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Samarium(II) Surrounded by Only Oxygen Donor Ligands: $[KSm(\mu\text{-}OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_3(THF)]_n$

William J. Evans,* Reiner Anwander, Mohammad A. Ansari, and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, California 92717

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Sm(II) chemistry is being extensively studied due to the strong reduction potential of this $4f^6$ ion.[1] Definitive structural information on the nature of Sm(II) starting materials has been restricted primarily to cyclopentadienyl complexes,[2] although some X-ray crystallographic data have been reported for halide,[3] amide,[4] heterocyclopentadienyl,[5] and polypyrazolylborate[6] complexes. Curiously, no structural evidence has been reported for Sm(II) surrounded by only oxygen-containing ligands, although oxygen donor coordination environments are quite common and stable for the f elements. Both colorless and purple Sm(II) alkoxide complexes have been described in the literature,[7] but X-ray crystallographic information for divalent f element complexes of oxygen donor ligands has been limited to the less strongly reducing Yb(II) systems.[8] In this report, we describe the synthesis of and first X-ray crystallographic data for Sm(II) aryloxide complexes as well as an example of the stabilizing effect of forming anionic "ate" complexes of highly reactive Sm(II) compounds.

Sublimed 2,6-di-*tert*-butyl-4-methylphenol reacts immediately with a purple hexane solution of $Sm[N(SiMe_3)_2]_2(THF)_2$, **1**,[4] to form a dark brown precipitate and $HN(SiMe_3)_2$ (eq 1). After 24 h, the solvent and amine were removed by rotary evaporation and the solid was washed with hexane. Crystallization of this material from toluene gave **3** in 70% yield.[9] Similiarly, a dark brown hexane solution of $\{KSm[N(SiMe_3)_2]_3\}_n$, **2**,[10] prepared from SmI_2 and 3 equiv of $KN(SiMe_3)_2$, yielded **4** in 90% yield (eq 2). Both **2** and **4** were characterized by elemental analysis and by ^1H NMR and IR spectroscopy.[9]

$$\underset{\mathbf{1}}{Sm[N(SiMe_3)_2]_2(THF)_2} + 2HOAr \xrightarrow{\text{hexane}} \underset{\mathbf{3}}{Sm(OAr)_2(THF)_3} + 2HN(SiMe_3)_2 \quad (1)$$

$$\underset{\mathbf{2}}{\{KSm[N(SiMe_3)_2]_3\}_n} + 3nHOAr \xrightarrow{\text{hexane}} \underset{\mathbf{4}}{[KSm(OAr)_3]_n} + 3nHN(SiMe_3)_2 \quad (2)$$

Crystals of **3** proved to be extremely sensitive to moisture and decomposed during data collection on the diffractometer.[11] However, the data obtained revealed a monomeric structure for **3**, similiar to that of $Yb(OAr)_2(THF)_3$[8a] despite the larger size of samarium.[12] The "ate" complex **4** proved to be more stable than **3**, but crystallization of **4** from toluene resulted in thin plates unsuitable for X-ray analysis. After addition of THF to **4**, black single crystals of the solvated "ate" complex $[KSm(\mu\text{-}OAr)_3(THF)]_n$, **5**, were obtained from benzene which provided the necessary crystallographic data[13] to fully define Sm(II) in an oxygen ligand environment (Figures 1 and 2).

Figure 1 shows that Sm(II) is surrounded by four oxygen atoms in a distorted tetrahedral coordination environment containing THF and three aryloxide ligands. The six O−Sm−O angles range from 87.0(2) to 133.3(2)°. The 2.635(7) Å Sm−O(THF) bond distance in **3** is comparable to other Sm(II)−O(THF) distances in complexes such as $Sm[N(SiMe_3)_2]_2(THF)_2$ (2.586(9), 2.607(9) Å)[4] and $(C_5Me_5)_2Sm(THF)_2$ (2.62(1)−2.66(1) Å).[2]

The Sm−O(OAr) distances [O(1), 2.336(7); O(2), 2.362(6); O(3), 2.319(9) Å] are surprisingly similar considering that one ligand is terminal and two appear to be bridging (see below). Extensive studies of alkoxide and aryloxide complexes show that bridging distances are typically longer than terminal distances.[14] The 2.339(9) Å average Sm−O(Ar) bond length is consistent with the 2.14(1)−2.22(1) Å range of terminal aryloxide distances in the Yb(II) complexes[8] $Yb(OAr)_2(L)_2$ (L

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(9) (a) Anal. Calcd for **3** ($C_{42}H_{70}O_5Sm$): Sm, 18.67. Found: Sm, 18.7. ^1H NMR (concentration dependent): (C_6D_6) δ 9.2 (br, $\Delta\nu_{1/2}$ = 170 Hz, THF), 4.1 (br, $\Delta\nu_{1/2}$ = 80 Hz, THF), 0.1 ($\Delta\nu_{1/2}$ = 320 Hz), −1.6 ($\Delta\nu_{1/2}$ = 190); (C_4D_8O) δ −0.58 (br, $\Delta\nu_{1/2}$ = 40 Hz, 18H, CMe_3), −1.19 (2H, $C_6\mathit{H}_2Bu^t_2$-2,6-Me-4), −1.87 (3H, Me). IR (Nujol, cm^{-1}): 1416 s, 1279 s, 1257 s, 1234 s, 1218 m, 1200 m, 1120 w, 1092 w, 1035 m, 991 w, 958 w, 921 w, 911 w, 889 m, 877 m, 861 m, 826 s, 802 m, 790 w, 779 w, 670 w, 605 w, 527 m, 499 m, 355 w, 300 w. (b) Anal. Calcd for **4** ($C_{45}H_{69}KO_3Sm$): Sm, 17.74. Found: Sm, 17.6. ^1H NMR (concentration dependent) (C_6D_6): δ 6.1 (br, $\Delta\nu_{1/2}$ = 150 Hz, CMe_3), 2.8 (br, $\Delta\nu_{1/2}$ = 80 Hz), −0.78 ($\Delta\nu_{1/2}$ = 40 Hz). **4** dissociates to **3** and KOAr in THF. IR (Nujol, cm^{-1}): 1416 s, 1290 m, 1268 s, 1255 s, 1216 m, 1200 m, 1119 w, 1091 w, 1030 m, 921 w, 888 m, 875 m, 862 m, 816 m, 799 s, 496 m, 357 w, 307 w, 301 w.

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(11) Crystal data for **3** ($C_{42}H_{70}O_5Sm{\cdot}C_7H_8$): monoclinic space group $P2_1/c$, $a = 15.480(2)$ Å, $b = 16.146(3)$ Å, $c = 19.816(4)$ Å, $\beta = 97.45(1)°$, $V = 4911(1)$ Å^3, $D_{calcd} = 1.214$ g cm^{-3} for $Z = 4$.

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(13) Crystal data for **5** ($C_{49}H_{77}KO_4Sm{\cdot}2C_6D_6$): monoclinic space group $C2/c$, $a = 32.11(2)$ Å, $b = 18.219(6)$ Å, $c = 25.10(2)$ Å, $\beta = 128.42(4)°$, $V = 11503(12)$ Å^3, $D_{calcd} = 1.242$ g cm^{-3} for $Z = 8$. Least-squares refinement of the model based on 5919 reflections [$|F_o| > 4\sigma(|F_o|)$] converged to a final $R_F = 6.9\%$. See supplementary material for details.

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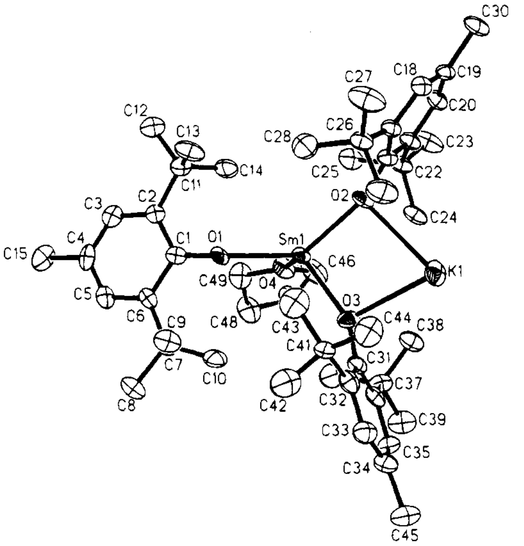

Figure 1. Themal ellipsoid plot of [KSm(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_3$(THF)]$_n$, **3**. *tert*-Butyl and methyl substituents on the aryl rings have been deleted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å) and angles (deg) for **2** are as follows: Sm−O(1) 2.336(7), Sm−O(2) 2.362(6), Sm−O(3) 2.319(9), Sm−O(4) 2.635(7), K−O(2) 2.967(9), K−O(3) 2.778(6), K−C(1A) 3.235(10), K−C(2A) 3.343(12), K−C(3A) 3.512(12), K−C(4A) 3.585(12), K−C(5A) 3.421(8), K−C(6A) 3.239(9), K−C(9A) 3.425(13), K−C(16) 3.534(13), K−C(29) 3.418(11), K−C(31) 3.310(10); O(1)−Sm−O(2) 133.3(2), O(1)−Sm−O(3) 120.5(3), O(1)−Sm−O(4) 87.0(2), O(2)−Sm−O(3) 91.4(3), O(2)−Sm−O(4) 116.8(3), O(3)−Sm−O(4) 107.6(2), Sm−O(1)−C(1) 152.2(7), Sm−O(2)−C(16) 160.8(7), Sm−O(3)−C(31) 155.5(6).

= THF, Et$_2$O, hexamethylphosphoramide), Yb(OAr)$_2$(THF)$_3$, and [Yb(OC$_6$H$_2$^{t}Bu$_3$-2,4,6)$_2$(THF)$_3$](THF) considering the larger size of samarium.[12] As expected, the Sm(II)−O(Ar) distance in **3** is longer than that in the Sm(III) aryloxide (C$_5$Me$_5$)$_2$Sm(OC$_6$HMe$_4$-2,3,5,6) (2.13(1) Å).[15] The Sm−O−C angles for the terminal and bridging OAr groups (O(1),152.2(7); O(2), 160.8(7); O(3), 155.5(6)°) are also unexpectedly similar and contrast sharply with the 78.5(9)−87.9(7)° Sm−S−C angles in the trivalent thiolate complex Sm(SC$_6$H$_2$^{t}Bu$_3$-2,4,6)$_3$.[16]

As shown in Figure 2, **3** exists as polymeric chains in the solid state which arise because the potassium is surrounded not only by the aryloxides containing O(2) and O(3) but also by an aryl ring from the O(1a) aryloxide located in another monomeric unit. The K−O(aryloxide) distances are not equivalent. The 2.778(6) Å K−O(3) distance is comparable to the bridging K−O distances in K[Nd(OC$_6$H$_3$^{i}Pr-2,6)$_4$] (2.760(9) Å)[17] and K$_8$(OSiPh$_3$)$_8$(DME)$_3$ (2.592(3)−2.757(3) Å).[18] The 2.967(9) Å K−O(2) distance is considerably longer and falls in the range of the K−O(DME) distances in (K$_8$(OSiPh$_3$)$_8$(DME)$_3$ (2.680(3)−2.958(3) Å).[18] The 3.89 Å K−O(1) and 5.79 Å K−O(THF) distances are beyond the range of significant interaction.

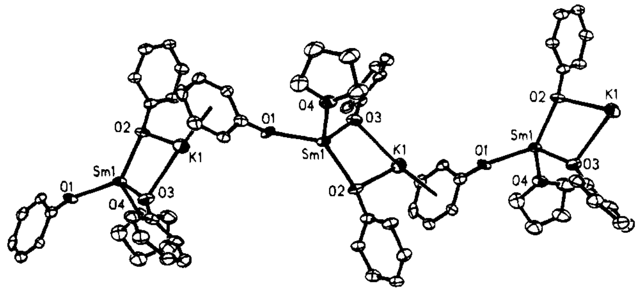

Figure 2. Extended structure of [KSm(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_3$(THF)]$_n$ with aryl substituents omitted for clarity.

The potassium is also unsymmetrically located with respect to the arene. The shortest potassium arene contacts (3.235(10) K−C(1A) and K−C(6A) 3.239(9) Å) are in the range observed in other complexes containing arenes oriented near potassium[19] and are comparable to the shortest K−C(arene) distances in K[Nd(OC$_6$H$_3$^{i}Pr-2,6)$_4$] (3.097(10)−3.473(11) Å)[17] and KBPh$_4$ (3.191(5) Å).[20] The other K−C(arene) distances range from 3.343(12) to 3.585(12) Å. Additional short K−C distances are present in **3** involving a 3.310(10) Å length to C(31), an ipso carbon of another aryloxide attached to O(3), and the 3.425(13) Å K−C(9A) distance to the quaternary carbon of the *tert*-butyl group attached to the O(1) aryloxide. Hence, an unsymmetrical coordination environment composed of a variety of oxygen and carbon donor atoms has assembled around potassium.

The formation of f element complexes which contain additional alkali metal ligand units is very common. Most examples are found in trivalent systems,[21] although some Eu(II) and Yb(II)[22] compounds are known. **3** is only the third structurally characterized [SmZ$_3$]$^-$ "ate" complex after [NaSm(C$_5$H$_4$^{t}Bu)$_3$(THF)]$_n$[23] and **1**.[10] Recently, heteroatom stabilization was used to generate new types of coordination environments for trivalent yttrium and lanthanides.[24] Comparison of **2**−**4** shows that heteroatom stabilization is also useful in Sm(II) chemistry, which in this case allowed a Sm(II) center to be crystallographically characterized in an oxygen donor atom environment for the first time. The reactivity of Sm(II) in this oxygen coordination environment as well as the effect of the "ate" complex on the chemistry is under investigation.

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Supplementary Material Available: A discussion of the X-ray experimental work and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (17 pages). Ordering information is given on any current masthead page.

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