

Tris(2,6-di-*tert*-butyl-4-methylphenolato-O)(triphenylphosphine oxide-O)-samarium(III)

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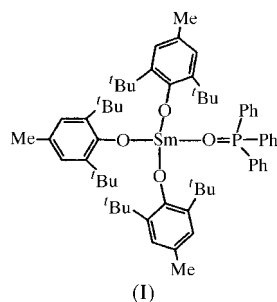
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In the title complex, $[\text{Sm}(\text{C}_{15}\text{H}_{23}\text{O})_3(\text{C}_{18}\text{H}_{15}\text{OP})]$, the central metal atom is coordinated by three O atoms of the aryloxo ligands and by one O atom of the triphenylphosphine oxide molecule resulting in a distorted tetrahedral geometry. The Sm—O_{Ar} distances (Ar is aryl) range from 2.122 (2) to 2.190 (2) Å and the Sm—O_{PPh₃} bond length is 2.306 (2) Å.

Comment

In recent years, lanthanide aryloxides have found a variety of applications as homogeneous catalysts for organic reactions (Shibasaki *et al.*, 1997), and as precursors for organolanthanide syntheses (Clark *et al.*, 1994) and high purity oxide materials (Hubert-Pfalzgraf, 1995). The syntheses, structures and reactivities of aryloxo–lanthanide complexes have attracted a great deal of attention and the investigation of the chemistry of lanthanide complexes containing aryloxo ligands has produced complexes exhibiting a variety of structural types (Evans *et al.*, 1997; Deacon *et al.*, 1997). In our study of the syntheses and reactivities of lanthanide aryloxides (Qi *et al.*, 1995; Yao *et al.*, 1998), the title complex, (I), was obtained from the reaction of $[(\text{ArO})_2\text{Sm}(\text{thf})_3]$ (ArO = OC₆H₂-2,6-di-*tert*-butyl-4-Me and thf is tetrahydrofuran) with excess triphenylphosphine oxide in toluene.



The crystal structure determination indicates that (I) consists of one Sm atom, three aryloxo ligands and one triphenylphosphine oxide molecule. The Sm atom is coordinated

by four O atoms, resulting in a distorted tetrahedral geometry. The coordination geometry around the central metal atom is similar to that in $[\text{Sm}(\text{OAr})_3(\text{thf})]\cdot\text{thf}$ (Qi *et al.*, 1995), but different from that in $[\text{Nd}(\text{Odpp})_3(\text{thf})]$, which has a distorted trigonal–bipyramidal stereochemistry as a result of intra-molecular π -bonding (Deacon *et al.*, 1995).

The $\Sigma\text{O}—\text{Sm}—\text{O}$ of the three aryloxo O atoms around samarium is 345.0° ; this value is comparable with those in $[\text{Sm}(\text{OAr})_3(\text{thf})]\cdot\text{thf}$ (351.9° ; Qi *et al.*, 1995) and $[\text{Nd}(\text{Odpp})_3(\text{thf})]$ (353.2°). However, the three O_{Ar}—Sm—O_{Ar} bond angles range from $99.42(8)$ to $138.29(8)^\circ$; this is different from the case in $[\text{Sm}(\text{OAr})_3(\text{thf})]\cdot\text{thf}$, where the three bond angles are nearly equal, and this may be attributed to the presence of the triphenylphosphine oxide ligand which is more bulky than the tetrahydrofuran ligand. The three Sm—O_{Ar}—C bond angles range from $172.9(2)$ to $175.3(2)^\circ$; they are all somewhat larger than those in $[\text{Sm}(\text{OAr})_3(\text{thf})]\cdot\text{thf}$ (Qi *et al.*, 1995) and are comparable with those in $[\text{Sm}(\text{OAr})_2(\text{thf})_3]\cdot\text{thf}$ (Qi *et al.*, 1994) and $[\text{La}(\text{OC}_6\text{H}_3\text{Me}_2-2,6)_3\{\text{MeO}(\text{CH}_2\text{CH}_2\text{O})_4\text{Me}\}]$ (Aspinall & Williams, 1996). The Sm—O—P angle of $170.06(14)^\circ$ is comparable with those found for lanthanide–triphenylphosphine oxide complexes (Evans *et al.*, 1985; Deacon *et al.*, 1989).

The three Sm—O_{Ar} bond lengths range from 2.112 (2) to 2.190 (2) Å, with an average of 2.155 Å; this value is similar to that of $[\text{Sm}(\text{OAr})_3(\text{thf})]\cdot\text{thf}$ (2.151 Å; Qi *et al.*, 1995). Subtraction of the estimated radius for four-coordinate trivalent samarium (0.84 Å; Shannon, 1976) from the Sm—O distance gives a value of 1.31 Å, which is in the range 1.24–1.31 Å found for a similar treatment of Ln—O_{Ar} distances in

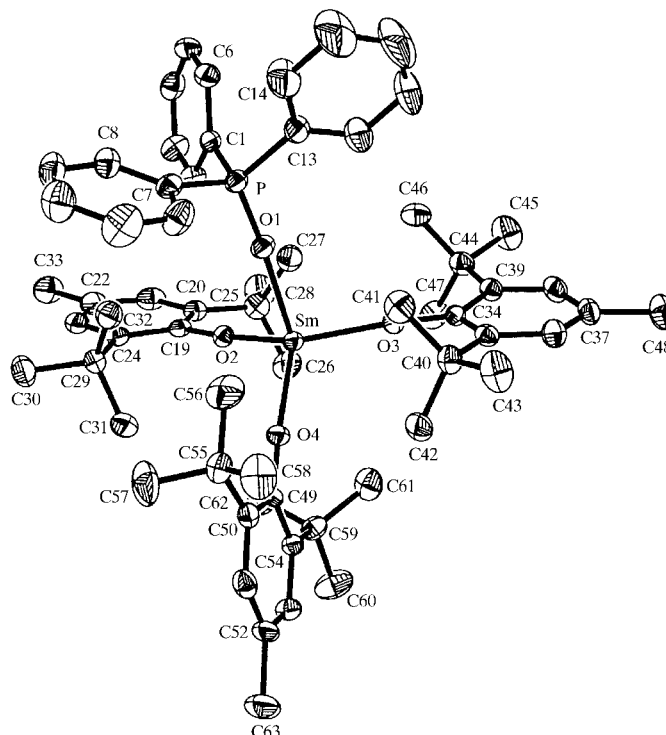


Figure 1

The molecule of (I) showing 40% probability displacement ellipsoids. H atoms have been omitted for clarity.

other aryloxo–lanthanide complexes (Hitchcock *et al.*, 1983, 1987). The Sm–O_{PPh₃} distance of 2.306 (2) Å is comparable with the values in [(C₅Me₅)₂[(C₆H₅)₃PO]Sm]₂(μ–OCH=CHO) (Evans *et al.*, 1985) and [(C₅H₅)₂Yb(OPPh₃)₂] (Deacon *et al.*, 1989) if the difference in the ionic radii is considered.

Experimental

The title complex is very sensitive to air and moisture. Consequently, all manipulations were carried out under argon by Schlenk techniques. Crystals were obtained from the reaction of [Sm(OAr)₂(thf)₃] with excess triphenylphosphine oxide in toluene at 353 K, followed by crystallization from a toluene solution at 263 K. A crystal suitable for single-crystal structure determination was sealed in a thin-walled glass capillary.

Crystal data

[Sm(C ₁₅ H ₂₃ O) ₃ (C ₁₈ H ₁₅ OP)]	$D_x = 1.231 \text{ Mg m}^{-3}$
$M_r = 1086.62$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 38 reflections
$a = 11.682(2) \text{ Å}$	$\theta = 2.99\text{--}16.50^\circ$
$b = 38.168(6) \text{ Å}$	$\mu = 1.072 \text{ mm}^{-1}$
$c = 14.245(2) \text{ Å}$	$T = 297(2) \text{ K}$
$\beta = 112.630(10)^\circ$	Prismatic, yellow
$V = 5862.5(16) \text{ Å}^3$	$0.50 \times 0.40 \times 0.24 \text{ mm}$
$Z = 4$	

Data collection

Siemens P4 diffractometer	$R_{\text{int}} = 0.025$
ω scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 13$
$T_{\text{min}} = 0.851$, $T_{\text{max}} = 0.984$	$k = 0 \rightarrow 45$
11 426 measured reflections	$l = -16 \rightarrow 15$
10 332 independent reflections	3 standard reflections
6845 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: 2.94%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.057$	$(\Delta/\sigma)_{\text{max}} = -0.006$
$S = 0.972$	$\Delta\rho_{\text{max}} = 0.31 \text{ e Å}^{-3}$
10 320 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e Å}^{-3}$
644 parameters	Extinction correction: <i>SHELXL93</i>
H-atom parameters constrained	Extinction coefficient:
	$2.7(3) \times 10^{-4}$

All H atoms were generated geometrically (C–H = 0.96 Å) and not refined.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s)

Table 1

Selected geometric parameters (Å, °).

Sm–O4	2.112 (2)	Sm–O1	2.306 (2)
Sm–O2	2.163 (2)	P–O1	1.509 (2)
Sm–O3	2.190 (2)		
O4–Sm–O2	99.42 (8)	O3–Sm–O1	94.86 (8)
O4–Sm–O3	107.30 (8)	P–O1–Sm	170.06 (14)
O2–Sm–O3	138.29 (8)	C19–O2–Sm	174.3 (2)
O4–Sm–O1	127.73 (8)	C34–O3–Sm	172.9 (2)
O2–Sm–O1	93.36 (8)	C49–O4–Sm	175.3 (2)

used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL*; 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: SK1411). Services for accessing these data are described at the back of the journal.

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