An optically active heteroleptic cerium camphorate: [bis(trimethylsilyl)amido-κN]bis[(+)-(1R,4R)-3-( trifluoroacetyl)camphorato-κ²O,O'](1,3,5-trimethyl-1,3,5-triazacyclohexane-κ³N,N',N'')cerium(III)

The title compound, [Ce(C₁₂H₁₄F₃O₂)₂(C₆H₁₈NSi₂)(C₆H₁₅N₃)], is a rare example of a structurally characterized lanthanide(III) camphorate. The Ce³⁺ 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 η²-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 Ce³⁺-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 (1R,4R)-(+) -3-trifluoroacetyl-camphor in the presence of the chelating N-donor 1,3,5-trimethyl-1,3,5-triazacyclohexane (tmta).

The molecular structure of (I) shows monomeric units (Fig. 1), in which the eight-coordinate Ce³⁺ atom is bonded to one N atom of the silylamido ligand, four O atoms of the η²-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 Ce³⁺ 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...
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(SiMe3)2}3](Rees et al., 1999), which contains a three-coordinate metal atom. Taking into account the small difference in the ionic radii of CeIII and PrIII (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(dmfa)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 = dimethylformamide; Cunningham & Sievers, 1975].

Finally, it may be noted that the asymmetric bonding of the chelating tmta donor, with Ce—N3n (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 η1 to η2-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 = O3SCF3; average Pr—N 2.673 (2) Å; Köhn et al., 2002].

**Experimental**

Under an atmosphere of purified argon, a solution of [Ce[N(SiMe3)2]3] (0.56 g, 0.90 mmol), (1R,4R)-(−)-3-trifluorocycloalkylcamphor (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%).

The trifluoromethyl group in one of the camphor 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 (CH2) and 0.98 Å (CH3) and refined in a riding-model approximation, including free rotation for methyl groups. The assigned Uiso 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,
(+)-(1R,4R)-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.

References


