

Tris[(pentafluorophenyl)trimethylsilylamido](tetrahydrofuran)-samarium(III)

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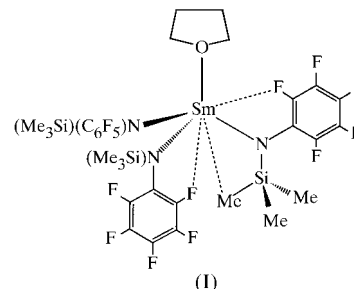
In the title complex, $[\text{Sm}(\text{C}_9\text{H}_9\text{F}_5\text{NSi})_3(\text{C}_4\text{H}_8\text{O})]$, the Sm metal center is coordinated in a highly distorted tetrahedral geometry by the three N atoms of the amido ligands and by the O atom of the tetrahydrofuran ligand. Principal bond lengths include: Sm–N 2.299 (4), 2.339 (4) and 2.366 (4) Å, and Sm–O 2.446 (3) Å, close Sm···F contacts of 2.536 (3) and 2.556 (3) Å, and an 'agostic' Sm···C interaction of 3.154 (4) Å.

Comment

The chemistry of transition metals coordinated by mono-, di- and triamido ligands has recently generated a considerable amount of interest due to many interesting observations of catalytic activity (Baumann *et al.*, 1997), small molecule activation (Johnson *et al.*, 1998) and unusual coordination modes of neutral ligands (Roussel & Scott, 1998). A number of these studies have involved amido ligands which have electron-withdrawing fluorophenyl groups directly attached to nitrogen (Rosenberger *et al.*, 1997; Memmler *et al.*, 1996). We are currently interested in the chemistry of highly electrophilic metal–amido complexes as potential catalysts for olefin polymerization. We have recently described the structural characterization of a series of lanthanide complexes bearing highly fluorinated amido ligands and have shown that the electrophilic metal centers entered into multiple close contacts with both the C–F and C–H bonds of the ligands (Click *et al.*, 1999). In one of these molecules, $[\text{Sm}\{\text{N}(\text{C}_6\text{F}_5)(\text{SiMe}_3)_3\}_3]$, the metal center displayed significant interactions with the three *ortho*-F atoms of the pentafluorophenyl groups and with three separate methyl groups from the trimethylsilyl portion of the ligands. We report here a structural study of the monotetrahydrofuran (thf) adduct, *i.e.* $[\text{Sm}\{\text{N}(\text{C}_6\text{F}_5)(\text{SiMe}_3)_3\}_3](\text{thf})$, (I), and describe the differences in C–F···Sm and C–H···Sm interactions between the base-free and single-Lewis-base adducts.

Complex (I) crystallizes in space group $P2_1/c$ with no unusual intermolecular contacts. The Sm metal center is

coordinated in a highly distorted tetrahedral geometry by the three N atoms of the amido ligands and the O atom of the thf ligand. The largest deviations from tetrahedral geometry are found in the rather acute N3–Sm1–O1 angle of 86.14 (13)° and the significantly larger N2–Sm1–O1 angle of



137.14 (13)°. The Sm–N distances of 2.299 (4), 2.338 (4) and 2.365 (4) Å are very similar to those of 2.329 (8), 2.330 (7) and 2.362 (8) Å found in the base-free analog $[\text{Sm}\{\text{N}(\text{C}_6\text{F}_5)(\text{SiMe}_3)_3\}_3]$ (Click *et al.*, 1999), while the Sm–O distance of 2.446 (3) Å to the thf ligand is comparable with those found in other thf adducts of Sm^{III} (Clark *et al.*, 1996; Butcher *et al.*, 1999).

In addition to the amido and thf ligands, significant interactions with the metal center are also made by the *ortho*-F atoms from two pentafluorophenyl groups [Sm1···F11 = 2.536 (3) and Sm1···F17 = 2.555 (3) Å] and by the C–H bonds of one methyl group [Sm1···C1 = 3.154 (4) Å]. The Sm···F interactions are very similar in magnitude to those of 2.561 (6), 2.566 (5) and 2.587 (6) Å observed in the base-free complex (Click *et al.*, 1999), while the Sm···C1 agostic interaction distance is typical of those observed in many *f*-element complexes containing bis(trimethylsilyl)amido ligands (Jeske *et al.*, 1985; Schaverien *et al.*, 1989). The third pentafluorophenyl group features no C–F···Sm interactions closer than 3.915 (3) Å, while the next-closest Sm···C interactions are made by C8 at 3.623 (4) Å and C6 at 3.761 (4) Å. The metal center may therefore be considered a seven-coordinate

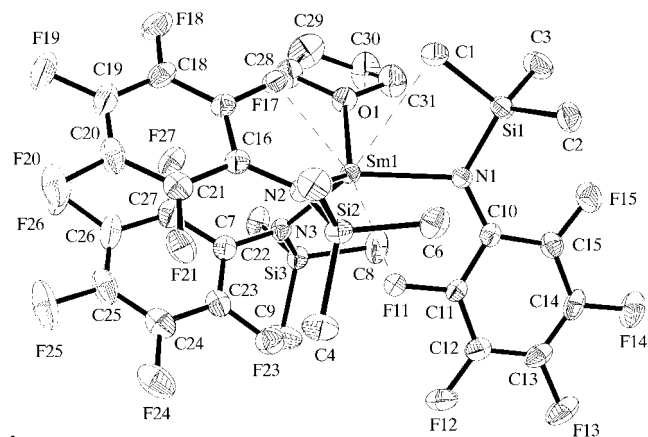


Figure 1
ORTEP plot (Johnson, 1965; 30% probability ellipsoids) showing the molecular structure of (I) and the atom-numbering scheme. F atoms, other than those interacting with the metal center, have been omitted for clarity, as have all the H atoms.

moiety, although the coordination geometry of the ON₃F₂C donor-atom set does not define any readily identifiable geometry. As previously mentioned, the base-free complex [Sm{N(C₆F₅)(SiMe₃)₃}₃] features a nine-coordinate geometry with an N₃F₃C₃ donor-atom set, and thus the coordination of a single thf molecule has displaced two Si—C ··· Sm interactions and one C—F ··· Sm interaction.

Experimental

[Sm{N(SiMe₃)₂}₃] (0.500 g, 0.792 mmol) was dissolved in toluene (10 ml) and *N*-trimethylsilylpentafluoroaniline (0.868 g, 3.40 mmol) was added. The reaction was stirred at room temperature for 18 h and the resulting solution filtered through a Celite pad. The filtrate was pumped to dryness and the resulting yellow–orange solid was washed three times with hexane. The solid was then redissolved in toluene (10 ml), thf (0.1 ml) was added, and the solution was placed in a freezer at 238 K to produce crystals of (I) over a period of several days. The crystals were isolated, washed with hexane and allowed to dry. Analysis calculated for C₃₁H₃₅N₃F₁₅Si₃Sm: C 37.79, H 3.58, N 4.26%; found: C 37.03, H 3.49, N 4.04%.

Crystal data

[Sm(C ₉ H ₉ F ₅ NSi) ₃ (C ₄ H ₈ O)]	$D_x = 1.675 \text{ Mg m}^{-3}$
$M_r = 985.24$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 31 reflections
$a = 17.447(3) \text{ \AA}$	$\theta = 13.0\text{--}13.5^\circ$
$b = 10.467(2) \text{ \AA}$	$\mu = 1.70 \text{ mm}^{-1}$
$c = 21.934(4) \text{ \AA}$	$T = 203(2) \text{ K}$
$\beta = 102.77(1)^\circ$	Block, yellow
$V = 3906.5(12) \text{ \AA}^3$	$0.45 \times 0.33 \times 0.25 \text{ mm}$
$Z = 4$	

Data collection

Siemens P4/PC diffractometer	$R_{\text{int}} = 0.041$
ω scans	$\theta_{\text{max}} = 25.01^\circ$
Absorption correction: empirical	$h = -20 \rightarrow 20$
(XSCANS; Siemens, 1994)	$k = -12 \rightarrow 1$
$T_{\text{min}} = 0.46$, $T_{\text{max}} = 0.65$	$l = -1 \rightarrow 26$
8237 measured reflections	3 standard reflections
6811 independent reflections	every 97 reflections
5303 reflections with $I > 2\sigma(I)$	intensity decay: 13% (linear)

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 4.7821P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.043$	$\Delta\rho_{\text{max}} = 0.99 \text{ e \AA}^{-3}$ (1.0 \AA from Sm1)
6811 reflections	$\Delta\rho_{\text{min}} = -1.02 \text{ e \AA}^{-3}$ (1.0 \AA from Sm1)
487 parameters	
H-atom parameters constrained	

The H-atom positions were idealized, with C—H = 0.96 Å for methyl and 0.97 Å for methylene and were refined using a riding model, with isotropic displacement parameters set to 1.5 (methyl) or 1.2 (methylene) times the equivalent U_{iso} of the atom to which they were bonded.

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS86 (Sheldrick, 1985); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXL97; software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1269). Services for accessing these data are described at the back of the journal.

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