

Bis[μ -*N*-(diethylamino- κ *N*)dimethylsilylanilido- κ^2 *N:N*]bis[chloridocobalt(II)]

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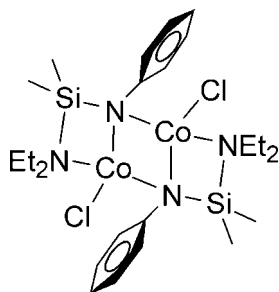
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.013$ Å; R factor = 0.072; wR factor = 0.227; data-to-parameter ratio = 18.7.

In the title binuclear Co^{II} complex, $[\text{Co}_2(\text{C}_{12}\text{H}_{21}\text{N}_2\text{Si})_2\text{Cl}_2]$, an inversion center is located at the mid-point between the two Co atoms in the dimeric molecule. The bidentate *N*-silylated anilide ligand coordinates the Co^{II} atom in an *N,N'*-chelating mode and provides the anilide N atom as a bridge to link two Co^{II} atoms. The two ends of the $\text{N}-\text{Si}-\text{N}$ chelating unit exhibit different affinities for the metal atom. The $\text{Co}-\text{N}_{\text{anilide}}$ bond is 2.031 (6) Å and $\text{Co}-\text{N}_{\text{amino}}$ bond is 2.214 (6) Å. The four-coordinate Co atom presents a distorted tetrahedral geometry, while the dimeric aggregation exhibits a $(\text{CoN})_2$ rhombus core with 1.998 (6) Å as the shortest sides and shows a ladder structure composed of Co, N and Si atoms.

Related literature

For related reviews of metal amides, see: Holm *et al.* (1996); Kempe (2000). For catalytic applications of related *N*-silylated anilido group 4 metal compounds towards olefin polymerization, see: Gibson *et al.* (1998); Hill & Hitchcock (2002); Yuan *et al.* (2010). For related organometallic compounds supported by analogous anilido ligands, see: Schumann *et al.* (2000); Chen (2008, 2009). For related cobalt amides, see: Murray & Power (1984); Hope *et al.* (1985).



Experimental

Crystal data

$[\text{Co}_2(\text{C}_{12}\text{H}_{21}\text{N}_2\text{Si})_2\text{Cl}_2]$
 $M_r = 631.56$
 Orthorhombic, *Pccn*
 $a = 12.180$ (1) Å
 $b = 15.6753$ (13) Å
 $c = 16.0235$ (13) Å

$V = 3059.3$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.36$ mm⁻¹
 $T = 293$ K
 $0.20 \times 0.15 \times 0.10$ mm

Data collection

Bruker SMART area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.773$, $T_{\text{max}} = 0.876$

16361 measured reflections
 2885 independent reflections
 1795 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.093$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.072$
 $wR(F^2) = 0.227$
 $S = 1.17$
 2885 reflections
 154 parameters

48 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.97$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JJ2112).

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supplementary materials

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Comment

Metal amides are important substitutes for cyclopentadienyl derivatives and are found to have valuable applications in various industrial and biological processes (Holm *et al.*, 1996; Kempe, 2000). Group 4 metal amides supported with *N*-silylated anilido ligands are active catalysts for olefin polymerization reactions (Gibson *et al.*, 1998; Hill & Hitchcock, 2002). Recently, a class of monoionic *N*-silylated anilido ligands bearing a pendant amino group were the subject of focus presuming that the empty *d*-orbitals on silicon would interact with the lone-pair electrons on the *p*-orbital of nitrogen center through a *d*- π interaction throughout the N—Si—N motif. Analogous compounds with different metals including Zn (Schumann *et al.*, 2000), Zr (Chen, 2009) and Fe (Chen, 2008) have been synthesized. In addition, a group of zirconium amides with a similar ligand were reported showing good performance in ethylene polymerization reactions (Yuan *et al.*, 2010). In view of the importance of these compounds, the synthesis and crystal structure of a new cobalt(II) anilido complex, (I), is reported.

The title compound, [Co(C₁₂H₂₁N₂Si)Cl]₂, is a binuclear Co^{II} complex with an inversion center located at the mid-point between two Co atoms in the dimeric molecule (Fig. 1). Each Co(II) atom is bound to three nitrogen atoms and one chlorine atom, resulting in a distorted tetrahedral geometry at the metal center. The bidentate *N*-silylated anilide ligand coordinates a metal center in an *N,N'*-chelating mode and provides the anilido nitrogen as a bridge to link the two Co atoms. The two ends of the N—Si—N chelating unit exhibit different affinities for the metal center. The Co—Co distance is 2.5682 (19) Å, which is similar to 2.583 (1) Å in [Co{N(SiMe₃)₂}₂]₂ and 2.566 (3) Å in [Co(NPh₂)₂]₂ (Murray & Power, 1984; Hope *et al.*, 1985). The N—Si—N angle is constrained to be 98.8 (3)°. The Co—N_{anilido} bond is 2.031 (2) Å and Co—N_{amino} bond is 2.214 (6) Å. The four-coordinate Co atom presents a distorted tetrahedral geometry while the dimeric aggregation exhibits a (CoN)₂ rhombus core with 2.0 Å sides and shows a ladder structure composed of Co, N and Si atoms.

Experimental

The title compound was prepared by a one-pot reaction of LiBu^{*n*}, *N*-[(diethylamino)dimethylsilyl]aniline and CoCl₂ as follows: A solution of LiBu^{*n*} (1.6 M, 1.75 ml, 2.8 mmol) in hexane was slowly added into a solution of *N*-[(diethylamino)dimethylsilyl]aniline (0.62 g, 2.8 mmol) in Et₂O (20 ml) at 273 K by syringe. The mixture was stirred at room temperature for two hours and then added to a stirring suspension of CoCl₂ (0.37 g, 2.8 mmol) in Et₂O (20 ml) at 273 K. The resulting mixture was stirred at room temperature for 8 h. Then all the volatiles were removed under vacuum. The residue was extracted with toluene (25 ml). The filtrate was concentrated and suitable green single-crystals of the title compound were obtained by recrystallization in toluene. (yield 0.25 g, 28%). Anal. Calc. for C₂₄H₄₂Cl₂Co₂N₄Si₂: C, 45.64; H, 6.70; N, 8.87%. Found: C, 45.48; H, 6.65; N, 9.05%.

Refinement

All of the H atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms with calculated positions and then refined using the riding model with Atom—H lengths of 0.93 Å (CH), 0.97 Å (CH₂) or 0.96 Å (CH₃). Isotropic displacement parameters for these atoms were set to 1.2 (CH, CH₂) or 1.5 (CH₃) times U_{eq} of the parent atom. The N—Si—N angle is constrained to be 98.8 (3)°.

Figures

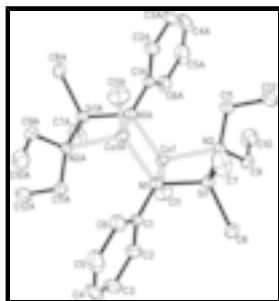


Fig. 1. The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. An inversion center is located at the midpoint between two Co atoms in the dimeric molecule. H atoms have been omitted for clarity.

\ Bis[μ -N-(diethylamino- κ N)dimethylsilylanilido- κ^2 N:N]bis[chloridocobalt(II)]

Crystal data

[Co₂(C₁₂H₂₁N₂Si)₂Cl₂]

$M_r = 631.56$

Orthorhombic, *Pccn*

Hall symbol: -P 2ab 2ac

$a = 12.180$ (1) Å

$b = 15.6753$ (13) Å

$c = 16.0235$ (13) Å

$V = 3059.3$ (4) Å³

$Z = 4$

$F(000) = 1320$

$D_x = 1.371$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3365 reflections

$\theta = 2.3$ – 26.3°

$\mu = 1.36$ mm⁻¹

$T = 293$ K

Block, green

$0.20 \times 0.15 \times 0.10$ mm

Data collection

Bruker SMART area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

Detector resolution: 7.9 pixels mm⁻¹

ϕ and ω scan

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

$T_{min} = 0.773$, $T_{max} = 0.876$

16361 measured reflections

2885 independent reflections

1795 reflections with $I > 2\sigma(I)$

$R_{int} = 0.093$

$\theta_{max} = 25.6^\circ$, $\theta_{min} = 2.1^\circ$

$h = -14 \rightarrow 14$

$k = -17 \rightarrow 19$

$l = -13 \rightarrow 19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.072$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.227$	H-atom parameters constrained
$S = 1.17$	$w = 1/[\sigma^2(F_o^2) + (0.0945P)^2 + 13.3754P]$
2885 reflections	where $P = (F_o^2 + 2F_c^2)/3$
154 parameters	$(\Delta/\sigma)_{\max} < 0.001$
48 restraints	$\Delta\rho_{\max} = 1.97 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.51 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. MS (EI, 70 eV): m/z 632 $[M]^+$.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.55911 (8)	0.48017 (6)	0.43654 (6)	0.0307 (3)
Si1	0.37762 (17)	0.55954 (13)	0.36970 (13)	0.0356 (5)
Cl1	0.71974 (18)	0.48946 (17)	0.37397 (16)	0.0617 (7)
N1	0.4612 (5)	0.5831 (4)	0.4563 (4)	0.0328 (14)
N2	0.4195 (5)	0.4511 (4)	0.3528 (4)	0.0303 (13)
C1	0.4863 (7)	0.6714 (5)	0.4684 (6)	0.0472 (14)
C2	0.5770 (8)	0.7089 (5)	0.4330 (6)	0.0534 (14)
H2A	0.6230	0.6770	0.3988	0.064*
C3	0.6006 (9)	0.7956 (6)	0.4482 (6)	0.0601 (15)
H3A	0.6627	0.8207	0.4250	0.072*
C4	0.5322 (9)	0.8417 (6)	0.4969 (6)	0.0620 (15)
H4A	0.5474	0.8991	0.5059	0.074*
C5	0.4443 (8)	0.8075 (6)	0.5320 (7)	0.0607 (15)
H5A	0.3997	0.8408	0.5660	0.073*
C6	0.4175 (8)	0.7207 (5)	0.5182 (6)	0.0536 (14)
H6A	0.3549	0.6971	0.5420	0.064*
C7	0.2306 (8)	0.5722 (7)	0.3939 (8)	0.079 (4)

supplementary materials

H7A	0.1963	0.6064	0.3516	0.119*
H7B	0.2226	0.5996	0.4472	0.119*
H7C	0.1962	0.5171	0.3957	0.119*
C8	0.4136 (10)	0.6277 (6)	0.2788 (6)	0.073 (3)
H8A	0.3484	0.6541	0.2573	0.109*
H8B	0.4465	0.5932	0.2361	0.109*
H8C	0.4646	0.6710	0.2960	0.109*
C9	0.4621 (7)	0.4311 (5)	0.2680 (5)	0.0456 (18)
H9A	0.5153	0.4742	0.2523	0.055*
H9B	0.4019	0.4338	0.2285	0.055*
C10	0.5154 (8)	0.3447 (6)	0.2621 (6)	0.057 (2)
H10A	0.5407	0.3355	0.2060	0.085*
H10B	0.4629	0.3014	0.2765	0.085*
H10C	0.5765	0.3420	0.2998	0.085*
C11	0.3406 (7)	0.3856 (5)	0.3839 (5)	0.0468 (19)
H11A	0.3119	0.4042	0.4374	0.056*
H11B	0.3800	0.3326	0.3930	0.056*
C12	0.2441 (8)	0.3683 (6)	0.3251 (6)	0.056 (2)
H12A	0.1971	0.3257	0.3492	0.083*
H12B	0.2714	0.3483	0.2724	0.083*
H12C	0.2032	0.4200	0.3169	0.083*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0344 (5)	0.0272 (5)	0.0305 (6)	0.0036 (4)	0.0043 (4)	0.0027 (4)
Si1	0.0450 (12)	0.0250 (11)	0.0369 (12)	0.0043 (9)	-0.0108 (10)	0.0007 (9)
Cl1	0.0470 (12)	0.0727 (17)	0.0655 (15)	0.0029 (11)	0.0246 (11)	0.0051 (12)
N1	0.040 (3)	0.023 (3)	0.036 (4)	0.005 (2)	-0.006 (3)	0.001 (2)
N2	0.045 (3)	0.018 (3)	0.028 (3)	0.000 (2)	-0.004 (3)	-0.002 (2)
C1	0.064 (3)	0.024 (3)	0.053 (3)	0.001 (2)	-0.020 (3)	0.003 (2)
C2	0.069 (3)	0.030 (3)	0.061 (3)	-0.004 (2)	-0.019 (3)	0.006 (2)
C3	0.077 (3)	0.035 (3)	0.068 (3)	-0.006 (3)	-0.022 (3)	0.007 (3)
C4	0.082 (3)	0.035 (3)	0.069 (3)	-0.001 (3)	-0.025 (3)	0.002 (2)
C5	0.081 (3)	0.036 (3)	0.066 (3)	0.007 (3)	-0.022 (3)	-0.003 (2)
C6	0.072 (3)	0.030 (3)	0.059 (3)	0.005 (2)	-0.020 (3)	-0.001 (2)
C7	0.058 (6)	0.079 (8)	0.100 (9)	0.027 (6)	-0.024 (6)	-0.027 (7)
C8	0.139 (10)	0.036 (5)	0.042 (5)	-0.014 (6)	-0.035 (6)	0.010 (4)
C9	0.060 (5)	0.043 (4)	0.034 (4)	-0.003 (4)	0.005 (3)	0.001 (3)
C10	0.074 (5)	0.051 (5)	0.046 (4)	0.004 (4)	0.007 (4)	-0.011 (4)
C11	0.056 (4)	0.036 (4)	0.048 (4)	-0.008 (3)	-0.012 (4)	0.006 (3)
C12	0.062 (4)	0.043 (4)	0.062 (5)	-0.014 (4)	-0.017 (4)	0.007 (4)

Geometric parameters (\AA , $^\circ$)

Co1—N1 ⁱ	1.998 (6)	C5—C6	1.416 (12)
Co1—N1	2.031 (6)	C5—H5A	0.9300
Co1—Cl1	2.203 (2)	C6—H6A	0.9300

Co1—N2	2.214 (6)	C7—H7A	0.9600
Co1—Co1 ⁱ	2.5682 (19)	C7—H7B	0.9600
Co1—Si1	2.754 (2)	C7—H7C	0.9600
Si1—N1	1.760 (6)	C8—H8A	0.9600
Si1—N2	1.795 (6)	C8—H8B	0.9600
Si1—C7	1.843 (10)	C8—H8C	0.9600
Si1—C8	1.859 (9)	C9—C10	1.505 (12)
N1—C1	1.431 (9)	C9—H9A	0.9700
N1—Co1 ⁱ	1.998 (6)	C9—H9B	0.9700
N2—C9	1.487 (10)	C10—H10A	0.9600
N2—C11	1.492 (10)	C10—H10B	0.9600
C1—C2	1.375 (13)	C10—H10C	0.9600
C1—C6	1.391 (13)	C11—C12	1.531 (11)
C2—C3	1.410 (12)	C11—H11A	0.9700
C2—H2A	0.9300	C11—H11B	0.9700
C3—C4	1.351 (14)	C12—H12A	0.9600
C3—H3A	0.9300	C12—H12B	0.9600
C4—C5	1.323 (14)	C12—H12C	0.9600
C4—H4A	0.9300		
N1 ⁱ —Co1—N1	100.8 (2)	C5—C4—C3	121.9 (10)
N1 ⁱ —Co1—C11	122.26 (18)	C5—C4—H4A	119.1
N1—Co1—C11	122.67 (19)	C3—C4—H4A	119.1
N1 ⁱ —Co1—N2	108.9 (2)	C4—C5—C6	120.6 (10)
N1—Co1—N2	78.9 (2)	C4—C5—H5A	119.7
C11—Co1—N2	114.83 (18)	C6—C5—H5A	119.7
N1 ⁱ —Co1—Co1 ⁱ	50.96 (17)	C1—C6—C5	119.0 (9)
N1—Co1—Co1 ⁱ	49.84 (17)	C1—C6—H6A	120.5
C11—Co1—Co1 ⁱ	147.37 (10)	C5—C6—H6A	120.5
N2—Co1—Co1 ⁱ	95.69 (16)	Si1—C7—H7A	109.5
N1 ⁱ —Co1—Si1	117.33 (18)	Si1—C7—H7B	109.5
N1—Co1—Si1	39.67 (17)	H7A—C7—H7B	109.5
C11—Co1—Si1	120.40 (9)	Si1—C7—H7C	109.5
N2—Co1—Si1	40.57 (15)	H7A—C7—H7C	109.5
Co1 ⁱ —Co1—Si1	75.44 (6)	H7B—C7—H7C	109.5
N1—Si1—N2	98.8 (3)	Si1—C8—H8A	109.5
N1—Si1—C7	111.9 (4)	Si1—C8—H8B	109.5
N2—Si1—C7	114.2 (4)	H8A—C8—H8B	109.5
N1—Si1—C8	111.2 (4)	Si1—C8—H8C	109.5
N2—Si1—C8	111.0 (4)	H8A—C8—H8C	109.5
C7—Si1—C8	109.4 (6)	H8B—C8—H8C	109.5
N1—Si1—Co1	47.44 (19)	N2—C9—C10	113.5 (7)
N2—Si1—Co1	53.33 (19)	N2—C9—H9A	108.9
C7—Si1—Co1	138.3 (4)	C10—C9—H9A	108.9
C8—Si1—Co1	112.0 (4)	N2—C9—H9B	108.9
C1—N1—Si1	115.7 (5)	C10—C9—H9B	108.9
C1—N1—Co1 ⁱ	112.9 (5)	H9A—C9—H9B	107.7

supplementary materials

Si1—N1—Co1 ⁱ	120.1 (3)	C9—C10—H10A	109.5
C1—N1—Co1	131.6 (5)	C9—C10—H10B	109.5
Si1—N1—Co1	92.9 (3)	H10A—C10—H10B	109.5
Co1 ⁱ —N1—Co1	79.2 (2)	C9—C10—H10C	109.5
C9—N2—C11	112.6 (6)	H10A—C10—H10C	109.5
C9—N2—Si1	115.9 (5)	H10B—C10—H10C	109.5
C11—N2—Si1	114.7 (5)	N2—C11—C12	114.2 (7)
C9—N2—Co1	109.2 (5)	N2—C11—H11A	108.7
C11—N2—Co1	115.7 (4)	C12—C11—H11A	108.7
Si1—N2—Co1	86.1 (2)	N2—C11—H11B	108.7
C2—C1—C6	118.9 (8)	C12—C11—H11B	108.7
C2—C1—N1	122.0 (8)	H11A—C11—H11B	107.6
C6—C1—N1	119.2 (8)	C11—C12—H12A	109.5
C1—C2—C3	120.4 (10)	C11—C12—H12B	109.5
C1—C2—H2A	119.8	H12A—C12—H12B	109.5
C3—C2—H2A	119.8	C11—C12—H12C	109.5
C4—C3—C2	119.3 (10)	H12A—C12—H12C	109.5
C4—C3—H3A	120.4	H12B—C12—H12C	109.5
C2—C3—H3A	120.4		

Symmetry codes: (i) $-x+1, -y+1, -z+1$.

Fig. 1

