J. Am. Chem. Soc. **1995,** *117,* 8999–9002

Coordination Chemistry of Samarium Diiodide with Ethers Including the Crystal Structure of Tetrahydrofuran-Solvated Samarium Diiodide, SmI$_2$(THF)$_5$[1]

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Received May 18, 1995[⊗]

Abstract: The tetrahydrofuran adduct of samarium diiodide, a reagent used extensively in organic synthesis as a unique one-electron reductant, crystallizes from THF as the seven-coordinate solvate SmI$_2$(THF)$_5$, **1**. Crystallization of this reagent in the presence of 1,2-dimethoxyethane (DME) generates related seven-coordinate mixed ether solvate derivatives SmI$_2$(DME)$_2$(THF), **2**, and SmI$_2$(DME)(THF)$_3$, **3**. These solid state studies show that in the presence of excess oxygen donors like ethers, the SmI$_2$ moiety prefers a seven-coordinate pentagonal bipyramidal geometry with iodide ligands in the axial positions. **1** crystallizes from THF at −35 °C in space group $P2_1/n$ with unit cell parameters at 163 K of $a = 23.154(12)$ Å, $b = 26.033(6)$ Å, $c = 23.866(10)$ Å, $\beta = 111.69(4)°$, $V = 13367(11)$ Å^3, and $Z = 16$. **2** crystallizes from THF/DME at −35 °C in space group $C2/c$ with unit cell parameters at 168 K of $a = 13.0111(14)$ Å, $b = 11.3727(10)$ Å, $c = 15.383(2)$ Å, $\beta = 114.989(8)°$, $V = 2063.2(4)$ Å^3, and $Z = 4$ for $D_{\text{calcd}} = 2.113$ g/cm^3. Least-squares refinement of the model based on 1826 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 4.0\%$. **3** crystallizes from THF/DME at −35 °C in space group $P2_1/c$ with unit cell parameters at 158 K of $a = 17.177(2)$ Å, $b = 8.8869(8)$ Å, $c = 16.137(4)$ Å, $\beta = 99.556(11)°$, $V = 2429.0(7)$ Å^3, and $Z = 4$ for $D_{\text{calcd}} = 1.943$ g/cm^3. Least-squares refinement of the model based on 5971 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 4.4\%$. The Sm−I distances are 3.231(1) to 3.246(1) Å in these structures and the Sm−O(ether) distances vary from 2.530(5) to 2.646(4) Å.

Introduction

In 1977 Kagan and co-workers published the first in a series of papers which showed that samarium diiodide can be a very useful one-electron reductant in organic synthesis.[2] Since these seminal studies, the utility of this compound has been examined in scores of laboratories and its successful use in many diverse applications has established it as a standard one-electron reducing reagent in synthetic organic laboratories.[2,3]

Despite the extensive use of the THF adduct of samarium diiodide, little is known about how THF and oxygen-containing substrates coordinate to the metal in the course of the reductive reactions. Although variable degrees of solvation have been reported depending upon the method of isolation,[4] complexometric analysis of the dry powder is consistent with the formula SmI$_2$(THF)$_2$. However, it is unlikely that this large metal ion has a four-coordinate geometry in solution in the presence of available oxygen donors. Since the samarium diiodide reagent is often generated *in situ* in THF, its effective coordination number when it interacts with a substrate is likely to be larger than four, but structural evidence on THF adducts has been lacking. Structural studies of samarium diiodide in the presence of donor solvents other than simple ethers do suggest that this unit prefers a coordination number greater than four. Hence, in the presence of the chelating diethylene glycol dimethyl ether (diglyme), samarium diiodide crystallizes as the eight-coordinate *cis*- and *trans*-SmI$_2$[O(CH$_2$CH$_2$OMe)$_2$]$_2$.[5,6] With nitrogen donor ligands, the six-coordinate structures [Sm(μ-I)$_2$(NCCMe$_3$)$_2$]$_n$[6] and [SmI(μ-I)(*N*-MeIm)$_3$]$_2$[7] (*N*-MeIm = *N*-methylimidazole) have been observed. Recently, the six-coordinate hexamethylphosphoramide complex, SmI$_2$(HMPA)$_4$, has been structurally characterized.[8] However, extrapolation of these data to THF-containing systems is uncertain.

We report here three structural studies on THF adducts of samarium diiodide: SmI$_2$(THF)$_5$, **1**, SmI$_2$(DME)$_2$(THF), **2**, and SmI$_2$(DME)(THF)$_3$, **3**. Compounds **2** and **3** were characterized by conventional crystallographic means, but the extreme thermal instability of single crystals of **1** required special low-temperature handling and the use of a rotating anode X-ray source to obtain data. The details of the structures and the prevalence of seven coordination for samarium diiodide in the presence of THF are described.

Experimental Section

The manipulations described below were conducted under nitrogen using standard glovebox, Schlenk, and high-vacuum techniques. ^{1}H and ^{13}C NMR spectra were obtained on either GN 500-MHz, Ω 500-MHz or QE 300-MHz NMR spectrometers. Chemical shifts were assigned relative to residual protons in THF-d_8. Infrared spectra were

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1995.

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0002-7863/95/1517-8999$09.00/0

recorded on a Perkin-Elmer 283 Fourier transform infrared spectrometer. Complexometric metal analyses were conducted as previously described.[9] Tetrahydrofuran (THF) was freshly distilled under nitrogen from a solution of sodium benzophenone ketyl. 1,2-Dimethoxyethane (DME) was dried using sodium benzophenone ketyl, degassed, and vacuum transferred prior to use. $SmI_2(THF)_2$ was prepared as previously described.[2b]

$SmI_2(THF)_5$, 1. A concentrated solution of $SmI_2(THF)_2$ in THF was cooled to −35 °C. After approximately 24 h, dark blue crystals had formed. Upon warming to glovebox temperature, however, the crystals redissolved. Rapid removal of the mother liquor from the cold crystals by pipet and addition of Paratone D also caused the crystals to dissolve before they could be transferred to a diffractometer. Hence, the hydrocarbon oil mounting technique[10] could not be used. To avoid these problems, the mother liquor was removed from a vial of freshly grown crystals by pipet and the capped vial was quickly removed from the glovebox and placed into a cold Dewar which had previously been filled with liquid nitrogen. The crystals were then transferred to a Buchner funnel whose mouth was fitted with a Kimwipe held in place by a rubber band. The stem of the funnel was inserted into a two-hole stopper which was placed on a Dewar filled with liquid nitrogen. Nitrogen gas was bubbled into the other hole of the stopper to generate a stream of cold nitrogen through the funnel and Kimwipe. Under this cold nitrogen stream, a crystal was secured with oil to a glass fiber attached to an elongated brass mounting pin. The entire apparatus was carefully moved to the diffractometer where the mounted crystal was transferred to the nitrogen stream of the low-temperature system of the diffractometer. Several crystals were mounted in this manner and examined. The intensity profiles of all of the crystals examined were broad, which indicated that the crystal quality was poor. Since these crystals were the best obtained to date, data collection was initiated.

$SmI_2(DME)_2(THF)$, 2. In the course of using samarium diiodide as a starting material, dark purple X-ray quality crystals of $SmI_2(DME)_2(THF)$ were isolated from a recrystallization containing SmI_2 using a 1:10 mixture of DME:THF at −35 °C. Attempts to make **2** deliberately produced **3** as described below.

$SmI_2(DME)(THF)_3$, 3. $SmI_2(THF)_2$ (753 mg, 1.4 mmol) was dissolved in a 1:10 mixture of DME:THF and cooled to −35 °C. After 3 days, red/purple X-ray quality crystals formed. Several crystals were removed and placed in Paratone D oil for the X-ray diffraction study. The remaining crystals were dried *in vacuo* (668 mg, 1.2 mmol, 86% yield). ^1H NMR (THF-d_8) δ 3.18 (s, 6H, $CH_3OCH_2CH_2OCH_3$), 3.36 (s, 4H, $CH_3OCH_2CH_2OCH_3$). ^{13}C NMR (THF-d_8) δ 61.2 ($CH_3OCH_2CH_2OCH_3$), 74.6 ($CH_3OCH_2CH_2OCH_3$). IR (KBr) 2955 m, 2874 m, 2346 w, 1452 w, 1259 w, 1091 m, 1027 s, 915 w, 867 s, 674 w cm^{-1}. Anal. Calcd for $SmI_2(DME)(THF)$: 26.5. Found: 26.6.

X-ray Data Collection, Structure Determination, and Refinement for 1−3. In each structural study, after the crystal was mounted on the diffractometer, subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature intensity data were carried out using standard procedures[11] similar to those of Churchill.[12] Details appear in Table 1. The crystallographic calculations were carried out using either a locally modified version of the UCLA Crystallographic Computing Package[13] or the SHELXTL PLUS program set.[14] The analytical scattering factors for neutral atoms were used throughout the analysis;[15] both the real ($\Delta f'$) and the imaginary ($i\Delta f''$) components of anomalous dispersion were included.

Table 1. Crystallographic Data for $SmI_2(DME)_2(THF)$, **2**, and $SmI_2(DME)(THF)_3$, **3**

	2	**3**
formula	$C_{12}H_{28}O_5I_2Sm$	$C_{16}H_{34}O_5I_2Sm$
mol wt	656.5	710.6
crystal system	monoclinic	monoclinic
space group	$C2/c$ [C_{2h}^6; No. 15]	$P2_1/c$ [C_{2h}^5; No. 14]
cell constants		
a, Å	13.0111(14)	17.177(2)
b, Å	11.3727(10)	8.8869(8)
c, Å	15.383(2)	16.137(4)
β, deg	114.989(8)	99.556(11)
cell vol, Å^3	2063.2(4)	2429.0(7)
Z	4	4
D_{calcd}, g/cm^3	2.113	1.943
diffractometer	Siemens P3	Siemens P4RA
temp, K	168	158
μ_{calcd}, mm^{-1}	5.851	4.978
R_F, %	4.0	4.4
R_{wF}, %	5.0	5.4
GOF	1.60	1.59
λ(Mo Kα), Å	0.710730	0.710730

$SmI_2(THF)_5$. Crystals were mounted as described above. Intensity data (17957 total) were collected on a Siemens P4 rotating-anode diffractometer system using monochromatized Mo Kα radiation via a $\theta - 2\theta$ scan technique.[9] Those 7014 reflections with $|F_o| > 6.0\sigma(|F_o|)$ were considered observed. The structure was solved by direct methods.[13−15] There are five molecules in the asymmetric unit, three of which occupy general positions while two are located about inversion centers. This is consistent with the observed value of $Z = 16$. The SmI_2 moiety of two of the molecules in general positions is ordered while this unit is disordered in the remaining three molecules. Although the overall geometry of the complex has been established, location and refinement of all of the light atoms (C, O) was not possible. Some THF of solvation was also present, but due to the poor quality of the data, the exact number could not be determined. The best refinement of the model yielded $R_F = 15\%$. The space group is $P2_1/n$ with cell parameters of $a = 23.154(12)$ Å, $b = 26.033(6)$ Å, $c = 23.866(10)$ Å, $\beta = 111.69(4)°$, $V = 13367(11)$ Å^3, and $Z = 16$.

$SmI_2(DME)_2(THF)$. A dark-purple crystal of approximate dimensions 0.23 × 0.23 × 0.26 mm was oil-mounted[10] on a glass fiber and transferred to the Siemens P3 diffractometer. All 2610 data were corrected for absorption[16] and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. The two possible monoclinic space groups are the noncentrosymmetric Cc or the centrosymmetric $C2/c$. It was later determined that space group $C2/c$ was correct.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(C-H) = 0.96$ Å and $U(iso) = 0.06$ Å^2. The molecule is located about a 2-fold rotation axis. Atoms Sm(1) and O(3) lie directly on the 2-fold axis and were each assigned site-occupancy factors of $^1/_2$. Refinement of positional and thermal parameters led to convergence with $R_F = 4.0\%$; $R_{wF} = 5.0\%$ and GOF = 1.60 for 93 variables refined against those 1826 data with $F > 3.0\sigma(F)$. A final difference-Fourier synthesis yielded $\varrho(max) = 1.24$ eÅ^{-3}.

$SmI_2(DME)(THF)_3$. A red/purple crystal of approximate dimensions 0.12 × 0.20 × 0.20 mm was oil-mounted[10] on a glass fiber and transferred to the Siemens P4 rotating-anode diffractometer. All 7756 data were corrected for decay (20%), absorption,[16] and Lorentz and polarization effects and then placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ is therefore uniquely defined.

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(10) The crystal is immersed in a lube-oil additive which allows for manipulation on the bench-top and prevents decomposition due to air or moisture. The crystal is secured to a glass fiber (the oil acts as the adhesive) which is attached to an elongated brass mounting pin. Further details appear in the following: Hope, H. *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*, ACS Symp. Ser. No. 357; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987.

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The structure was solved via an automated Patterson routine (SHELXTL) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(C-H) = 0.96$ Å and $U(iso) = 0.08$ Å^2. Refinement of positional and thermal parameters led to convergence with $R_F = 4.4\%$; $R_{wF} = 5.4\%$ and GOF = 1.59 for 281 variables refined against those 5971 data with $F > 3.0\sigma(F)$. A final difference-Fourier synthesis yielded $\varrho(\max) = 2.14$ eÅ^{-3} at a distance of 0.83 Å from I(2).

Results and Discussion

Samarium diiodide is commonly obtained from samarium metal and ICH_2CH_2I or I_2CH_2 in THF. It is often used *in situ*, but it can be conveniently obtained as a dry powder by removal of THF under vacuum. This generates a solid which has a complexometric analysis consistent with the formula $SmI_2(THF)_2$.

This $SmI_2(THF)_2$ is likely to be oligomeric in the solid state, since it is improbable that this compound exists as a simple four-coordinate structure. Sm^{2+} is a large ion[17] which can support coordination numbers as large as ten,[18] and X-ray crystallographic studies have shown that eight-coordinate structures are quite common for Sm^{2+}.[18] Low-coordinate Sm^{2+} complexes have been found only with very large ligands, e.g. in $[(Me_3Si)_2N]_2Sm(THF)_2$,[19] $(4\text{-}Me\text{-}2,6\text{-}Bu^t_2C_6H_2O)_2Sm(THF)_3$,[20] and $(4\text{-}Me\text{-}2,6\text{-}Bu^t_2C_6H_2O)_3SmK$,[21] and even in these cases, agostic interactions can occur to give higher effective coordination numbers.[19]

Solvated samarium diiodide has been crystallographically characterized in the presence of diglyme, *tert*-butyl nitrile, *N*-methylimidazole, and hexamethylphosphoramide (HMPA). The tridentate chelating ether generates eight-coordinate structures of *cis*- and *trans*-$SmI_2[O(CH_2CH_2OMe)_2]_2$,[5,6] **4** and **5**, respectively, whereas the nitrogen donor atom ligands form six-coordinate complexes, $[Sm(\mu\text{-}I)_2(NCCMe_3)_2]_n$,[6] **6**, and $[SmI(\mu\text{-}I)(N\text{-}MeIm)_3]_2$,[7] **7**. The latter structures show how the iodide ligands can bridge to increase the coordination number of the Sm^{2+} ion as is likely in $SmI_2(THF)_2$. With the strong donor ligand HMPA, a six-coordinate complex, $SmI_2(HMPA)_4$, could be structurally characterized.[8]

Attempts to obtain structural data from single crystals isolated from THF solutions of samarium diiodide were hampered by the thermal instability of the crystals which dissolved as soon as they began to warm to ambient temperature. However, by growing the crystals at −35 °C, immediately removing the mother liquor at low temperature, and continuously manipulating the crystals under cold nitrogen until a crystal was mounted on the diffractometer, structural data were finally obtained. The crystallographic data reveal that five THF molecules solvate the SmI_2 moiety to form the seven-coordinate complex, $SmI_2(THF)_5$, **1**, (Figure 1). THF was also present in the lattice. The fact that a seven-coordinate complex forms in the presence of excess THF suggests that this coordination number is preferred for the SmI_2 moiety in the presence of THF and similar ligands. Unfortunately, due to the limited quality of the crystallographic data, only the connectivity of the atoms in **1** could be established.

More stable samarium diiodide derivatives were obtained from THF in the presence of 1,2-dimethoxyethane and better crystallographic data were obtainable on $SmI_2(DME)_2(THF)$, **2**, and $SmI_2(DME)(THF)_3$, **3** (Figures 2 and 3, respectively).[22] In both cases, as in **1**, seven-coordinate pentagonal bipyramidal structures were observed in which the iodide ligands were located in the axial positions.

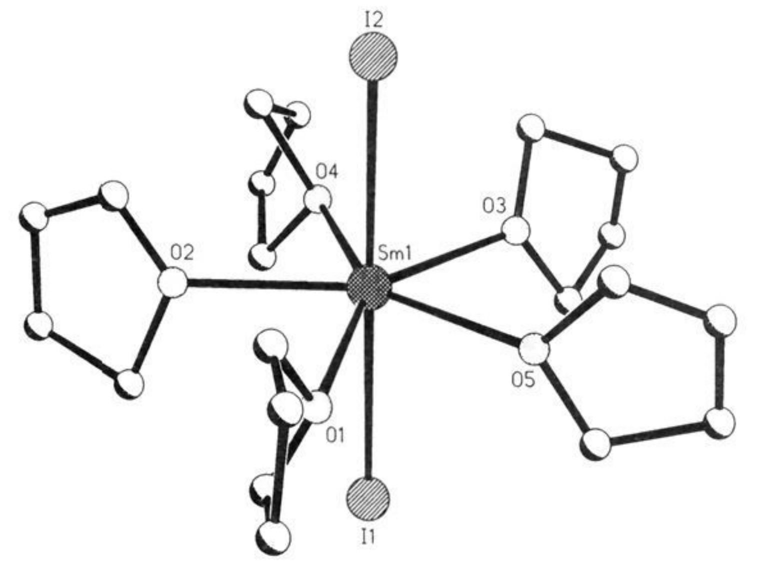

Figure 1. Ball and stick plot of $SmI_2(THF)_5$, **1**.

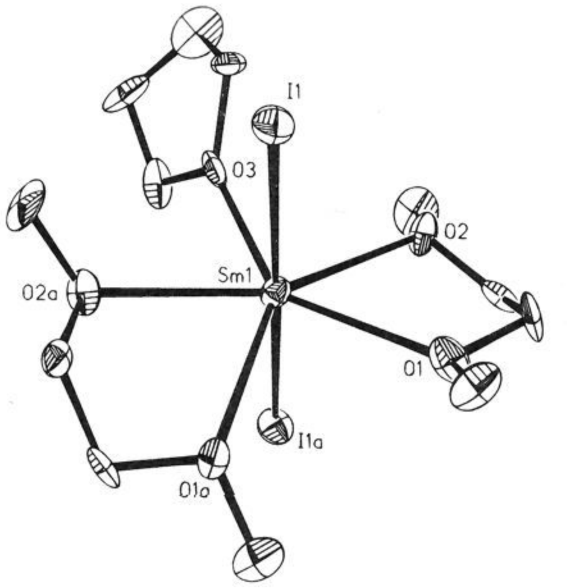

Figure 2. Thermal ellipsoid plot of $SmI_2(DME)_2(THF)$, **2**, drawn at the 50% probability level.

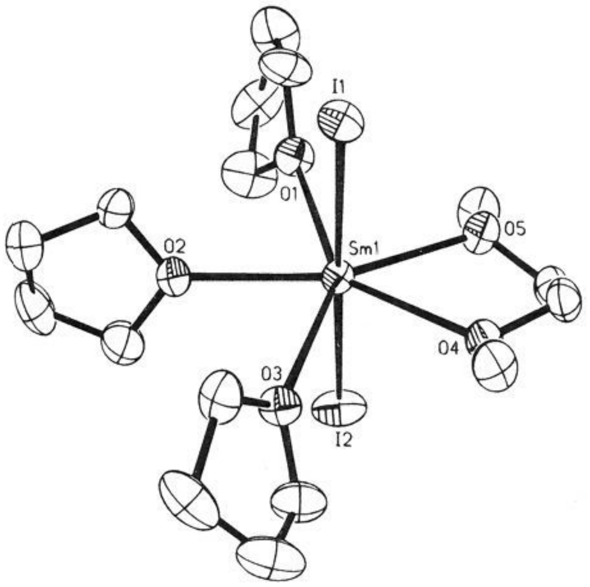

Figure 3. Thermal ellipsoid plot of $SmI_2(DME)(THF)_3$, **3**, drawn at the 50% probability level.

The geometry observed for $SmI_2(THF)_5$, $SmI_2(DME)_2(THF)$, and $SmI_2(DME)(THF)_3$ is common for a variety of lanthanide complexes containing at least two anionic ligands. Examples include $[SmI_2(THF)_5]^+$,[23] $[CeCl_2(THF)_5]^+$,[24] $[TbCl_2(THF)_5]^+$,[25] $[YCl(OCMe_3)(THF)_5]^+$,[26] $YCl_3(DME)_2$,[27] $GdCl_3(DME)_2$,[28] $LnCl_3$-

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[22] Once the crystals of $SmI_2(DME)(THF)_3$, **3**, were dried *in vacuo*, the resulting material analyzed as 26.6% Sm by complexometric titration. This is consistent with the formula $SmI_2(DME)(THF)$.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $SmI_2(DME)_2(THF)$, **2**

	Bond Distances		
Sm−I(1)	3.246(1)	Sm−O(1)	2.595(5)
Sm−O(2)	2.640(5)	Sm−O(3)	2.530(5)
	Bond Angles		
I(1)−Sm−I(1a)	178.8(1)	O(1)−Sm−O(2)	64.7(1)
O(2)−Sm−O(3)	77.3(1)	O(1)−Sm−O(1a)	80.2(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $SmI_2(DME)(THF)_3$, **3**

	Bond Distances		
Sm−I(1)	3.235(1)	Sm−I(2)	3.231(1)
Sm−O(1)	2.581(4)	Sm−O(2)	2.553(4)
Sm−O(3)	2.579(4)	Sm−O(4)	2.636(4)
Sm−O(5)	2.646(4)		
	Bond Angles		
I(1)−Sm−I(2)	178.8(1)	O(1)−Sm−O(2)	73.0(1)
O(2)−Sm−O(3)	72.0(1)	O(3)−Sm−O(4)	75.6(1)
O(4)−Sm−O(5)	63.6(1)	O(5)−Sm−O(1)	77.9(1)

$(THF)_4$, (Ln = Eu,[29] Nd[30]), $SmCl_3(DME)(THF)_2$,[31] and $EuCl_3(pyridine)_4$.[32] Hence, the nearly linear (anion)−lanthanide−(anion) unit surrounded by five other ligands appears to be favored in a variety of systems.

This pentagonal bipyramidal geometry has also recently been reported for the radially similar strontium complex, $SrI_2(THF)_5$.[33] The Shannon radii[17] for Sr(II) and Sm(II) are 1.21 and 1.22 Å, respectively. However, for the smaller metal, ytterbium, which has a 1.08-Å seven-coordinate Shannon radius, the diiodide crystallizes as the six-coordinate complex $YbI_2(THF)_4$.[34] Coordination number preferences can also be affected by strong donor ligands as shown by the structure of six-coordinate $SmI_2(HMPA)_4$.[8]

Both **2** and **3** are quite similar in their structural parameters (Tables 2 and 3) and comparisons with other samarium iodide structures (Table 4) show no unusual bonding features. The narrow 3.231(1)−3.246(1) Å range of Sm−I distances in seven-coordinate **2** and **3** matches the 3.242(1) Å average Sm−(*μ*-I) distance in six-coordinate $[Sm(\mu\text{-}I)_2(NCCMe_3)_2]_n$,[5] **6**, and the 3.237(1) Å terminal Sm−I distances in six-coordinate $[SmI(\mu\text{-}I)(N\text{-}MeIm)_3]_2$,[7] **7**. These Sm−I distances are all smaller than the 3.322(1) and 3.333(1) Å terminal Sm−I distances in the higher-coordinate *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$,[5] **4**, and the 3.390 (2) Å distance in $SmI_2(HMPA)_4$, which has unusually long Sm−I bond lengths.[8]

In both **2** and **3**, the Sm−O(THF) distances are shorter than the Sm−O(DME) distances. This is similar to the situation in $\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$ in which the Sm−O(THF) and the two Sm−O(DME) distances are 2.592(6), 2.679(8), and 2.691(8) Å, respectively.[19] However, in the carbazole derivative $Yb(C_{12}H_6N)_2(DME)(THF)_2$, the two Yb−O(THF) distances are 2.41(2) and 2.48(2) Å while the two Yb-O(DME) distances are 2.44(2) and 2.46(1) Å.[35]

Table 4. Summary of Sm−I Bond Distances (Å) and Angles (deg) for **2**−**7**

	bond distances, Å		bond angles, deg
	Sm-I	Sm-(*μ*-I)	I-Sm-I
$SmI_2(DME)_2(THF)$, **2**[a]	3.246(1)		178.8(1)
$SmI_2(DME)(THF)_3$, **3**[a]	3.235(1)		178.8(1)
	3.231(1)		
cis-SmI_2-$[O(CH_2CH_2OMe)_2]_2$,**4**[b]	3.322(1)		92.0(1)
	3.333(1)		
trans-SmI_2-$[O(CH_2CH_2OMe)_2$, **5**[c]	3.265(1)		180
$[Sm(\mu\text{-}I)_2(NCCMe_3)_2]_n$, **6**[c]		3.260(1)	173.04(2)
		3.225(1)	101.07(10)
			96.68(1)
			87.75(1)
$[SmI(\mu\text{-}I)(N\text{-}MeIm)_3]_2$, **7**[d]	3.237(1)	3.280(1)	175.7(1)
		3.307(1)	100.2(1)
			84.0(1)

[a] This work. [b] Reference 4. [c] Reference 5. [d] Reference 6.

The 178.8(1)° I−Sm−I angles in both **2** and **3** are consistent with a rather regular pentagonal bipyramid, but the O−Sm−O angles vary considerably from the idealized 72° due the fact that the five equatorial ligands are not all the same. The O-Sm-O angles in a single DME molecule are smaller than 72° and the O−Sm−O angles between DME molecules or between a DME and a THF molecule are larger than 72°. However, the O−Sm−O angles between THF molecules in **3** are 72.0(1)° and 73.0(1)°.

Conclusion

Structural studies on $SmI_2(THF)_5$, $SmI_2(DME)_2(THF)$, and $SmI_2(DME)(THF)_3$ show that in the presence of THF, the samarium diiodide moiety prefers to surround itself with five oxygen donor atom ligands in a pentagonal bipyramidal coordination environment. The uniformity of this geometry in these samarium diiodide structures and the high frequency of the $Ln(anion)_2(ligand)_5$ structure in a variety of other systems suggest that this geometry is both easily formed and energetically favorable upon crystallization. Although these data do not establish the structure of samarium diiodide in solution, they suggest that in the absence of strong donor ligands such as HMPA, similar seven-coordinate structures may be preferred in THF.

Acknowledgment. We thank the National Science Foundation for support for this research and the Department of Education for a Graduate Assistance in Areas of National Need (GAANN) fellowship to T.S.G. We also thank the National Science Foundation for Grant No. CHE-9300266 for the rotating anode X-ray diffractometer.

Supporting Information Available: Tables of atomic coordinates, atomic displacement parameters, and bond distances and angles (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9516120

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