Tris[bis(trimethylsilyl)amido]samarium tetrahydrofuran solvate

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(Si–C) = 0.007 Å
R factor = 0.061
wR factor = 0.104
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecular structure of the title complex, [Sm{N(SiMe$_3$)$_2$}$_3$]·C$_4$H$_8$O, an important key compound in lanthanide chemistry, has been determined. The crystal structure analysis reveals a trigonal–pyramidal structure, isotype to other structurally characterized lanthanide tris-silylamides. The molecule is disordered due to the D_3 site symmetry.

Comment

Homoleptic silylamides of the rare earth elements are well established starting materials for the synthesis of more complex functionalized compounds of the lanthanides *via* amine metathesis reactions with OH-, NH- and CH-acidic ligands (Anwander, 1996). The title compound, (I), was first described by Bradley *et al.* (1973); however, its molecular structure has never been established. It serves as a catalyst for the ring-opening polymerization of lactones (Agarwal *et al.*, 1999). Samarium, with an Sm^{3+} radius of 1.13 Å, is the largest of the lanthanide(III) cations and we were therefore interested to compare the molecular structure with those of other [Ln{N(SiMe$_3$)$_2$}$_3$] compounds (Niemeyer, 2002, and references therein; Hitchcock, 2004).


(I)
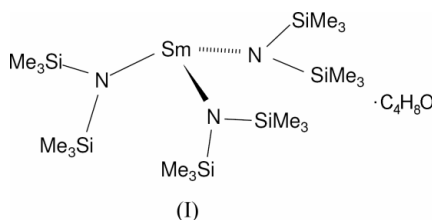
Compound (I) crystallizes in the trigonal space group $P\overline{3}1c$ with Z = 2 and is isotypic to the other [Ln{N(SiMe$_3$)$_2$}$_3$] compounds and therefore shows similar structural features: (i) the three-coordinate pyramidal Sm atom is disordered and adopts a position on a threefold axis 0.515 (2) Å above and below the N$_3$ plane; (ii) there are short 'agostic' interactions between Sm and the trimethylsilyl groups, with Sm1···C1 = 2.988 (6) Å [see Niemeyer (2002) for details about this interaction]; (iii) heavily disordered solvent (tetrahydrofuran) is present in solvent-accessible channels.

Experimental

The title compound was prepared using NaN(SiMe$_3$)$_2$ instead of LiN(SiMe$_3$)$_2$ in a modification of a literature procedure (Bradley *et al.*, 1973). SmCl$_3$ (3.76 g, 14.63 mmol) was suspended at 273 K in THF (70 ml) and a solution of NaN(SiMe$_3$)$_2$ (8.05 g, 43.86 mmol) in THF (30 ml) was added over a period of 2–3 min. After stirring for 24 h at room temperature, all solvent was removed under reduced pressure. The residue was extracted from a glass frit with 5 × 50 ml boiling
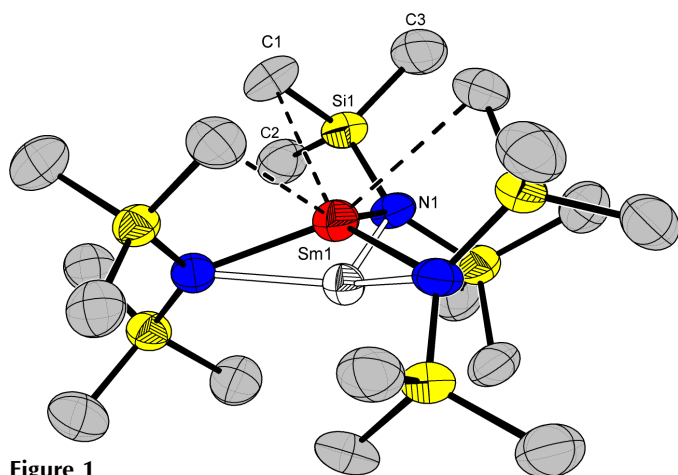
Figure 1
A view of (I) showing the Sm⋯C contacts (dashed lines). Displacement ellipsoids are drawn at the 50% probability level. H atoms and the disordered tetrahydrofuran molecule have been omitted. Atoms of the asymmetric unit are labelled.
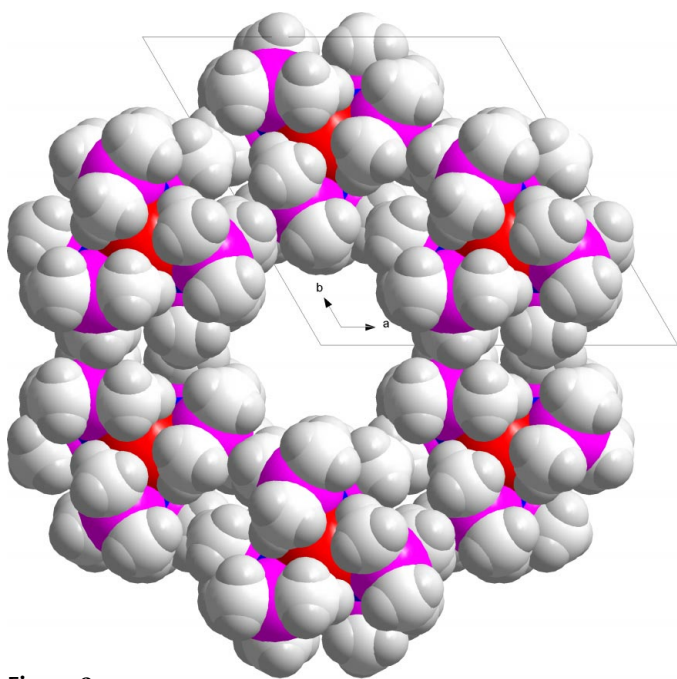
Figure 2
Space-filling packing diagram of (I), showing a solvent-accessible channel.

hexane. The extract was evaporated to dryness and the residue was sublimed at 363 K/10^{-4} mbar (yield: 6.85 g, 74%, literature 50–70%; yellow, crystalline; m.p. 431–432 K, literature m.p. 428–431 K). ^{1}H NMR (200.1 MHz, C_6D_6): δ −1.58. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 2.2. Single crystals were grown by cooling a hexane/THF solution.

Crystal data

$[Sm(C_6H_{18}NSi_2)_3]\cdot C_4H_8O$	Mo $K\alpha$ radiation
$M_r = 703.64$	Cell parameters from 2000
Trigonal, $P\bar{3}1c$	reflections
$a = 16.490 (3)$ Å	$\theta = 2$–$25°$
$c = 8.3485 (11)$ Å	$\mu = 1.69$ mm^{-1}
$V = 1966.0 (6)$ Å^3	$T = 193 (2)$ K
$Z = 2$	Needle, colourless
$D_x = 1.189$ Mg m^{-3}	$0.33 \times 0.06 \times 0.06$ mm

Data collection

Stoe IPDS-2 diffractometer	784 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.118$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(Blessing, 1995)	$h = -19 \rightarrow 19$
$T_{min} = 0.855$, $T_{max} = 0.903$	$k = -19 \rightarrow 13$
8924 measured reflections	$l = -8 \rightarrow 9$
1154 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.061$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
1154 reflections	$\Delta\rho_{min} = -0.92$ e Å^{-3}
92 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0145 (16)

Table 1
Selected geometric parameters (Å, °) for (I).

Sm1—N1	2.294 (6)	Si1—C3	1.861 (7)
Sm1—C1	2.988 (6)	Si1—C1	1.873 (6)
Si1—N1	1.709 (3)	Si1—C2	1.875 (6)
N1^{ii}—Sm1—N1	115.11 (3)	C3—Si1—C2	107.6 (3)
N1—Si1—C3	113.5 (3)	C1—Si1—C2	107.1 (3)
N1—Si1—C1	108.2 (3)	Si1—N1—Si1^{iii}	126.1 (4)
C3—Si1—C1	106.7 (3)	Si1—C1—Sm1	79.8 (2)
N1—Si1—C2	113.3 (2)		

Symmetry codes: (i) $1 - y, 1 - x, -\frac{1}{2} - z$; (ii) $1 - y, x - y, z$; (iii) $x, x - y, -\frac{1}{2} - z$.

There was substantial residual electron density present in the solvent-accessible channels in the structure of the title compound. A complete tetrahydrofuran molecule was modelled with restraints for 1,2- and 1,3-distances and was anisotropically refined with restraints for the displacement parameters. A common occupation factor refined to 0.171 (5) and was fixed at 0.16667. This leads to two solvent molecules in the unit cell with a sixfold disorder due to crystallographic symmetry. This heavy disorder and the disorder of the Sm atom may explain the weakness of the data set ($R_\sigma = 0.081$) and the relatively high R_{int} value (0.118). All H atoms were included in calculated positions and refined using a riding model [C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 atoms, and C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for CH_2 atoms]. Although a refinement in the non-centrosymmetric space group $P31c$ gave slightly better R values, it was finally not successful. The same disorder for the Sm atom and for the tetrahydrofuran molecule was present as in space group $P\bar{3}1c$. There were large correlations between parameters, high standard deviations and a distorted geometry. Some displacement parameters of the tetrahydrofuran molecule were non-positive definite.

Data collection: *X-AREA* (Stoe & Cie, 2003); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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