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SYNTHESIS AND CRYSTAL STRUCTURE OF A FOUR-COORDINATE ARYLOXO SAMARIUM COMPLEX [Sm(OAr)$_3$(THF)](THF) (OAr = 2.6-DITERTBUTYL-4-METHYLPHENOXO)

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Abstract—The aryloxo samarium complex [Sm(ArO)$_3$(THF)](THF) has been prepared by the reaction of $SmCl_3$ with 3 equiv. of NaOAr in THF. An X-ray crystallographic analysis shows the complex to be a four-coordinate aryloxide complex. Three oxygen atoms of aryloxo and one oxygen atom of THF coordinate to the samarium to form a distorted tetrahedron. The average Sm—O(Ar) distance is 2.151(7) Å.

Due to the excellent precursors for the deposition of metal oxide[1–4] the chemistry of the Sc, Y and lanthanide aryloxides is reasonably well documented. However, because of the high solubility, disorder phenomenon and twinning problems, only a few of homoleptic low-coordinate (<6) lanthanide aryloxides have been structurally characterized, such as $Sc(OC_6H_2Bu^t_2\text{-}2.6\text{-}Me\text{-}4)_3$,[5] $Y(OC_6H_3Me_2\text{-}2.6)_3$,[6] $Ce(OC_6H_3Bu^t_2\text{-}2.6)_3$,[7] $Ce(OC_6H_3Bu^t_2\text{-}2.6)_3(CNBu^t)_2$,[7] $Yb(OC_6H_3Ph_2\text{-}2.6)_3$[8] and $Yb(OC_6H_2Bu^t_3\text{-}2.4.6)_3(THF)$.[9] The structure of an aryloxide of a middle lanthanide element appears not to have been reported yet. We report here the synthesis and X-ray crystal of [Sm(OAr)$_3$(THF)](THF).

EXPERIMENTAL

All operations were performed under argon using the Schlenk technique. Hexane was washed with sulphuric acid and H_2O, dried over $CaCl_2$ and refluxed over Na. THF and toluene were distilled from sodium benzophenone ketyl before use. ArONa was prepared from ArOH and NaH in THF. Analysis of the metal was accomplished using direct titration method. MS spectra was obtained on a VG-Quattro spectrometer by the EI^+ method at $T = 200°C$ and EV = 70 eV. Isotopes refer to ^{12}C, ^{1}H, ^{15}O, ^{152}Sm.

Synthetic procedures

To a suspension of $SmCl_3$ (2.93 g, 11.40 mmol) in 20 cm^3 THF was slowly added a solution of ArONa (34.5 mmol) in 74 cm^3 THF at room temperature. After being stirred for 48 h, the reaction mixture was transferred to a centrifuge tube and centrifuged. The solution was decanted from the residue. The solvent was concentrated *in vacuo* and a certain amount of hexane was added until the solution became slightly turbid. After centrifugation, the resulting solution was cooled to −5°C for crystallization. The yellow crystals (4.67 g) were

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obtained (yield 43.1%). Found: Sm 15.3 for $C_{53}H_{85}O_5Sm$: Sm 15.7%, M.P. 135–137°C.

X-ray data collection, structure determination and refinement

A crystal of dimensions $0.24 \times 0.42 \times 0.56$ mm was sealed under argon in a glass capillary and mounted on an Nicolet R3M/E diffractometer. Intensity data were measured with an ω-scan mode with Mo-K_α radiation. Crystallographic data are listed in Table 1. The structure was solved by heavy atom methods, and was refined by full-matrix least-squares using anisotropic temperature factors. The intensities were corrected for Lorentz polarization and empirical absorption effects. The weighting scheme was $W = 1/[\sigma^2(F) + 0.00002F^2]$ $R = 0.0429$, $R_w = 0.0407$. All calculations were made on an Eclipse S/140 minicomputer with the SHELXTL programme system.

RESULTS AND DISCUSSION

The samarium complex [Sm(OC$_6$H$_2$Bu$^t_2$-2.6 Me-4)$_3$(THF)](THF) was prepared by the reaction of $SmCl_3$ with Na(OC$_6$H$_2$Bu$^t_2$-2.6-Me-4) in a 1:3 molar ratio at room temperature in good yield.

$$SmCl_3 + 3NaOAr \longrightarrow Sm(OAr)_3 + NaCl$$

The title complex is sensitive to air and became red when it was exposed to air. The mass spectrum of the complex (Table 2) clearly revealed a molecular ion $[M]^+$ without THF, and related fragments.

The molecular structure is displayed in Fig. 1, selected bond distances and bond angles are listed in Table 3.

The complex is a four-coordinate monomer with three aryloxo oxygen atoms and one THF oxygen atom around the samarium forming a distorted tetrahedron. The Sm—O(Ar) distances are as follows: Sm—O(1) = 2.142(6), Sm—O(2) = 2.163(7), Sm—O(3) = 2.148(7) Å. The average

Table 2. Composition, m/z and relative abundance of fragments of Sm(OAr)$_3$

Symbol	Formula	m/z	Relative abundance %
M^+	$C_{45}H_{69}O_3Sm$	809	1
a	$C_{30}H_{46}O_2Sm$	590	4.8
b	$C_{29}H_{43}O_2Sm$	575	0.8
c	$C_{15}H_{23}OSm$	371	0.9
d	$C_{14}H_{20}OSm$	356	3.7
e	$C_{15}H_{23}O$	219	41
f	$C_{14}H_{20}O$	204	100

Table 1. Summary of crystal and intensity collection data

Formula	$C_{53}H_{85}O_5Sm$
Molecular weight	952.6
Crystal system	Monoclinic
Space group	Cn
β (°)	103.29
Cell constants, a (Å)	25.928(9)
b (Å)	10.527(1)
c (Å)	20.163(9)
Cell volume (Å^3)	5 355
Molecules/unit cell	4
D (g cm^{-3})	1.18
Temperature (K)	298
μ (cm^{-1})	11.6
$F(000)$	2020
Radiation	Mo-K_α, $\lambda = 0.71069$ Å
Crystal dimension (mm)	$0.24 \times 0.42 \times 0.56$
Scan width (°)	1.2
Scan rate (° min^{-1})	7
$2\theta_{max}$ (°)	50
Total unique data	4896
Unique data with $I \geqslant 3\sigma(I)$	3492
Number of parameters varied	512
G.O.F	1.83
R	0.0429
R_w	0.0407

Table 3. Some important bond lengths (Å) and angles (°) in [Sm(OC$_6$H$_2$Bu$^t_2$-2.6-Me-4)$_3$(THF)](THF)

Bond lengths	
Sm—O(1)	2.142(6)
Sm—O(2)	2.163(7)
Sm—O(3)	2.148(7)
Sm—O(4)	2.431(7)
O(1)—C(1)	1.359(10)
O(2)—C(16)	1.365(13)
O(3)—C(31)	1.284(14)
Bond angles	
O(1)—Sm—O(2)	118.7(3)
O(1)—Sm—O(3)	116.9(2)
O(2)—Sm—O(3)	116.3(3)
O(1)—Sm—O(4)	101.3(2)
O(2)—Sm—O(4)	89.2(3)
O(3)—Sm—O(4)	108.1(3)
Sm-O(1)—C(1)	160.7(7)
Sm-O(2)—C(16)	155.3(6)
Sm-O(3)—C(31)	148.4(6)
Sm-O(4)—C(46)	119.8(6)
Sm-O(4)—C(49)	130.1(7)

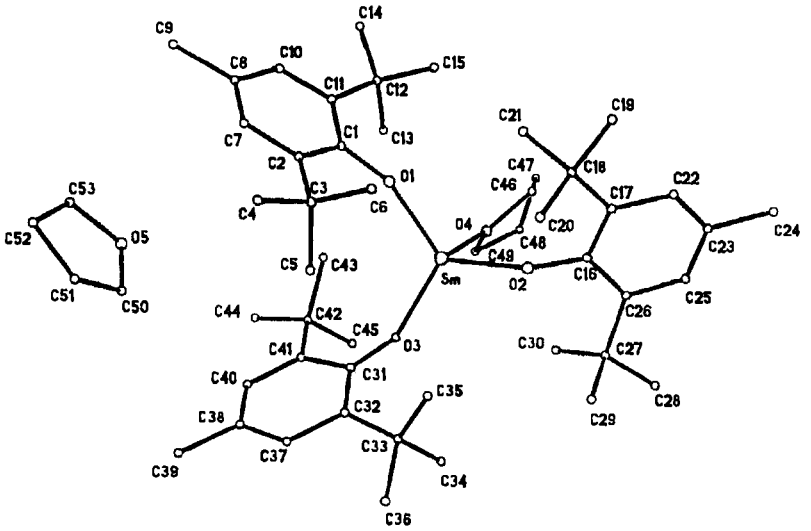

Fig. 1. The molecular structure of $[Sm(OAr)_3(THF)](THF)$.

Sm—O(Ar) distances is 2.151(7) Å. Subtraction of the estimated radius (0.84 Å) for four-coordinate trivalent Sm[10] from the Sm—O distance 2.151(7) Å gives 1.31 Å. This is in the range 1.24–1.31 Å for similar treatment of Ln—O(Ar) distances for the other aryloxo complexes.[1–4,6] The Sm—O(THF) distance 2.431(7) Å is similar to Yb—O(THF) 2.35(1) Å in the other four-coordinate lanthanide aryloxide of $Yb(OC_6H_2Bu^t_3\text{-}2.6)_3(THF)$[9] if the difference of ionic radii is considered.

The O—Sm—O angles varies from 89.2(3) to 118.7(3)°, which is similar to the values of O—Yb—O angles in $Yb(OC_6H_2Bu^t_3\text{-}2.6)_3(THF)$.

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