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Bis(η^5-isopropyltetramethylcyclopentadienyl)(tetrahydroborato-κ^3H,H',H'')(tetrahydrofuran-*O*)samarium(III): a lanthanidocene complex with a tridentate tetrahydroborato ligand

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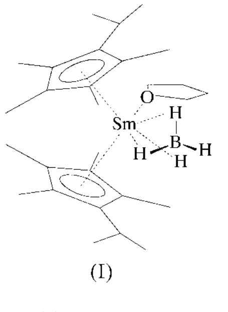
The lanthanidocene complex $[Sm(BH_4)(C_{12}H_{19})_2(C_4H_8O)]$, (I), shows a distorted tetrahedral arrangement around the central Sm^{III} atom. It consists of two η^5-isopropyltetramethylcyclopentadienyl ligands, one tetrahydroborato (BH_4^-) ligand bridging *via* H atoms to the lanthanide atom and one coordinating tetrahydrofuran (thf) molecule. The BH_4^- unit of (I) coordinates as a tridentate ligand with three bridging H atoms and one terminal H atom [Sm—B—H4 176 (2)°]. The η^5-isopropyltetramethylcyclopentadienyl ligands of this bent-sandwich complex [*Cp*1—Sm—*Cp*2 133.53 (1)° where *Cp* denotes the centroid of the cyclopentadienyl ring] adopt staggered conformations.

Comment

In the course of our work on lanthanidocene complexes for homogeneous catalysis (Schumann *et al.*, 1995), we have



(I)

synthesized compound (I), which represents an example of tridentate ligation by the tetrahydroborato ligand.

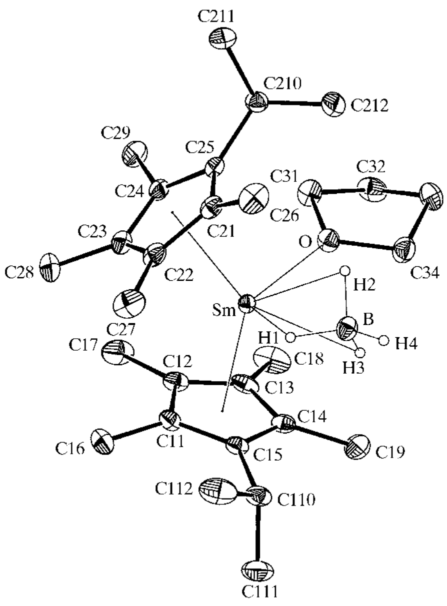


Figure 1
The molecular structure of (I) showing 40% probability displacement ellipsoids. H atoms have been omitted for clarity, except for those of the BH_4^- ligand.

The *Cp*—Sm distances of (I) are 2.4888 (2) and 2.4910 (2) Å, the Sm—O bond length is 2.470 (2) Å and the Sm—B distance is 2.624 (3) Å. Our related work on tetrahydroborato metallocenes (Schumann *et al.*, 1998) revealed that $(\eta^5\text{-EtMe}_4C_5)_2Y(BH_4\text{-}\kappa^2H)$(thf) contains a bidentate BH_4^- ligand with *Cp*—Y distances of 2.385 (2) and 2.392 (2) Å, a Y—O bond length of 2.389 (2) Å and a Y—B distance of 2.669 (4) Å. The constitution of the Sm^{III} complex (I) and the constitution of the Y^{III} complex differ only regarding the metal centre and the substitution of the cyclopentadienyl rings (^{i}Pr instead of Et). The *Cp*—Sm distance of (I) is about 0.1 Å longer than the *Cp*—Y distance of the Y^{III} complex, and the Sm—O bond is also 0.081 Å longer than the analogous Y—O bond due to the larger ionic radius of Sm^{III} [Sm^{III} 1.098 Å and Y^{III} 1.04 Å (Shannon, 1976)]. However, the Sm—B distance [2.624 (3) Å] is 0.045 Å shorter than the Y—B distance [2.669 (4) Å] which is, contrary to expectations, based on the ionic radii. This can be explained by the observation that the Sm^{III} complex (I) has a BH_4^- ligand with three bridging H atoms whereas the Y^{III} complex contains only two bridging H atoms. In the case of a tridentate complexation of BH_4^-, (I), the resulting geometry reduces the Sm—B distance and compensates for the larger ionic radius of Sm^{III}. Generally, for larger lanthanide atoms, tridentate complexation is favoured (Lappert *et al.*, 1983). It was observed earlier that an increased number of bridging H atoms leads to a shorter distance between the two corresponding central atoms (Mayo *et al.*, 1994). In agreement with these results, the single-crystal structure of $(\eta^5\text{-Me}_5C_5)_2SmBH_4$(thf) (Schumann *et al.*, 1998) with two molecules per asymmetric unit and Sm—B distances of 2.58 (2) and 2.62 (2) Å correspond to parameters for tridentate ligation; however, in this structure, the H atoms of the BH_4^- moiety could not be located. Tetrahydroborato lanthanide complexes with the larger Pr^{III} and Nd^{III} atoms and the distances Pr—B = 2.757 Å and Nd—B = 2.664 Å were also suggested to have tridentate BH_4^- ligation (Deng *et al.*, 1994). These examples show that the variation of the lanthanide centre influences the steric behaviour of lanthanidocene complexes, and there are further examples published in the literature (Evans *et al.*, 1999). The geometrical parameters of the three bridging H atoms of (I) indicate that only H2 and H3 are equivalent [B—H2 1.13 (3), B—H3 1.13 (3), Sm—H2 2.51 (3), Sm—H3 2.49 (3) Å, Sm—H2—B 83 (2) and Sm—H3—B 84 (2)°]. The H1 atom is located slightly closer to the Sm atom [B—H1 1.18 (3), Sm—H1 2.36 (3) Å and Sm—H1—B 89 (2)°]. As a result, the Sm—B—H4 angle, involving the terminal H4 atom, is 176 (2)°. As expected regarding the bridging H atoms, the average Y—H distance of 2.35 Å of the complex $(\eta^5\text{-EtMe}_4\text{C}_5)_2\text{Y}(\text{BH}_4\text{-}\kappa^2 H)(\text{thf})$ is shorter than the average Sm—H distance of 2.45 Å in (I).

The average *Cp*—Sm distances of $(\eta^5\text{-Me}_5\text{C}_5)_2\text{SmBH}_4(\text{thf})$ [2.456 (8) Å] and of $(\eta^5\text{-Me}_5\text{C}_5)_2\text{SmMe}(\text{thf})$ (2.458 Å) (Evans *et al.*, 1988) are slightly shorter than in (I) [2.490 (2) Å], probably due to the larger cyclopentadienyl ring substituent (isopropyl group) of (I).

Experimental

The synthesis of (I) was conducted by the reaction of samarium trichloride and isopropyltetramethylcyclopentadienyl sodium (molar ratio 1:2) refluxing in anhydrous tetrahydrofuran solution for 3 h followed by the addition of one equivalent of NaBH_4 and further refluxing for 3 h yielding 54% of (I). The lanthanidocene complex is air and moisture sensitive. Single crystals were obtained by slow cooling of an *n*-hexane solution to 245 K. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker ARX 200.

$[\text{C}_3\text{H}_7(\text{CH}_3)_4\text{C}_5]_2\text{Sm}(\text{BH}_4\text{-}\kappa^3 H)(\text{thf})$: ^{1}H NMR (200 MHz, C_6D_6, p.p.m.): δ 2.27 (*m*, 2H, CH), 1.96 (*s*, 12H, CH_3), 0.88 (*s*, 12H, CH_3), −0.30 [*s*, 12H, $(\text{CH}_3)_2$], −1.36 (*s*, 4H, thf), −1.97 (*s*, 4H, thf), −16.36 (s_{br}, 4H, BH_4). ^{13}C{^{1}H} NMR (50.32 MHz, C_6D_6, p.p.m.): δ 123.43 (CC_3H_7), 116.24 (CCH_3), 115.76 (CCH_3), 65.92 (thf), 32.62 [$\text{CH}(\text{CH}_3)_2$], 21.47 (thf), 21.17 [$(\text{CH}_3)_2$], 19.17 (CH_3), 18.58 (CH_3).

Crystal data

$[\text{Sm}(\text{C}_{12}\text{H}_{19})_2(\text{C}_4\text{H}_8\text{O})(\text{BH}_4)]$
$M_r = 563.84$
Orthorhombic, $P2_12_12_1$
$a = 8.9875$ (1) Å
$b = 15.4363$ (1) Å
$c = 20.0845$ (2) Å
$V = 2786.40$ (5) Å^3
$Z = 4$
$D_x = 1.344$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 1.66$–$30.45°$
$\mu = 2.124$ mm^{-1}
$T = 173$ (2) K
Prismatic, orange
0.42 × 0.26 × 0.18 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.507$, $T_{\max} = 0.682$
26 346 measured reflections
8462 independent reflections
7687 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.057$
$\theta_{\max} = 30.45°$
$h = -12 \rightarrow 12$
$k = -22 \rightarrow 21$
$l = -28 \rightarrow 25$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.050$
$S = 1.005$
8462 reflections
480 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0020P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.064$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.90$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.022 (9)

Table 1
Selected geometric parameters (Å, °).

Sm—*Cp*1	2.4888 (2)	Sm—H3	2.49 (3)
Sm—*Cp*2	2.4910 (2)	B—H1	1.18 (3)
Sm—O	2.470 (2)	B—H2	1.13 (3)
Sm—B	2.624 (3)	B—H3	1.13 (3)
Sm—H1	2.36 (3)	B—H4	1.01 (5)
Sm—H2	2.51 (3)		
*Cp*1—Sm—*Cp*2	133.53 (1)	Sm—H3—B	84 (2)
*Cp*1—Sm—O	102.45 (5)	Sm—B—H4	176 (2)
*Cp*2—Sm—O	105.44 (5)	H1—B—H2	99 (2)
*Cp*1—Sm—B	109.35 (8)	H1—B—H3	117 (2)
*Cp*2—Sm—B	107.01 (8)	H1—B—H4	112 (3)
O—Sm—B	90.11 (9)	H2—B—H3	106 (3)
Sm—H1—B	89 (2)	H2—B—H4	111 (4)
Sm—H2—B	83 (2)	H3—B—H4	111 (3)

The peaks for the H atoms of the BH_4^- ligand (peak height 0.57 to 0.40 e Å^{-3}) were located in the last difference Fourier maps. All H atoms were refined with isotropic displacement parameters. The Flack parameter was based on 3741 Friedel pairs.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997); molecular graphics: *PLATON*99 (Spek, 1990); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1369). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (2000). C**56**, 48–49 Herbert Schumann *et al.* • $[\text{Sm}(\text{C}_{12}\text{H}_{19})_2(\text{C}_4\text{H}_8\text{O})(\text{BH}_4)]$ **49**