Dichloridobis{*N*-[(dimethylamino)-dimethylsilyl]-2,6-dimethylanilido-κ^2N,N'}hafnium(IV)

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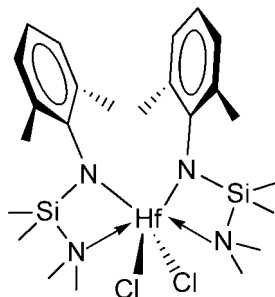Correspondence e-mail: guojp@sxu.edu.cn

In the monomeric hafnium(IV) title compound, [Hf(C$_{12}$H$_{21}$N$_2$Si)$_2$Cl$_2$], the Hf atom is *N,N'*-chelated by the *N*-silylated anilido ligand. The two ligands around the Hf atom are arranged *cis* to each other; a twofold rotation axis passes through the Hf atom. The two ends of the N—Si—N chelating unit exhibit different affinities to the metal center. The Zn—N$_{amino}$ bond is longer than the Zn—N$_{anilido}$ bond. Along with two Cl atoms, the six–coordinate Hf atom demonstrates a highly distorted octahedral geometry.

Related literature

For the catalytic applications of related *N*-silylated anilido group 4 metal compounds towards olefin polymerization, see: Gibson *et al.* (1998); Hill & Hitchcock (2002). For related amidinate or guanidinate hafnium(IV) compounds with the same geometry as the title compound, see: Wood *et al.* (1999); Milanov *et al.* (2005). For related zinc compounds supported by analogous anilido ligands, see: Schumann *et al.* (2000).

Experimental

Crystal data

[Hf(C$_{12}$H$_{21}$N$_2$Si)$_2$Cl$_2$]
M_r = 692.19
Monoclinic, *C*2/*c*
a = 16.074 (6) Å
b = 10.209 (4) Å
c = 18.736 (7) Å
β = 112.117 (4)°

V = 2848.4 (18) Å^3
Z = 4
Mo *Kα* radiation
μ = 3.95 mm^{-1}
T = 203 (2) K
0.10 × 0.10 × 0.05 mm

Data collection

Bruker SMART area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.693, T_{max} = 0.827

6574 measured reflections
2510 independent reflections
2428 reflections with *I* > 2σ(*I*)
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.081
S = 1.03
2510 reflections

153 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.74 e Å^{-3}
$\Delta\rho_{min}$ = −1.44 e Å^{-3}

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2062).

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supplementary materials

Dichloridobis{*N*-[(dimethylamino)dimethylsilyl]-2,6-dimethylanilido-κ^2*N,N'*}hafnium(IV)

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Comment

Group 4 metal amides supported with the *N*–silylated anilido ligands were found to be highly active in catalyzing olefin polymerization reactions (Gibson *et al.*, 1998; Hill & Hitchcock, 2002), which attracted us to the subject.

The *N*–silylated anilido ligand in the title compound has a pendant amino group. It results in an N—Si—N chelating moiety, which is presumed to be a "quasi" conjugated unit owing to *d*–π interaction between Si and N atoms. The zinc compounds coordinated with the analogous ligand have been reported by Schumann *et al.*, (2000). The title compound is the first example of hafnium species. It is monomeric and contains two *N*–silylated anilido ligands, which are arranged in *cis* to each other and obey the C_2 symmetrical operation. Such arrangement makes Hf atom right in the triangular plane of (N1···N2A···Cl1) and its symmetrical counterpart. Moreover, it presents the perpendicular relationship between the two planes and leads the molecule to display a highly distorted octahedral geometry. In the title compound, the Hf center is chelated, with an average N1—Hf—N2 angle of 68.04 (14)°. The corresponding N1—Si1—N2 angle 92.40 (18)° of the ligand is constrained nearly to be a right angle. The two values are quite different from those in the related amidinate and guanidinate hafnium(IV) compounds bearing the same geometry (Wood *et al.*, 1999; Milanov *et al.*, 2005), N—Hf—N being about 60° and N—C—N being larger than 110°. The Hf—N$_{anilido}$ (Hf—N1) bond is 2.100 (4)Å whereas the Hf—-N$_{amino}$ (Hf—N2) bond is 2.397 (4)Å in the title compound. In the reported amidinate and guanidinate hafnium(IV) compounds, all Hf—N bonds are about 2.2 Å. Therefore by comparison, the N—C—N chelating unit is rigid and the N—Si—N group is much more flexible.

Experimental

HfCl$_4$ (0.81 g, 2.53 mmol) was added into the solution of [LiN(Si*Me*$_2$N*Me*$_2$)(2,6–*Me*$_2$C$_6$H$_3$)]$_2$ (1.15 g, 2.53 mmol) in *Et*$_2$O (30 ml) at 273 K. The reaction mixture was warmed to room temperature and kept stirring for 12 h. It was dried in vacuum to remove all volatiles and the residue was extracted with CH$_2$Cl$_2$ (30 ml). Concentration of the filtrate under reduced pressure gave the title compound as colorless crystals (yield 1.15 g, 66%).

Refinement

The methyl H atoms were then constrained to an ideal geometry, with C—H distances of 0.97Å and U_{iso}(H) = 1.5U_{eq}(C), but each group was allowed to rotate freely about its C—C bond. The other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.94Å and U_{iso}(H) = 1.2U_{eq}(C).

The highest residual peak of 1.74 e.Å^{-3} is 0.88Å from Hf1.
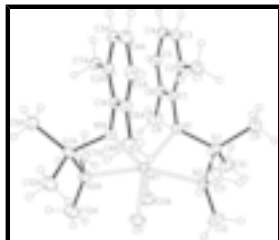
supplementary materials

Figures

Fig. 1. The molecular structure, showing the atom–numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as spheres of arbitrary radius. Symmetry code: (i) $-x + 1$, y, $-z + 3/2$.

Dichloridobis{*N*-[(dimethylamino)dimethylsilyl]-2,6-dimethylanilido- $\kappa^2 N,N'$}hafnium(IV)

Crystal data

[Hf(C$_{12}$H$_{21}$N$_2$Si)$_2$Cl$_2$]	$F_{000} = 1392$
$M_r = 692.19$	$D_x = 1.614$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 5767 reflections
$a = 16.074 (6)$ Å	$\theta = 2.4–27.5°$
$b = 10.209 (4)$ Å	$\mu = 3.95$ mm^{-1}
$c = 18.736 (7)$ Å	$T = 203 (2)$ K
$\beta = 112.117 (4)°$	Block, colourless
$V = 2848.4 (18)$ Å^3	$0.10 \times 0.10 \times 0.05$ mm
$Z = 4$	

Data collection

Bruker SMART area-detector diffractometer	2510 independent reflections
Radiation source: fine–focus sealed tube	2428 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.035$
$T = 203(2)$ K	$\theta_{max} = 25.0°$
$\varphi–$ and $\omega–$scan	$\theta_{min} = 2.4°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -19\rightarrow18$
$T_{min} = 0.693$, $T_{max} = 0.827$	$k = -12\rightarrow11$
6574 measured reflections	$l = -22\rightarrow14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 9.7887P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{max} = 0.001$

$S = 1.03$

$\Delta\rho_{max} = 1.74$ e Å^{-3}

2510 reflections

$\Delta\rho_{min} = -1.44$ e Å^{-3}

153 parameters

Extinction correction: SHELXL,
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.00099 (12)

Secondary atom site location: difference Fourier map

Special details

Geometry. All s.u. (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u. are taken into account individually in the estimation of s.u. in distances, angles and torsion angles; correlations between s.u. in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u. 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 $F^2 > 2\sigma(F^2)$ 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}
Hf1	0.5000	0.73483 (2)	0.7500	0.02959 (14)
Cl1	0.60246 (9)	0.57611 (12)	0.83593 (8)	0.0482 (3)
Si1	0.53880 (8)	0.80201 (14)	0.60910 (8)	0.0341 (3)
N1	0.4877 (2)	0.8749 (3)	0.6645 (2)	0.0280 (8)
N2	0.5989 (3)	0.6903 (4)	0.6840 (2)	0.0373 (9)
C1	0.4422 (3)	0.9973 (4)	0.6421 (2)	0.0277 (9)
C2	0.4898 (3)	1.1150 (4)	0.6592 (2)	0.0309 (9)
C3	0.4435 (4)	1.2323 (4)	0.6394 (3)	0.0367 (11)
H3A	0.4757	1.3114	0.6520	0.044*
C4	0.3524 (4)	1.2361 (4)	0.6022 (3)	0.0400 (12)
H4A	0.3220	1.3167	0.5901	0.048*
C5	0.3060 (3)	1.1205 (5)	0.5826 (3)	0.0361 (10)
H5A	0.2435	1.1228	0.5557	0.043*
C6	0.3487 (3)	1.0006 (5)	0.6012 (2)	0.0322 (10)
C7	0.5897 (3)	1.1225 (5)	0.6996 (3)	0.0352 (10)
H7A	0.6174	1.1279	0.6618	0.053*
H7B	0.6112	1.0447	0.7310	0.053*
H7C	0.6053	1.1996	0.7323	0.053*
C8	0.2938 (3)	0.8783 (5)	0.5747 (3)	0.0476 (13)
H8A	0.2540	0.8683	0.6025	0.071*
H8B	0.3334	0.8031	0.5845	0.071*
H8C	0.2584	0.8845	0.5199	0.071*
C9	0.6134 (3)	0.9025 (5)	0.5765 (3)	0.0442 (12)
H9A	0.5982	0.8890	0.5218	0.066*
H9B	0.6753	0.8770	0.6046	0.066*

H9C	0.6058	0.9943	0.5861	0.066*
C10	0.4649 (4)	0.7144 (6)	0.5218 (3)	0.0509 (14)
H10A	0.4802	0.7395	0.4783	0.076*
H10B	0.4028	0.7370	0.5113	0.076*
H10C	0.4730	0.6207	0.5300	0.076*
C11	0.6884 (4)	0.7404 (5)	0.7317 (4)	0.0527 (15)
H11A	0.7298	0.7234	0.7063	0.079*
H11B	0.7095	0.6970	0.7814	0.079*
H11C	0.6849	0.8340	0.7390	0.079*
C12	0.6097 (4)	0.5532 (5)	0.6616 (4)	0.0588 (16)
H12A	0.6518	0.5517	0.6357	0.088*
H12B	0.5520	0.5199	0.6272	0.088*
H12C	0.6324	0.4989	0.7074	0.088*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hf1	0.02721 (18)	0.02347 (18)	0.0387 (2)	0.000	0.01318 (12)	0.000
Cl1	0.0491 (7)	0.0331 (6)	0.0634 (8)	0.0120 (5)	0.0225 (6)	0.0153 (6)
Si1	0.0308 (6)	0.0344 (7)	0.0372 (7)	0.0026 (5)	0.0129 (5)	−0.0024 (5)
N1	0.0227 (17)	0.0279 (19)	0.0297 (18)	0.0008 (13)	0.0056 (14)	0.0014 (15)
N2	0.033 (2)	0.033 (2)	0.048 (2)	0.0074 (17)	0.0184 (18)	0.0058 (18)
C1	0.026 (2)	0.031 (2)	0.024 (2)	0.0005 (17)	0.0069 (17)	−0.0024 (17)
C2	0.029 (2)	0.035 (2)	0.027 (2)	−0.0016 (17)	0.0092 (18)	0.0008 (18)
C3	0.044 (3)	0.027 (2)	0.038 (3)	−0.0012 (18)	0.014 (2)	0.0016 (18)
C4	0.042 (3)	0.037 (3)	0.039 (3)	0.009 (2)	0.012 (2)	0.004 (2)
C5	0.027 (2)	0.046 (3)	0.030 (2)	0.0072 (19)	0.0058 (18)	0.001 (2)
C6	0.028 (2)	0.036 (2)	0.031 (2)	0.0004 (18)	0.0089 (18)	−0.0032 (18)
C7	0.031 (2)	0.036 (3)	0.036 (2)	−0.0066 (18)	0.0085 (19)	−0.004 (2)
C8	0.029 (2)	0.044 (3)	0.056 (3)	−0.005 (2)	0.000 (2)	−0.011 (2)
C9	0.046 (3)	0.045 (3)	0.045 (3)	0.003 (2)	0.022 (2)	0.002 (2)
C10	0.056 (3)	0.052 (3)	0.041 (3)	−0.007 (3)	0.014 (3)	−0.014 (3)
C11	0.030 (3)	0.064 (4)	0.059 (4)	0.011 (2)	0.011 (3)	0.015 (3)
C12	0.070 (4)	0.036 (3)	0.084 (4)	0.019 (3)	0.045 (3)	0.006 (3)

Geometric parameters (Å, °)

Hf1—N1^i	2.100 (4)	C5—C6	1.382 (6)
Hf1—N1	2.100 (4)	C5—H5A	0.9400
Hf1—N2	2.397 (4)	C6—C8	1.501 (6)
Hf1—N2^i	2.397 (4)	C7—H7A	0.9700
Hf1—Cl1^i	2.4359 (13)	C7—H7B	0.9700
Hf1—Cl1	2.4359 (13)	C7—H7C	0.9700
Hf1—Si1^i	3.0114 (16)	C8—H8A	0.9700
Si1—N1	1.717 (4)	C8—H8B	0.9700
Si1—N2	1.784 (4)	C8—H8C	0.9700
Si1—C9	1.848 (5)	C9—H9A	0.9700
Si1—C10	1.851 (5)	C9—H9B	0.9700

N1—C1	1.429 (5)	C9—H9C	0.9700
N2—C11	1.470 (7)	C10—H10A	0.9700
N2—C12	1.489 (7)	C10—H10B	0.9700
C1—C2	1.395 (6)	C10—H10C	0.9700
C1—C6	1.407 (6)	C11—H11A	0.9700
C2—C3	1.384 (6)	C11—H11B	0.9700
C2—C7	1.498 (6)	C11—H11C	0.9700
C3—C4	1.365 (8)	C12—H12A	0.9700
C3—H3A	0.9400	C12—H12B	0.9700
C4—C5	1.371 (7)	C12—H12C	0.9700
C4—H4A	0.9400		
N1^i—Hf1—N1	94.2 (2)	C3—C4—C5	118.9 (4)
N1^i—Hf1—N2	129.21 (14)	C3—C4—H4A	120.6
N1—Hf1—N2	68.04 (14)	C5—C4—H4A	120.6
N1^i—Hf1—N2^i	68.04 (14)	C4—C5—C6	121.8 (4)
N1—Hf1—N2^i	129.21 (14)	C4—C5—H5A	119.1
N2—Hf1—N2^i	158.1 (2)	C6—C5—H5A	119.1
N1^i—Hf1—Cl1^i	143.43 (10)	C5—C6—C1	119.0 (4)
N1—Hf1—Cl1^i	95.91 (10)	C5—C6—C8	118.6 (4)
N2—Hf1—Cl1^i	87.01 (11)	C1—C6—C8	122.4 (4)
N2^i—Hf1—Cl1^i	78.46 (10)	C2—C7—H7A	109.5
N1^i—Hf1—Cl1	95.91 (10)	C2—C7—H7B	109.5
N1—Hf1—Cl1	143.43 (10)	H7A—C7—H7B	109.5
N2—Hf1—Cl1	78.46 (10)	C2—C7—H7C	109.5
N2^i—Hf1—Cl1	87.01 (11)	H7A—C7—H7C	109.5
Cl1^i—Hf1—Cl1	96.60 (7)	H7B—C7—H7C	109.5
N1^i—Hf1—Si1^i	33.65 (10)	C6—C8—H8A	109.5
N1—Hf1—Si1^i	121.48 (10)	C6—C8—H8B	109.5
N2—Hf1—Si1^i	153.13 (10)	H8A—C8—H8B	109.5
N2^i—Hf1—Si1^i	36.33 (10)	C6—C8—H8C	109.5
Cl1^i—Hf1—Si1^i	114.79 (4)	H8A—C8—H8C	109.5
Cl1—Hf1—Si1^i	83.32 (5)	H8B—C8—H8C	109.5
N1—Si1—N2	92.40 (18)	Si1—C9—H9A	109.5
N1—Si1—C9	118.5 (2)	Si1—C9—H9B	109.5
N2—Si1—C9	112.8 (2)	H9A—C9—H9B	109.5
N1—Si1—C10	116.7 (2)	Si1—C9—H9C	109.5
N2—Si1—C10	111.3 (3)	H9A—C9—H9C	109.5
C9—Si1—C10	104.9 (3)	H9B—C9—H9C	109.5
C1—N1—Si1	120.6 (3)	Si1—C10—H10A	109.5
C1—N1—Hf1	135.3 (3)	Si1—C10—H10B	109.5
Si1—N1—Hf1	103.71 (17)	H10A—C10—H10B	109.5
C11—N2—C12	107.9 (4)	Si1—C10—H10C	109.5
C11—N2—Si1	111.8 (3)	H10A—C10—H10C	109.5
C12—N2—Si1	117.7 (4)	H10B—C10—H10C	109.5
C11—N2—Hf1	107.9 (4)	N2—C11—H11A	109.5

C12—N2—Hf1	119.6 (3)	N2—C11—H11B	109.5
Si1—N2—Hf1	90.94 (16)	H11A—C11—H11B	109.5
C2—C1—C6	119.1 (4)	N2—C11—H11C	109.5
C2—C1—N1	120.6 (4)	H11A—C11—H11C	109.5
C6—C1—N1	120.3 (4)	H11B—C11—H11C	109.5
C3—C2—C1	119.4 (4)	N2—C12—H12A	109.5
C3—C2—C7	117.2 (4)	N2—C12—H12B	109.5
C1—C2—C7	123.4 (4)	H12A—C12—H12B	109.5
C4—C3—C2	121.8 (4)	N2—C12—H12C	109.5
C4—C3—H3A	119.1	H12A—C12—H12C	109.5
C2—C3—H3A	119.1	H12B—C12—H12C	109.5

Symmetry codes: (i) −x+1, y, −z+3/2.

Fig. 1