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An optically active heteroleptic cerium camphorate: [bis(trimethylsilyl)amido-κ*N*]bis[(+)-(1*R*,4*R*)-3-(trifluoroacetyl)camphorato-κ^2*O*,*O*′](1,3,5-trimethyl-1,3,5-triazacyclohexane-κ^3*N*,*N*′,*N*″)cerium(III)

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Key indicators

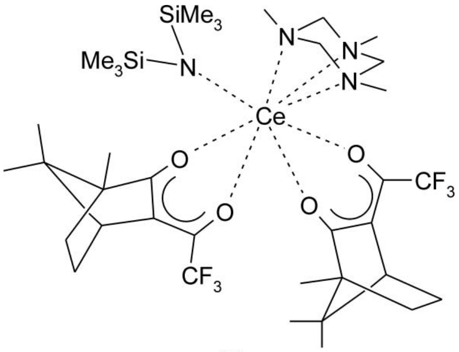
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.041
wR factor = 0.103
Data-to-parameter ratio = 14.4

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

The title compound, [Ce($C_{12}H_{14}F_3O_2$)$_2$($C_6H_{18}NSi_2$)($C_6H_{15}N_3$)], is a rare example of a structurally characterized lanthanide(III) camphorate. The Ce^{III} atom shows a distorted trigonal–dodecahedral coordination, formed by the N atom of the amido ligand [Ce—N = 2.428 (5) Å], four O atoms of two η^2-bonded camphorate groups [average Ce—O = 2.459 (4) Å] and three N atoms of a chelating triazacyclohexane donor [average Ce—N = 2.808 (6) Å].

Comment

The Ce^{III}-catalyzed α-hydroxylation of β-diketo compounds with molecular oxygen is a mild atom-economic and environmentally friendly method for the synthesis of the biologically important α-hydroxy-β-dicarbonyl group (Christoffers & Werner, 2002; Christoffers *et al.*, 2003, 2004; Rössle *et al.*, 2004). The structure determination of the title compound, (I), was performed as part of a project on the preparation of well defined chiral cerium(III) complexes which might be used for enantioselective oxidation reactions. Crystals of (I) were obtained by the reaction of cerium-tris{bis(trimethylsilyl)amide} with an excess of (1*R*,4*R*)-(+)-3-trifluoroacetylcamphor in the presence of the chelating *N*-donor 1,3,5-trimethyl-1,3,5-triazacyclohexane (tmta).



(I)

The molecular structure of (I) shows monomeric units (Fig. 1), in which the eight-coordinate Ce^{III} atom is bonded to one N atom of the silylamido ligand, four O atoms of the η^2-chelating camphorate groups and three N atoms of the neutral donor tmta. The evaluation of characteristic dihedral angles (Muetterties & Guggenberger, 1974) indicates that the coordination polyhedron around the Ce^{III} atom is best described as a distorted trigonal dodecahedron (Fig. 2). In an alternative view, pairs of O atoms (O1/O2 and O3/O4) of the camphorate and the three N atoms N31/N33/N35 of the tmta ligand are replaced by three centroids, thus resulting in a distorted

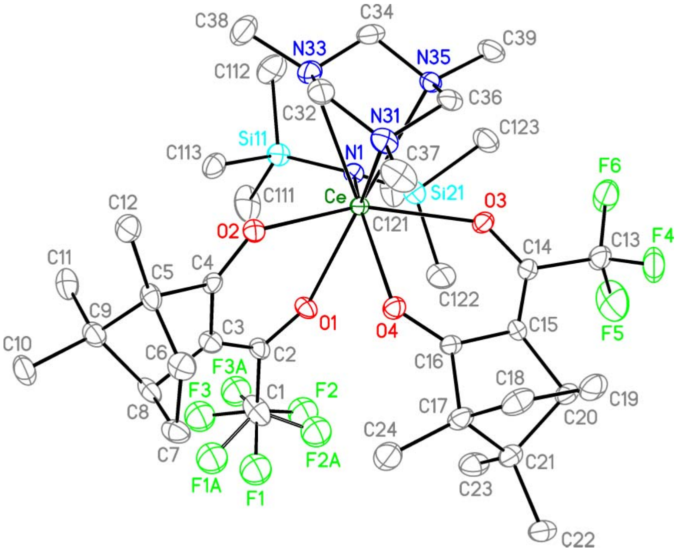


Figure 1
A drawing of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. H atoms have been omitted for clarity.

tetrahedral environment with interligand angles in the range 98.2 (2)–123.1 (2)°.

The Ce—N1 bond length of 2.428 (5) Å is longer than the distance of 2.320 (3) Å in the tris-amide $[Ce\{N(SiMe_3)_2\}_3]$ (Rees *et al.*, 1999), which contains a three-coordinate metal atom. Taking into account the small difference in the ionic radii of Ce^{III} and Pr^{III} (0.01 Å for coordination number 6; Emsley, 1991) the average Ce—O distance of 2.459 (4) Å is almost identical to the corresponding Pr—O bond length of 2.46 (3) Å in the nine-coordinate complex $[(Tfcam)_3Pr(\mu\text{-}dmf)_3Pr(Tfcam)_3]$, which is the only structurally characterized lanthanide camphorate currently available in the literature for comparison [Tfcam is 3-(trifluoroacetyl)camphorate and dmf is dimethylformamide; Cunningham & Sievers, 1975].

Finally, it may be noted that the asymmetric bonding of the chelating tmta donor, with Ce—N3*n* (*n* = 1, 3, 5) distances of 2.762 (6), 2.883 (6) and 2.780 (5) Å, respectively, indicates steric crowding and a transition from η^3- to η^2-coordination (Becker *et al.*, 2004). The average Ce—N bond length of 2.808 (6) Å is considerably longer than the corresponding value in the praseodymium trifluoromethanesulfonate complex $[Pr(OTf)_3(tmta)_2]$ [OTf = O_3SCF_3; average Pr—N 2.673 (2) Å; Köhn *et al.*, 2002].

Experimental

Under an atmosphere of purified argon, a solution of $[Ce\{N(SiMe_3)_2\}_3]$ (0.56 g, 0.90 mmol), (1*R*,4*R*)-(+)-3-trifluoroacetylcamphor (0.82 g, 3.3 mmol) and tmta (0.5 ml) in *n*-heptane (40 ml) was stirred for 2 d at 333 K, after which all volatile materials were removed under reduced pressure. The remaining solid was extracted with *n*-heptane (*ca* 15 ml) and solid by-products were separated by centrifugation. The volume of the resulting dark-amber solution was reduced to incipient crystallization. Redissolution by slight warming and storage at ambient temperature for 14 h afforded orange–brown crystals of (I) (m.p. 396–398 K; yield 0.47 g, 56%).

Crystal data

$[Ce(C_{12}H_{14}F_3O_2)_2(C_6H_{18}NSi_2)(C_6H_{15}N_3)]$
M_r = 924.19
Orthorhombic, $P2_12_12_1$
a = 10.170 (3) Å
b = 14.934 (4) Å
c = 29.568 (8) Å
V = 4491 (2) $Å^3$
Z = 4

D_x = 1.367 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 42 reflections
θ = 7.1–12.5°
μ = 1.13 mm^{-1}
T = 173 (2) K
Prism, orange–brown
0.50 × 0.45 × 0.35 mm

Data collection

Rebuilt Syntex $P2_1$/Siemens *P*3 four-circle diffractometer
ω scans
Absorption correction: *ψ* scan (North *et al.*, 1968)
T_{min} = 0.574, T_{max} = 0.673
7383 measured reflections
7081 independent reflections
6138 reflections with $I > 2\sigma(I)$

R_{int} = 0.023
θ_{max} = 28.0°
h = −1 → 13
k = −1 → 19
l = −1 → 39
2 standard reflections every 298 reflections intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.103
S = 1.47
7081 reflections
491 parameters
Only H-atom displacement parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.38 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.88 e $Å^{-3}$
Absolute structure: Flack (1983), with 1079 Friedel pairs
Flack parameter: −0.013 (17)

Table 1
Selected geometric parameters (Å, °).

Ce—O1	2.414 (3)	N1—Si21	1.712 (5)
Ce—O2	2.480 (4)	O1—C2	1.266 (6)
Ce—O3	2.415 (4)	O2—C4	1.238 (6)
Ce—O4	2.528 (4)	O3—C14	1.271 (7)
Ce—N1	2.428 (5)	O4—C16	1.248 (7)
Ce—N31	2.762 (6)	C2—C3	1.384 (8)
Ce—N33	2.883 (6)	C3—C4	1.436 (7)
Ce—N35	2.780 (5)	C14—C15	1.370 (8)
N1—Si11	1.705 (5)	C15—C16	1.429 (8)
O1—Ce—O2	72.10 (11)	O3—Ce—N31	85.12 (16)
O1—Ce—O3	108.57 (14)	O3—Ce—N33	116.24 (16)
O1—Ce—O4	72.12 (16)	O3—Ce—N35	68.68 (14)
O1—Ce—N1	84.03 (16)	O4—Ce—N1	144.28 (15)
O1—Ce—N31	135.94 (16)	O4—Ce—N31	74.00 (15)
O1—Ce—N33	135.07 (16)	O4—Ce—N33	119.68 (16)
O1—Ce—N35	173.88 (13)	O4—Ce—N35	111.18 (13)
O2—Ce—O3	140.37 (14)	N1—Ce—N31	138.11 (17)
O2—Ce—O4	72.64 (13)	N1—Ce—N33	96.01 (17)
O2—Ce—N1	125.16 (14)	N1—Ce—N35	90.64 (15)
O2—Ce—N31	71.50 (15)	N31—Ce—N33	49.28 (15)
O2—Ce—N33	71.56 (16)	N31—Ce—N35	49.98 (15)
O2—Ce—N35	113.61 (13)	N33—Ce—N35	48.40 (16)
O3—Ce—N1	93.65 (14)		

The trifluoromethyl group in one of the camphorate ligands is disordered and was modelled over two positions, with site occupation factors of 0.5 and a common isotropic displacement parameter. The corresponding C—F distances were refined with distance similarity restraints. The H atoms were positioned geometrically at distances of 1.00 (CH), 0.99 (CH_2) and 0.98 Å (CH_3) and refined in a riding-model approximation, including free rotation for methyl groups. The assigned U_{iso} was allowed to refine freely for groups of chemically equivalent atoms. The absolute configuration was assigned on the basis of the known absolute configuration of the starting material,

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(+)-(1*R*,4*R*)-3-trifluoroacetylcamphor, and confirmed by anomalous scattering effects.

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

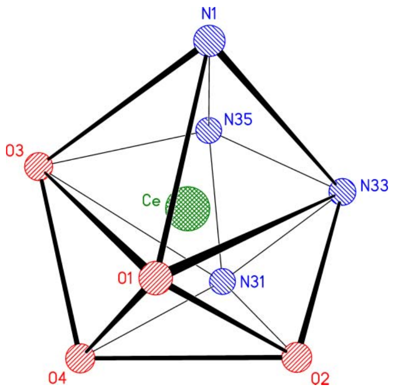

Figure 2

The trigonal–dodecahedral coordination of the $\mathrm{Ce^{III}}$ atom in (I). Characteristic dihedral angles (Muetterties & Guggenberger, 1974): O4—O1—O3—N1 = 150.7, O4—O3—N31—N35 = 158.8, O2—N31—N33—N35 = 127.4 and O2—O1—N33—N1 = 167.0°. In the ideal polyhedron, these values should equal 150.5°.

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