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*Crystallographic report*

# Crystal structure of bis(2,4,6-tri-*tert*-butylphenolato-*O*) bis(tetrahydrofuran-*O*) samarium (*N*,*N*-$\eta^2$-azobenzene) diethyl ether solvate

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**Reaction of divalent $Sm(OAr)_2(THF)_3$ (Ar = $C_6H_2$-*tert*-$Bu_3$-2,4,6; THF = tetrahydrofuran) with one equivalent of azobenzene in THF and crystallization of the product in diethyl ether afforded the title complex $(ArO)_2(THF)_2Sm(\eta^2\text{-}N_2Ph_2)\cdot Et_2O$ in good yield. In the complex, the N–N bond length for the azobenzene species is lengthened. The two Sm–N bonds are equivalent, and their bond lengths are intermediate between the donor bond and the single bond. Copyright © 2005 John Wiley & Sons, Ltd.**

**KEYWORDS:** samarium; aryloxide; azobenzene; X-ray

## COMMENT

Research on the reactivity of divalent lanthanide complexes has been one of the most active scopes in organolanthanide chemistry.[1–4] However, most attention has been focused upon the divalent lanthanides with substituted cyclopentadienyl ligands. The reactivity of divalent lanthanide aryloxides remains far less explored. To our knowledge, only a few examples of reactions of divalent lanthanide aryloxides with unsaturated substrates have been reported. Hou *et al.*[5] reported that reaction of $Sm(OAr')_2(THF)_3$ ($Ar' = C_6H_2$-*tert*-$Bu_2$-2,6-Me-4; THF = tetrahydrofuran) with fluorenone afforded the samarium(III) ketyl complex and led to the coupling of the radical units to give the pinacolate complex. We found that this divalent aryloxide complex can promote the reductive coupling of phenyl isocyanate to form a bimetallic complex.[6] In order to understand more about the structure and reactivity of divalent lanthanide aryloxide, we studied the reaction of $Sm(OAr)_2(THF)_3$ ($Ar = C_6H_2$-*tert*-$Bu_3$-2,4,6) with azobenzene. As a result, green crystals of $(ArO)_2(THF)_2Sm(\eta^2\text{-}N_2Ph_2)\cdot Et_2O$ ($Et_2O$ = diethyl ether) were obtained in 76.8% yield.

$$Sm(OAr)_2(THF)_3 + PhN{=}NPh \xrightarrow{THF} (ArO)_2(THF)_2Sm(\eta^2\text{-}N_2Ph_2)$$

From Fig. 1, we can see there is an azobenzene ligand in the molecule in the $\eta^2$-coordinating fashion. The phenyl rings are no longer trans and coplanar. They now have a cis orientation. The geometry of the $Ph_2N_2$ species is similar to that in $(C_5Me_5)_2(THF)Sm(\eta^2\text{-}N_2Ph_2)$[7] and $[HB(3,5\text{-}Me_2Pz)_3]_2Sm(\eta^2\text{-}N_2Ph_2)$.[8] The N–N bond length of 1.358(11) Å is obviously longer than the N=N double bond length (1.25 Å) in azobenzene, but shorter than the N–N single bond length (1.45 Å) in hydrazines. The two Sm–N bonds are equivalent. They have the same bond length (2.371(6) Å). This length is shorter than the typical Sm–N donor bond length (2.41–2.65 Å),[6] but longer than the typical Sm–N $\sigma$ bond length (2.284 Å).[9] These structural parameters demonstrate that considerable electron delocalization is present in the $Ph_2N_2$ ligand. The Sm–O(Ar) bond length (2.178(4) Å) is somewhat shorter than the analogous bond lengths (2.183(10) and 2.207(9) Å) in $[Sm(OAr')_2(DME)]_2[\mu\text{-}\eta^2\text{-}(PhN)OCCO(NPh)]$,[6] and the O(1)–Sm(1)–O(1A) angle of 137.3(2)° is comparable to

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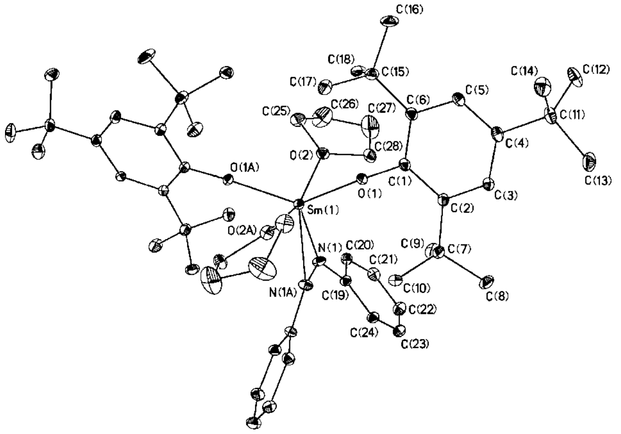

**Figure 1.** X-ray structure of the title complex. Key geometric parameters: Sm(1)–O(1) 2.178(4), Sm(1)–O(2) 2.465(5), Sm(1)–O(1A) 2.178(4), Sm(1)–O(2A) 2.465(5), Sm(1)–N(1) 2.371(6), Sm(1)–N(1A) 2.371(6), C(1)–O(1) 1.359(7), N(1)–N(1A) 1.358(11), C(19)–N(1) 1.407(9) Å; O(1)–Sm(1)–O(1A) 137.3(2), O(1)–Sm(1)–O(2) 87.05(17), O(1)–Sm(1)–O(2A) 86.02(17), O(1)–Sm(1)–N(1) 111.22(19), O(1)–Sm(1)–N(1A) 109.62(19), O(1A)–Sm(1)–O(2) 86.02(17), O(1A)–Sm(1)–N(1) 109.62(19), O(1A)–Sm(1)–N(1A) 111.22(19), O(2)–Sm(1)–O(2A) 160.9(2), N(1)–Sm(1)–N(1A) 33.3(3), N(1A)–N(1)–Sm(1) 73.36(13), N(1A)–N(1)–C(19) 122.2(4), C(19)–N(1)–Sm(1) 154.8(5), C(1)–O(1)–Sm(1) 176.5(4)°.

the 140.4(2)° in $[\mathrm{Sm(OAr')_2(DME)}]_2[\mu\text{-}\eta^2\text{-(PhN)OCCO(NPh)}]$. There is a diethyl ether molecule in the unit cell.

## EXPERIMENTAL

### Synthesis of the title complex

To a blue THF solution (about 40 ml) of $\mathrm{SmI_2}$ (3.45 mmol) was added a THF solution (about 14 ml) of ArONa (6.90 mmol) at room temperature. The color of the solution turned brown immediately. This was stirred at room temperature for 0.5 h, and then added to a THF solution (about 5 ml) of azobenzene (0.63 g, 3.45 mmol). The color of the solution turned green quickly. After stirring at room temperature for a day, the solution was evaporated under vacuum. The residue was extracted with diethyl ether and centrifuged to separate the NaI. The clear solution was kept at −20 °C. Green crystals were produced (2.85 g, 2.65 mmol, 76.8%); m.p. 110 °C (dec.). Anal. Found: C, 66.85; H, 8.94; N, 2.45; Sm, 13.50. Calc. for $\mathrm{C_{60}H_{94}N_2O_5Sm}$: C, 67.11; H, 8.82; N, 2.61; Sm, 14.00%. IR absorption ($\mathrm{cm^{-1}}$): 3448(s), 2928(m), 2337(m), 1649(m), 1120(w), 667(w).

### Crystallography

Intensity data for the title complex were collected at 193(2) K on a Rigaku Mercury CCD area detector. Crystallographic data: $\mathrm{C_{60}H_{94}N_2O_5Sm}$, $M = 1073.72$, monoclinic, $C2/c$, $a = 16.211(12)$, $b = 13.777(10)$, $c = 27.11(2)$ Å, $\beta = 102.395(8)°$, $V = 5914(7)$ Å$^3$, $Z = 4$, $D_c = 1.206\ \mathrm{g\,cm^{-3}}$; 23 693 data collected, 5401 unique data ($3.06 \leqslant \theta \leqslant 25.35°$), $R_{\mathrm{obs}} = 0.0860$, $wR = 0.1809$ (all data), $\rho_{\max} = 1.914\ \mathrm{e^-}$ Å$^{-3}$, $\rho_{\min} = -1.888\ \mathrm{e^-}$ Å$^{-3}$. Programs used: SHELXS-97, SHELXL-97. CCDC number: 236324.

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