b, c (Å)	8.8550 (5), 11.7359 (7), 24.0066 (14)
α, β, γ (°)	93.199 (1), 97.370 (1), 111.684 (1)
V (Å^3)	2284.6 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.70
Crystal size (mm)	0.45 × 0.20 × 0.02
Data collection	
Diffractometer	Bruker TXS Rotating anode, Pt^{135} CCD
Absorption correction	Numerical (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.820, 0.986
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	39360, 13897, 11154
R_{int}	0.051
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.112, 1.04
No. of reflections	13897
No. of parameters	385
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.87, −0.36

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2017* (Sheldrick, 2015*b*) and *Mercury* (Macrae *et al.*, 2006).

The packing of the molecules in the title compound is displayed in Fig. 2.

Synthesis and crystallization

In an argon-filled glove-box, to a solution of 1*M* titanium tetrachloride in toluene (1 mmol) in 5 ml of toluene at 243 K

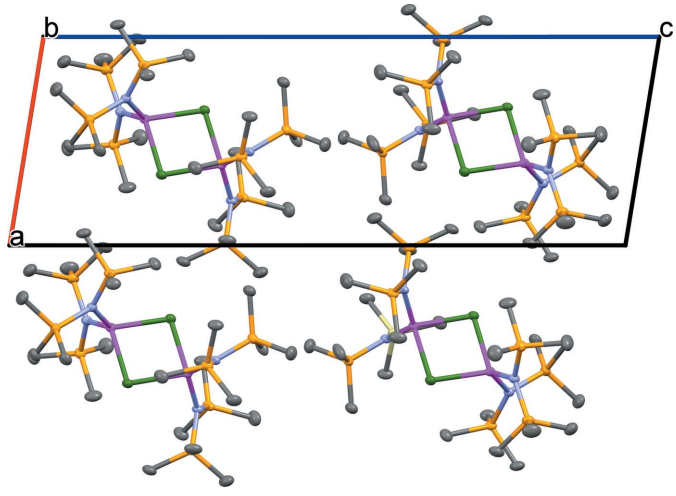


Figure 2
The crystal packing of the title compound seen down the *b* axis, showing four molecules, three of which are related to the unique one *via* inversion centres at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$. The packing is essentially based on van der Waals interactions only.

was added a pre-cooled solution at 243 K of lithium bis(trimethylsilyl)amide (334.6 mg, 2 mmol) in pentane (5 ml). The mixture was warmed to room temperature and stirred at that temperature overnight. The green solution was then centrifuged, filtered and dried under vacuum. Single crystals were obtained by preparing a concentrated solution of the reaction mixture in dichloromethane and cooling it for two days at 243 K.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

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Crystal data

$[Ti_2Cl_2(C_6H_{18}NSi_2)_4]$
M_r = 808.27
Triclinic, $P\overline{1}$
a = 8.8550 (5) Å
b = 11.7359 (7) Å
c = 24.0066 (14) Å
α = 93.199 (1)°
β = 97.370 (1)°
γ = 111.684 (1)°
V = 2284.6 (2) Å^3
Z = 2
$F(000)$ = 868
D_x = 1.175 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9927 reflections
θ = 2.4–30.4°
μ = 0.70 mm^{-1}
T = 103 K
Thin plate, blue
0.45 × 0.20 × 0.02 mm

Data collection

Bruker TXS Rotating anode, Pt^{135} CCD diffractometer
Radiation source: Bruker TXS Rotating anode
ω scans
Absorption correction: numerical (*SADABS*; Bruker, 2013)
T_{min} = 0.820, T_{max} = 0.986
39360 measured reflections
13897 independent reflections
11154 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 30.5°, θ_{min} = 1.9°
h = −12→12
k = −16→16
l = −34→34

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.112
S = 1.04
13897 reflections
385 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.0514P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.87 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ti1	0.39441 (3)	0.30081 (2)	0.18633 (2)	0.01492 (7)
Ti2	0.61439 (3)	0.34925 (2)	0.32250 (2)	0.01526 (7)
Cl1	0.35239 (5)	0.35207 (4)	0.28076 (2)	0.01844 (8)
Cl2	0.66257 (5)	0.30888 (4)	0.22823 (2)	0.01891 (8)
Si1	0.13473 (5)	0.01105 (4)	0.17059 (2)	0.01756 (9)
Si2	0.39903 (6)	0.10306 (4)	0.09651 (2)	0.01876 (10)
Si3	0.98553 (5)	0.51034 (4)	0.35013 (2)	0.01995 (10)
Si4	0.76984 (6)	0.65233 (4)	0.36573 (2)	0.01897 (10)
Si5	0.44682 (6)	0.22235 (4)	0.41948 (2)	0.01771 (9)
Si6	0.57789 (5)	0.06572 (4)	0.35238 (2)	0.01837 (10)
Si7	0.15997 (6)	0.39762 (4)	0.11156 (2)	0.02084 (10)
Si8	0.51671 (6)	0.57332 (4)	0.14338 (2)	0.01976 (10)
N1	0.29662 (16)	0.13254 (12)	0.15026 (6)	0.0158 (2)
N2	0.78674 (16)	0.51130 (12)	0.34860 (6)	0.0160 (3)
N3	0.55174 (16)	0.20568 (12)	0.36416 (6)	0.0156 (2)
N4	0.36078 (16)	0.42951 (12)	0.14546 (6)	0.0176 (3)
C1	−0.0578 (2)	−0.03685 (18)	0.11736 (8)	0.0283 (4)
H1A	−0.072271	0.036697	0.104347	0.042*
H1B	−0.152591	−0.084398	0.134768	0.042*
H1C	−0.049311	−0.087897	0.085113	0.042*
C2	0.0888 (2)	0.05425 (16)	0.24066 (8)	0.0258 (4)
H2A	0.187690	0.077064	0.269187	0.039*
H2B	0.000081	−0.016058	0.251365	0.039*
H2C	0.054419	0.124437	0.238195	0.039*
C3	0.1844 (2)	−0.12943 (16)	0.17834 (9)	0.0268 (4)
H3A	0.199665	−0.160639	0.141633	0.040*
H3B	0.093680	−0.193105	0.191919	0.040*
H3C	0.285746	−0.108184	0.205533	0.040*
C4	0.2520 (3)	0.00131 (19)	0.03467 (8)	0.0324 (4)
H4A	0.192094	−0.079915	0.046220	0.049*
H4B	0.312970	−0.007854	0.004563	0.049*
H4C	0.173595	0.038278	0.020768	0.049*
C5	0.5248 (2)	0.25066 (17)	0.07026 (8)	0.0258 (4)
H5A	0.452511	0.291751	0.055247	0.039*
H5B	0.580772	0.232561	0.040296	0.039*
H5C	0.606841	0.304826	0.101507	0.039*
C6	0.5450 (2)	0.02861 (17)	0.12106 (8)	0.0252 (4)
H6A	0.626317	0.081499	0.152805	0.038*
H6B	0.601530	0.016854	0.090005	0.038*
H6C	0.483962	−0.051629	0.133274	0.038*
C7	1.1301 (2)	0.6014 (2)	0.41457 (9)	0.0341 (4)
H7A	1.147275	0.688685	0.414021	0.051*
H7B	1.235718	0.591854	0.415281	0.051*
H7C	1.083416	0.571434	0.448297	0.051*
C8	1.0782 (2)	0.56924 (17)	0.28657 (8)	0.0266 (4)

H8A	0.997837	0.529646	0.252337	0.040*
H8B	1.176512	0.550135	0.285205	0.040*
H8C	1.108706	0.658789	0.288864	0.040*
C9	0.9760 (2)	0.34943 (17)	0.35218 (10)	0.0315 (4)
H9A	0.926157	0.315209	0.384758	0.047*
H9B	1.087588	0.349647	0.355531	0.047*
H9C	0.909278	0.298778	0.317337	0.047*
C10	0.9034 (2)	0.77735 (16)	0.32842 (9)	0.0294 (4)
H10A	1.019229	0.791738	0.341220	0.044*
H10B	0.884908	0.853369	0.336899	0.044*
H10C	0.876107	0.752524	0.287566	0.044*
C11	0.8290 (3)	0.70627 (18)	0.44330 (8)	0.0328 (4)
H11A	0.772775	0.638676	0.464706	0.049*
H11B	0.796714	0.775988	0.451647	0.049*
H11C	0.948386	0.732344	0.454096	0.049*
C12	0.5572 (2)	0.64757 (17)	0.34511 (10)	0.0314 (4)
H12A	0.520119	0.618943	0.304744	0.047*
H12B	0.556877	0.730410	0.352646	0.047*
H12C	0.482788	0.590862	0.367111	0.047*
C13	0.6293 (2)	0.04081 (17)	0.28093 (8)	0.0278 (4)
H13A	0.546336	0.049009	0.252003	0.042*
H13B	0.630805	−0.042073	0.275139	0.042*
H13C	0.737924	0.102421	0.278092	0.042*
C14	0.3826 (2)	−0.06827 (15)	0.35585 (9)	0.0257 (4)
H14A	0.357593	−0.067546	0.394443	0.038*
H14B	0.395844	−0.145440	0.345160	0.038*
H14C	0.292099	−0.061890	0.329758	0.038*
C15	0.7441 (2)	0.05277 (18)	0.40522 (9)	0.0287 (4)
H15A	0.851801	0.107772	0.397738	0.043*
H15B	0.737788	−0.032546	0.402178	0.043*
H15C	0.729713	0.076308	0.443402	0.043*
C16	0.5171 (3)	0.16823 (19)	0.48585 (8)	0.0312 (4)
H16A	0.480331	0.078108	0.480814	0.047*
H16B	0.470349	0.193116	0.516997	0.047*
H16C	0.637568	0.205033	0.494593	0.047*
C17	0.4886 (3)	0.38942 (17)	0.43672 (9)	0.0327 (4)
H17A	0.607722	0.435963	0.445805	0.049*
H17B	0.436739	0.399920	0.469278	0.049*
H17C	0.443294	0.420061	0.404112	0.049*
C18	0.2185 (2)	0.14155 (17)	0.40172 (8)	0.0250 (4)
H18A	0.179303	0.165442	0.365918	0.037*
H18B	0.166814	0.164665	0.431820	0.037*
H18C	0.189658	0.052111	0.398103	0.037*
C19	0.0103 (2)	0.30239 (18)	0.15467 (9)	0.0289 (4)
H19A	0.027150	0.225319	0.159410	0.043*
H19B	−0.102140	0.283538	0.135463	0.043*
H19C	0.026947	0.348153	0.191834	0.043*
C20	0.1197 (2)	0.3118 (2)	0.03996 (8)	0.0342 (4)

H20A	0.199961	0.360063	0.017228	0.051*
H20B	0.008229	0.298365	0.021457	0.051*
H20C	0.129617	0.232056	0.043589	0.051*
C21	0.1100 (3)	0.53780 (19)	0.10321 (11)	0.0381 (5)
H21A	0.122658	0.581663	0.140532	0.057*
H21B	−0.003813	0.512985	0.084098	0.057*
H21C	0.184923	0.592248	0.080617	0.057*
C22	0.7226 (2)	0.57858 (17)	0.17584 (10)	0.0329 (4)
H22A	0.721610	0.564799	0.215698	0.049*
H22B	0.806864	0.659555	0.173027	0.049*
H22C	0.747460	0.514162	0.155825	0.049*
C23	0.4826 (3)	0.70071 (17)	0.18345 (9)	0.0341 (4)
H23A	0.404100	0.725609	0.159716	0.051*
H23B	0.587397	0.771397	0.193897	0.051*
H23C	0.438453	0.671851	0.217725	0.051*
C24	0.5339 (3)	0.60785 (19)	0.06891 (8)	0.0363 (5)
H24A	0.563521	0.545918	0.048974	0.054*
H24B	0.619079	0.689924	0.068835	0.054*
H24C	0.428075	0.605825	0.049832	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti1	0.01427 (13)	0.01257 (13)	0.01745 (13)	0.00477 (10)	0.00199 (10)	0.00148 (10)
Ti2	0.01249 (13)	0.01240 (12)	0.01828 (14)	0.00156 (10)	0.00260 (10)	0.00260 (10)
Cl1	0.01564 (17)	0.02084 (18)	0.01963 (18)	0.00765 (14)	0.00376 (13)	0.00135 (14)
Cl2	0.01367 (16)	0.02160 (18)	0.02062 (18)	0.00591 (14)	0.00325 (13)	0.00018 (14)
Si1	0.0133 (2)	0.01390 (19)	0.0234 (2)	0.00310 (16)	0.00236 (16)	0.00136 (17)
Si2	0.0189 (2)	0.0202 (2)	0.0177 (2)	0.00803 (18)	0.00401 (17)	−0.00034 (17)
Si3	0.01163 (19)	0.0191 (2)	0.0268 (2)	0.00370 (17)	0.00232 (17)	0.00030 (18)
Si4	0.0164 (2)	0.0135 (2)	0.0258 (2)	0.00352 (16)	0.00683 (18)	0.00027 (17)
Si5	0.0183 (2)	0.0160 (2)	0.0182 (2)	0.00470 (17)	0.00558 (16)	0.00310 (16)
Si6	0.0145 (2)	0.0140 (2)	0.0268 (2)	0.00547 (16)	0.00364 (17)	0.00304 (17)
Si7	0.0166 (2)	0.0204 (2)	0.0267 (2)	0.00833 (18)	0.00247 (18)	0.00567 (18)
Si8	0.0204 (2)	0.0152 (2)	0.0218 (2)	0.00422 (17)	0.00358 (18)	0.00435 (17)
N1	0.0142 (6)	0.0142 (6)	0.0187 (6)	0.0052 (5)	0.0025 (5)	0.0012 (5)
N2	0.0118 (6)	0.0143 (6)	0.0210 (6)	0.0036 (5)	0.0038 (5)	0.0007 (5)
N3	0.0130 (6)	0.0135 (6)	0.0197 (6)	0.0042 (5)	0.0032 (5)	0.0023 (5)
N4	0.0150 (6)	0.0163 (6)	0.0214 (7)	0.0051 (5)	0.0043 (5)	0.0041 (5)
C1	0.0157 (8)	0.0279 (9)	0.0363 (10)	0.0048 (7)	−0.0013 (7)	−0.0009 (8)
C2	0.0265 (9)	0.0202 (8)	0.0293 (9)	0.0046 (7)	0.0110 (7)	0.0051 (7)
C3	0.0226 (8)	0.0164 (8)	0.0402 (10)	0.0062 (7)	0.0037 (8)	0.0036 (7)
C4	0.0326 (10)	0.0362 (11)	0.0239 (9)	0.0112 (9)	−0.0005 (8)	−0.0086 (8)
C5	0.0279 (9)	0.0300 (9)	0.0240 (8)	0.0130 (8)	0.0119 (7)	0.0078 (7)
C6	0.0253 (9)	0.0266 (9)	0.0290 (9)	0.0146 (7)	0.0095 (7)	0.0024 (7)
C7	0.0209 (9)	0.0390 (11)	0.0354 (11)	0.0069 (8)	−0.0024 (8)	−0.0049 (9)
C8	0.0173 (8)	0.0269 (9)	0.0351 (10)	0.0061 (7)	0.0100 (7)	0.0031 (7)
C9	0.0182 (8)	0.0250 (9)	0.0532 (13)	0.0098 (7)	0.0061 (8)	0.0067 (8)

C10	0.0298 (10)	0.0175 (8)	0.0394 (11)	0.0043 (7)	0.0143 (8)	0.0049 (7)
C11	0.0400 (11)	0.0269 (9)	0.0297 (10)	0.0101 (8)	0.0105 (8)	−0.0053 (8)
C12	0.0227 (9)	0.0180 (8)	0.0555 (13)	0.0095 (7)	0.0074 (9)	0.0057 (8)
C13	0.0304 (9)	0.0197 (8)	0.0352 (10)	0.0104 (7)	0.0106 (8)	−0.0007 (7)
C14	0.0186 (8)	0.0152 (7)	0.0409 (10)	0.0040 (6)	0.0044 (7)	0.0040 (7)
C15	0.0202 (8)	0.0271 (9)	0.0411 (11)	0.0114 (7)	0.0036 (8)	0.0097 (8)
C16	0.0342 (10)	0.0356 (10)	0.0218 (9)	0.0110 (8)	0.0024 (8)	0.0071 (8)
C17	0.0447 (12)	0.0203 (8)	0.0332 (10)	0.0078 (8)	0.0220 (9)	0.0007 (7)
C18	0.0200 (8)	0.0272 (9)	0.0279 (9)	0.0079 (7)	0.0081 (7)	0.0020 (7)
C19	0.0190 (8)	0.0291 (9)	0.0415 (11)	0.0105 (7)	0.0094 (8)	0.0086 (8)
C20	0.0266 (10)	0.0432 (12)	0.0284 (10)	0.0112 (9)	−0.0030 (8)	−0.0007 (8)
C21	0.0296 (10)	0.0298 (10)	0.0588 (14)	0.0162 (8)	0.0022 (10)	0.0139 (10)
C22	0.0208 (9)	0.0218 (9)	0.0494 (12)	0.0024 (7)	−0.0011 (8)	0.0051 (8)
C23	0.0440 (12)	0.0191 (8)	0.0398 (11)	0.0126 (8)	0.0078 (9)	0.0025 (8)
C24	0.0405 (12)	0.0307 (10)	0.0279 (10)	0.0003 (9)	0.0093 (8)	0.0096 (8)

Geometric parameters (Å, º)

Ti1—N1	1.9371 (13)	C6—H6A	0.9800
Ti1—N4	1.9379 (14)	C6—H6B	0.9800
Ti1—Cl1	2.4226 (5)	C6—H6C	0.9800
Ti1—Cl2	2.4227 (5)	C7—H7A	0.9800
Ti1—Si2	3.0937 (5)	C7—H7B	0.9800
Ti2—N3	1.9459 (13)	C7—H7C	0.9800
Ti2—N2	1.9534 (13)	C8—H8A	0.9800
Ti2—Cl2	2.4094 (5)	C8—H8B	0.9800
Ti2—Cl1	2.4190 (5)	C8—H8C	0.9800
Ti2—Si5	3.0790 (5)	C9—H9A	0.9800
Ti2—Si3	3.0861 (5)	C9—H9B	0.9800
Si1—N1	1.7530 (14)	C9—H9C	0.9800
Si1—C2	1.8668 (19)	C10—H10A	0.9800
Si1—C3	1.8693 (18)	C10—H10B	0.9800
Si1—C1	1.8731 (18)	C10—H10C	0.9800
Si2—N1	1.7576 (14)	C11—H11A	0.9800
Si2—C6	1.8652 (18)	C11—H11B	0.9800
Si2—C4	1.8661 (19)	C11—H11C	0.9800
Si2—C5	1.8746 (19)	C12—H12A	0.9800
Si3—N2	1.7601 (14)	C12—H12B	0.9800
Si3—C9	1.8627 (19)	C12—H12C	0.9800
Si3—C7	1.863 (2)	C13—H13A	0.9800
Si3—C8	1.8705 (19)	C13—H13B	0.9800
Si4—N2	1.7474 (14)	C13—H13C	0.9800
Si4—C12	1.8638 (19)	C14—H14A	0.9800
Si4—C10	1.8681 (19)	C14—H14B	0.9800
Si4—C11	1.875 (2)	C14—H14C	0.9800
Si5—N3	1.7570 (14)	C15—H15A	0.9800
Si5—C16	1.8656 (19)	C15—H15B	0.9800
Si5—C18	1.8666 (18)	C15—H15C	0.9800

Si5—C17	1.8672 (19)	C16—H16A	0.9800
Si6—N3	1.7544 (14)	C16—H16B	0.9800
Si6—C13	1.8651 (19)	C16—H16C	0.9800
Si6—C15	1.8725 (19)	C17—H17A	0.9800
Si6—C14	1.8743 (18)	C17—H17B	0.9800
Si7—N4	1.7513 (14)	C17—H17C	0.9800
Si7—C19	1.8610 (19)	C18—H18A	0.9800
Si7—C20	1.865 (2)	C18—H18B	0.9800
Si7—C21	1.869 (2)	C18—H18C	0.9800
Si8—N4	1.7499 (14)	C19—H19A	0.9800
Si8—C22	1.866 (2)	C19—H19B	0.9800
Si8—C24	1.868 (2)	C19—H19C	0.9800
Si8—C23	1.871 (2)	C20—H20A	0.9800
C1—H1A	0.9800	C20—H20B	0.9800
C1—H1B	0.9800	C20—H20C	0.9800
C1—H1C	0.9800	C21—H21A	0.9800
C2—H2A	0.9800	C21—H21B	0.9800
C2—H2B	0.9800	C21—H21C	0.9800
C2—H2C	0.9800	C22—H22A	0.9800
C3—H3A	0.9800	C22—H22B	0.9800
C3—H3B	0.9800	C22—H22C	0.9800
C3—H3C	0.9800	C23—H23A	0.9800
C4—H4A	0.9800	C23—H23B	0.9800
C4—H4B	0.9800	C23—H23C	0.9800
C4—H4C	0.9800	C24—H24A	0.9800
C5—H5A	0.9800	C24—H24B	0.9800
C5—H5B	0.9800	C24—H24C	0.9800
C5—H5C	0.9800		

N1—Ti1—N4	118.42 (6)	Si2—C5—H5A	109.5
N1—Ti1—Cl1	121.02 (4)	Si2—C5—H5B	109.5
N4—Ti1—Cl1	102.91 (4)	H5A—C5—H5B	109.5
N1—Ti1—Cl2	100.57 (4)	Si2—C5—H5C	109.5
N4—Ti1—Cl2	123.75 (4)	H5A—C5—H5C	109.5
Cl1—Ti1—Cl2	87.550 (16)	H5B—C5—H5C	109.5
N1—Ti1—Si2	31.37 (4)	Si2—C6—H6A	109.5
N4—Ti1—Si2	106.50 (4)	Si2—C6—H6B	109.5
Cl1—Ti1—Si2	148.298 (17)	H6A—C6—H6B	109.5
Cl2—Ti1—Si2	85.901 (15)	Si2—C6—H6C	109.5
N3—Ti2—N2	126.91 (6)	H6A—C6—H6C	109.5
N3—Ti2—Cl2	114.38 (4)	H6B—C6—H6C	109.5
N2—Ti2—Cl2	102.71 (4)	Si3—C7—H7A	109.5
N3—Ti2—Cl1	103.24 (4)	Si3—C7—H7B	109.5
N2—Ti2—Cl1	115.13 (4)	H7A—C7—H7B	109.5
Cl2—Ti2—Cl1	87.938 (16)	Si3—C7—H7C	109.5
N3—Ti2—Si5	31.84 (4)	H7A—C7—H7C	109.5
N2—Ti2—Si5	112.35 (4)	H7B—C7—H7C	109.5
Cl2—Ti2—Si5	142.757 (17)	Si3—C8—H8A	109.5

Cl1—Ti2—Si5	88.334 (15)	Si3—C8—H8B	109.5
N3—Ti2—Si3	112.82 (4)	H8A—C8—H8B	109.5
N2—Ti2—Si3	31.85 (4)	Si3—C8—H8C	109.5
Cl2—Ti2—Si3	86.479 (15)	H8A—C8—H8C	109.5
Cl1—Ti2—Si3	142.490 (17)	H8B—C8—H8C	109.5
Si5—Ti2—Si3	117.236 (16)	Si3—C9—H9A	109.5
Ti2—Cl1—Ti1	92.070 (16)	Si3—C9—H9B	109.5
Ti2—Cl2—Ti1	92.306 (16)	H9A—C9—H9B	109.5
N1—Si1—C2	111.33 (7)	Si3—C9—H9C	109.5
N1—Si1—C3	112.16 (7)	H9A—C9—H9C	109.5
C2—Si1—C3	106.10 (9)	H9B—C9—H9C	109.5
N1—Si1—C1	111.65 (8)	Si4—C10—H10A	109.5
C2—Si1—C1	108.60 (9)	Si4—C10—H10B	109.5
C3—Si1—C1	106.71 (9)	H10A—C10—H10B	109.5
N1—Si2—C6	112.71 (7)	Si4—C10—H10C	109.5
N1—Si2—C4	111.91 (8)	H10A—C10—H10C	109.5
C6—Si2—C4	107.62 (9)	H10B—C10—H10C	109.5
N1—Si2—C5	110.54 (7)	Si4—C11—H11A	109.5
C6—Si2—C5	106.29 (8)	Si4—C11—H11B	109.5
C4—Si2—C5	107.47 (9)	H11A—C11—H11B	109.5
C6—Si2—Ti1	113.02 (6)	Si4—C11—H11C	109.5
C4—Si2—Ti1	135.70 (7)	H11A—C11—H11C	109.5
C5—Si2—Ti1	77.57 (6)	H11B—C11—H11C	109.5
N2—Si3—C9	109.52 (8)	Si4—C12—H12A	109.5
N2—Si3—C7	112.45 (8)	Si4—C12—H12B	109.5
C9—Si3—C7	105.95 (10)	H12A—C12—H12B	109.5
N2—Si3—C8	112.74 (8)	Si4—C12—H12C	109.5
C9—Si3—C8	107.37 (9)	H12A—C12—H12C	109.5
C7—Si3—C8	108.46 (9)	H12B—C12—H12C	109.5
C9—Si3—Ti2	75.79 (6)	Si6—C13—H13A	109.5
C7—Si3—Ti2	135.46 (7)	Si6—C13—H13B	109.5
C8—Si3—Ti2	113.34 (6)	H13A—C13—H13B	109.5
N2—Si4—C12	112.97 (7)	Si6—C13—H13C	109.5
N2—Si4—C10	111.77 (8)	H13A—C13—H13C	109.5
C12—Si4—C10	105.39 (9)	H13B—C13—H13C	109.5
N2—Si4—C11	112.83 (8)	Si6—C14—H14A	109.5
C12—Si4—C11	106.38 (10)	Si6—C14—H14B	109.5
C10—Si4—C11	106.99 (9)	H14A—C14—H14B	109.5
N3—Si5—C16	112.68 (8)	Si6—C14—H14C	109.5
N3—Si5—C18	113.65 (7)	H14A—C14—H14C	109.5
C16—Si5—C18	107.98 (9)	H14B—C14—H14C	109.5
N3—Si5—C17	109.08 (8)	Si6—C15—H15A	109.5
C16—Si5—C17	106.48 (10)	Si6—C15—H15B	109.5
C18—Si5—C17	106.56 (9)	H15A—C15—H15B	109.5
C16—Si5—Ti2	134.95 (7)	Si6—C15—H15C	109.5
C18—Si5—Ti2	114.66 (6)	H15A—C15—H15C	109.5
C17—Si5—Ti2	75.09 (6)	H15B—C15—H15C	109.5
N3—Si6—C13	112.98 (8)	Si5—C16—H16A	109.5

N3—Si6—C15	112.70 (8)	Si5—C16—H16B	109.5
C13—Si6—C15	106.99 (9)	H16A—C16—H16B	109.5
N3—Si6—C14	110.68 (7)	Si5—C16—H16C	109.5
C13—Si6—C14	105.39 (9)	H16A—C16—H16C	109.5
C15—Si6—C14	107.67 (9)	H16B—C16—H16C	109.5
N4—Si7—C19	109.43 (8)	Si5—C17—H17A	109.5
N4—Si7—C20	111.34 (8)	Si5—C17—H17B	109.5
C19—Si7—C20	108.73 (10)	H17A—C17—H17B	109.5
N4—Si7—C21	114.02 (8)	Si5—C17—H17C	109.5
C19—Si7—C21	105.32 (10)	H17A—C17—H17C	109.5
C20—Si7—C21	107.72 (10)	H17B—C17—H17C	109.5
N4—Si8—C22	111.84 (8)	Si5—C18—H18A	109.5
N4—Si8—C24	110.95 (8)	Si5—C18—H18B	109.5
C22—Si8—C24	106.25 (10)	H18A—C18—H18B	109.5
N4—Si8—C23	111.98 (9)	Si5—C18—H18C	109.5
C22—Si8—C23	106.17 (10)	H18A—C18—H18C	109.5
C24—Si8—C23	109.37 (10)	H18B—C18—H18C	109.5
Si1—N1—Si2	119.76 (8)	Si7—C19—H19A	109.5
Si1—N1—Ti1	126.34 (8)	Si7—C19—H19B	109.5
Si2—N1—Ti1	113.63 (7)	H19A—C19—H19B	109.5
Si4—N2—Si3	117.90 (7)	Si7—C19—H19C	109.5
Si4—N2—Ti2	129.66 (7)	H19A—C19—H19C	109.5
Si3—N2—Ti2	112.31 (7)	H19B—C19—H19C	109.5
Si6—N3—Si5	117.87 (8)	Si7—C20—H20A	109.5
Si6—N3—Ti2	129.67 (8)	Si7—C20—H20B	109.5
Si5—N3—Ti2	112.41 (7)	H20A—C20—H20B	109.5
Si8—N4—Si7	120.13 (8)	Si7—C20—H20C	109.5
Si8—N4—Ti1	123.47 (8)	H20A—C20—H20C	109.5
Si7—N4—Ti1	116.36 (7)	H20B—C20—H20C	109.5
Si1—C1—H1A	109.5	Si7—C21—H21A	109.5
Si1—C1—H1B	109.5	Si7—C21—H21B	109.5
H1A—C1—H1B	109.5	H21A—C21—H21B	109.5
Si1—C1—H1C	109.5	Si7—C21—H21C	109.5
H1A—C1—H1C	109.5	H21A—C21—H21C	109.5
H1B—C1—H1C	109.5	H21B—C21—H21C	109.5
Si1—C2—H2A	109.5	Si8—C22—H22A	109.5
Si1—C2—H2B	109.5	Si8—C22—H22B	109.5
H2A—C2—H2B	109.5	H22A—C22—H22B	109.5
Si1—C2—H2C	109.5	Si8—C22—H22C	109.5
H2A—C2—H2C	109.5	H22A—C22—H22C	109.5
H2B—C2—H2C	109.5	H22B—C22—H22C	109.5
Si1—C3—H3A	109.5	Si8—C23—H23A	109.5
Si1—C3—H3B	109.5	Si8—C23—H23B	109.5
H3A—C3—H3B	109.5	H23A—C23—H23B	109.5
Si1—C3—H3C	109.5	Si8—C23—H23C	109.5
H3A—C3—H3C	109.5	H23A—C23—H23C	109.5
H3B—C3—H3C	109.5	H23B—C23—H23C	109.5
Si2—C4—H4A	109.5	Si8—C24—H24A	109.5

Si2—C4—H4B	109.5	Si8—C24—H24B	109.5
H4A—C4—H4B	109.5	H24A—C24—H24B	109.5
Si2—C4—H4C	109.5	Si8—C24—H24C	109.5
H4A—C4—H4C	109.5	H24A—C24—H24C	109.5
H4B—C4—H4C	109.5	H24B—C24—H24C	109.5
C2—Si1—N1—Si2	163.08 (9)	C13—Si6—N3—Si5	161.93 (9)
C3—Si1—N1—Si2	44.37 (12)	C15—Si6—N3—Si5	−76.63 (11)
C1—Si1—N1—Si2	−75.35 (11)	C14—Si6—N3—Si5	44.01 (11)
C2—Si1—N1—Ti1	−10.50 (12)	C13—Si6—N3—Ti2	−15.17 (13)
C3—Si1—N1—Ti1	−129.22 (10)	C15—Si6—N3—Ti2	106.27 (11)
C1—Si1—N1—Ti1	111.07 (10)	C14—Si6—N3—Ti2	−133.09 (10)
C6—Si2—N1—Si1	−76.23 (11)	C16—Si5—N3—Si6	45.52 (11)
C4—Si2—N1—Si1	45.24 (12)	C18—Si5—N3—Si6	−77.73 (10)
C5—Si2—N1—Si1	164.99 (9)	C17—Si5—N3—Si6	163.54 (10)
Ti1—Si2—N1—Si1	−174.36 (14)	Ti2—Si5—N3—Si6	−177.58 (13)
C6—Si2—N1—Ti1	98.13 (9)	C16—Si5—N3—Ti2	−136.90 (9)
C4—Si2—N1—Ti1	−140.40 (9)	C18—Si5—N3—Ti2	99.86 (9)
C5—Si2—N1—Ti1	−20.65 (10)	C17—Si5—N3—Ti2	−18.88 (11)
C12—Si4—N2—Si3	165.48 (10)	C22—Si8—N4—Si7	−173.96 (10)
C10—Si4—N2—Si3	46.82 (12)	C24—Si8—N4—Si7	−55.51 (12)
C11—Si4—N2—Si3	−73.81 (11)	C23—Si8—N4—Si7	67.00 (12)
C12—Si4—N2—Ti2	−10.18 (14)	C22—Si8—N4—Ti1	8.39 (13)
C10—Si4—N2—Ti2	−128.84 (11)	C24—Si8—N4—Ti1	126.83 (11)
C11—Si4—N2—Ti2	110.54 (11)	C23—Si8—N4—Ti1	−110.65 (11)
C9—Si3—N2—Si4	162.97 (10)	C19—Si7—N4—Si8	−142.94 (10)
C7—Si3—N2—Si4	45.45 (12)	C20—Si7—N4—Si8	96.82 (11)
C8—Si3—N2—Si4	−77.55 (11)	C21—Si7—N4—Si8	−25.30 (13)
Ti2—Si3—N2—Si4	−176.38 (14)	C19—Si7—N4—Ti1	34.87 (11)
C9—Si3—N2—Ti2	−20.65 (11)	C20—Si7—N4—Ti1	−85.36 (11)
C7—Si3—N2—Ti2	−138.16 (9)	C21—Si7—N4—Ti1	152.52 (10)
C8—Si3—N2—Ti2	98.83 (9)		