Autoionization of SmI_3 in Tetrahydrofuran. X-ray Crystal Structure of the Ionic Complex $[SmI_2(THF)_5][SmI_4(THF)_2]$

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Introduction

Lanthanide trihalides are common starting materials for the synthesis of many types of coordination compounds involving these metals. Under proper conditions of crystallization or in the presence of certain coordinating moieties, $LnCl_3$ can form various kinds of complexes. A rich variation in formation of neutral complexes vs ionics, six- vs seven- and eight-coordinate complexes, and homoleptic environments vs heteroleptic coordination can occur.[1−18] Many types of these coordination complexes including the ionic complexes $[TbCl_2(THF)_5][TbCl_4(THF)_2]$[1] and $[YCl_2(THF)_5][YCl_4(THF)_2]$[18] have been crystallographically characterized. In contrast, the coordination chemistry of lanthanide triiodide is largely unexplored. To date, no crystal structure of any LnI_3 complex has been reported to our knowledge. We here report the first observation of autoionization of lanthanide triiodide in tetrahydrofuran as well as the X-ray crystal structure of $[SmI_2(THF)_5][SmI_4(THF)_2]$.

Experimental Section

All experiments were performed under an atmosphere of dry dinitrogen using standard Schlenk techniques. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl and stored under nitrogen. SmI_2 was prepared according to the literature method.[19] Infrared spectrum was obtained on a Perkin-Elmer 1600 Fourier transform spectrometer.

Table 1. Crystallographic Data

formula	$C_{28}H_{56}I_6O_7Sm_2$
fw	1566.8
cryst syst	monoclinic
space group	*C*2/*c*
a, Å	12.974(1)
b, Å	12.256(1)
c, Å	29.106(1)
β, deg	97.37(1)
V, Å^3	4590(2)
Z	4
d_{calcd}, g/cm^3	2.268
λ (Mo Kα), Å	0.710 73
μ, mm^{-1}	6.603
temp, K	298
R, R_w^{a}	0.043, 0.044
no of indep reflcns	4598
no of obsd reflcns ($F > 6.0\sigma(F)$)	4031
data-to-param ratio	20.4:1

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg)

Sm(1)−I(1)	3.028(1)	Sm(2)−I(2)	3.051(1)
Sm(2)−I(3)	3.071(1)		
Sm(1)−O(1)	2.449(4)	Sm(1)−O(2)	2.441(4)
Sm(1)−O(3)	2.455(4)	Sm(2)−O(4)	2.386(4)
I(1)−Sm(1)−O(1)	90.5(1)	I(1)−Sm(1)−O(2)	88.5(1)
O(1)−Sm(1)−O(2)	143.7(1)	I(1)−Sm(1)−O(3)	89.2(1)
O(1)−Sm(1)−O(3)	71.7(1)	O(2)−Sm(1)−O(3)	144.5(1)
I(1)−Sm(1)−I(1a)^a	179.0(1)	I(2)−Sm(2)−I(3)	89.1(1)
I(2)−Sm(2)−O(4)	91.5(1)	I(3)−Sm(2)−O(4)	92.2(1)
I(2)−Sm(2)−I(2b)^a	180.0(1)	I(3)−Sm(2)−I(2b)	90.9(1)
O(4)−Sm(2)−I(2b)	88.5(1)	I(3)−Sm(2)−I(3b)	180.0(1)
O(4)−Sm(2)−I(3b)	87.8(1)	I(2b)−Sm(2)−I(3b)	89.1(1)

^{a} Symmetry transformations: a ($-x$, y, $0.5 - z$); b ($1 - x$, $1 - y$, $1 - z$).

$[SmI_2(THF)_5][SmI_4(THF)_2]$. Moisture-free oxygen was bubbled through the dark green THF solution of SmI_2 (10 mL, 0.5 mmol) until the color of the solution turned to yellow. The volume of the resulting solution was then reduced under vacuum to about 8 mL. After 2 days, the yellow crystals were filtered off and washed with a small amount of THF (81 mg, 31%). Anal. Calcd for $Sm_2I_6C_{28}H_{56}O_7$: C, 22.14; H, 3.72. Found: C, 21.95; H, 3.80. IR (KBr, cm^{-1}): 2982 m, 2895 m, 1020 w, 1004 s, 910 w, 850 s, 625 w.

X-ray Diffraction Study. The crystal data are summarized in Table 1, and selected bond distances and angles are given in Table 2. Single crystals were sealed under N_2 with Paraton-N oil in thin-walled glass capillaries. Data were collected on a MSC/Rigaku RAXIS-IIC Image Plate using Mo Kα radiation ($\lambda = 0.710\ 73$ Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. Absorption correction was applied by correlation of symmetry-equivalent reflections using the REQAB program.[20] The structure was solved by direct methods and refined using the Siemens SHELXTL PLUS program package (PC version).[21]

Results and Discussion

Samarium diiodide is a very strong reductant and can be easily oxidized to the triiodide by oxygen in THF. The ionic complex $[SmI_2(THF)_5][SmI_4(THF)_2]$ is probably the least soluble material in solution, so that it crystallizes out first upon slow evaporation of the solvent. The crystal structure consists of well-separated, alternating layers of discrete octahedral anions and pentagonal

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(1) Evans, W. J.; Shreeve, J. L.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1995**, *34*, 576−585.
(2) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5084−5092.
(3) Wei, G.; Gao, H.; Jin, Z.; Shen, Q. *J. Struct. Chem. (Jiegou Huaxue)* **1989**, *8*, 61.
(4) Lin, S.-H.; Dong, Z.-C.; Huang, J.-S.; Zhang, Q.-E.; Lu, X.-L. *Acta Crystallogr.* **1991**, *C47*, 426−427.
(5) Chen, W.; X ia, Z. *Inorg. Chim. Acta* **1987**, *130,* 125−129.
(6) Jin, Z.; Nie, G.; Hu, N.; Chen, W. *Chin. J. Appl. Chem. (Yingyong Huaxue)* **1989**, *6,* 68.
(7) Hu, N.; Liu, Y.; Shen, Q.; Xing, Y.,; Shi, E.. *Acta Chim. Sin. (Huaxue Xuebao)* **1986**, *44,* 388.
(8) Rogers, R. D.; Voss, E. J.; Etzenhouser, R. D. *Inorg. Chem.* **1988**, *27,* 533−542.
(9) Castellani, B. C.; Coda, A. *Acta Crystallogr.* **1985**, *C41,* 186−189.
(10) Evans, W. J.; Shreeve, J. L.; Doedens, R. J. *Inorg. Chem.* **1993**, *32*, 245−246.
(11) Castellani, B. C.; Tazzoli, V. *Acta Crystallogr.* **1984**, *C40*, 1832−1834.
(12) Radonovich, L. J.; Glick, M. D. *J. Inorg. Nucl. Chem.* **1973**, *35,* 2645−2752.
(13) Hou, Z.; Kobayashi, K.; Yamazaki, H. *Chem. Lett.* **1991**, 265−268.
(14) Deacon, G. B.; Feng, T.; Nickel, S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commum.* **1993**, 1328−1329.
(15) Magomedov, G. K.-L.; Voskoboinikov, A. Z.; Kirillova, N. I.; Gusev, A. I.; Parshina, I. N.; Beletskaya, I. P. *Organomet. Chem. USSR* **1992**, *5,* 330−332.
(16) Jin, Z.; Jin, S.; Wang, X.; Chen, W. *J. Struct. Chem. (Jiegou Huaxue)* **1988**, *7,* 181.
(17) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6,* 161−172.
(18) (a)Xie, Z.; Qian, C.; Sun, J. *J. Struct. Chem. (Jiegou Huaxue)* **1993**, *12,* 107−109. (b) Sobota, P.; Utko, J.; Szafert, S. *Inorg. Chem.* **1994**, *33,* 5203−5206.
(19) Miller, L. L.; Jacobson, R. A. *Comput. Chem.* **1989**, *13,* 1−3.
(20) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102,* 2693−2698.
(21) Sheldrick, D. SHELXTL PLUS program set. Siemens Analytical X-ray Instruments, Inc., Madison, WI 1990.

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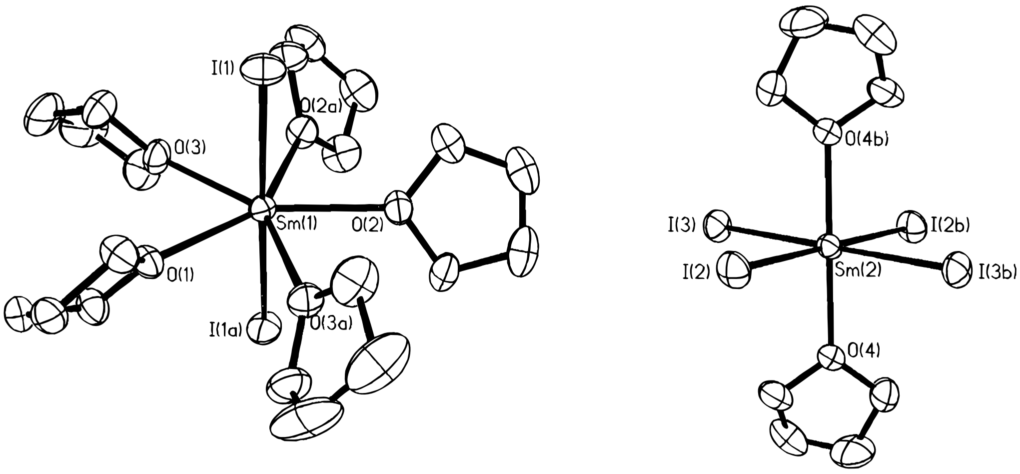

Figure 1. Perspective view of $[SmI_2(THF)_5][SmI_4(THF)_2]$. The thermal ellipsoids are drawn at the 35% probability level.

bipyramidal cations. The complementary sizes of the anion and cation probably contribute to the stabilization of the layered lattice. The shortest intermolecular Sm···I contact is 6.64 Å between Sm(1) of the cation and I(3) of the neighboring anion.

The cation shown in Figure 1 is similar in structure to other seven-coordinate cationic lanthanide complexes such as $[YCl(OCMe_3)(THF)_5]^+$,[22] $[CeCl_2(THF)_5]^+$,[16] $[TbCl_2(THF)_5]^+$,[1] and $[YCl_2(THF)_5]^+$.[18] As shown in Table 2, its structural features is almost identical to the cation in $[SmI_2(THF)_5][Co(CO)_4]$.[23] A crystallographic 2-fold rotation axis passes through Sm(1), O(1), and the midpoint of the C(2)−C(2a) bond, so that the iodo ligands and the THF molecules occupy the axial and equatorial sites, respectively, in a rather regular pentagonal bipyramidal geometry.

The centrosymmetric [*trans*-$SmI_4(THF)_2]^-$ anion exhibits an almost perfect coordination octahedron. The Sm(2)−I distances of 3.051(1) and 3.071(1) Å in the six-coordinate anion are significantly longer than the 3.028(1) Å Sm(1)−I distance in the seven-coordinate cation, but are comparable to the following values in eight-coordinate neutral Sm(III) compounds: $(C_5Me_5)_2SmI(THF)$,[24] 3.043(2) and 3.053(2) Å; $(Bu^tC_5H_4)_2SmI(THF)$,[25] 3.045 Å; $(MeOCH_2CH_2C_5H_4)_2SmI$,[26] 3.119(1) Å; $(MeOCH_2CH_2C_5H_4)SmI_2(THF)_2$,[26] 3.086(1) and 3.092(1) Å. In contrast, the 2.386(4) Å Sm(2)−O bond distance in the anion is significantly shorter than the average 2.448(4) Å Sm(1)−O distance in the cation or other THF coordinated Sm(III) compounds in the range 2.45−2.52 Å.[24−26]

In conclusion, the first X-ray crystal structure of a lanthanide triiodide THF complex has been determined. Similar to $TbCl_3$ and YCl_3, SmI_3 crystallizes as an ionic complex $[SmI_2(THF)_5][SmI_4(THF)_2]$ from THF rather than the simple coordination compound $SmI_3(THF)_3$. The occurrence of this autoionization may be due to favorable lattice energetics.

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Supporting Information Available: Tables of crystallographic data collection information, atomic coordinates, bond distances and angles, and anisotropic thermal parameters and an atom-numbering scheme (10 pages). Ordering information is given on any current masthead page.

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[22] Evans, W. J.; Olofson, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2308−2314.

[23] Evans, W. J.; Bloom, I.; Grate, J. W.; Hughes, L. A.; Hunter W. E.; Atwood, J. L. *Inorg. Chem.* **1985**, *24*, 4620−4623.

[24] Evans, W. J.; Grate, J. W.; Levan, K. R.; Doedens R. J.; Hunter W. E.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614−3619.

[25] Belskii, V. K.; Gun'ko, Yu. K.; Lobkovskii, E. B.; Bulychev, B. M.; Soloveichik, G. L. *Metallory. Khim.* **1991**, *4*, 420−425.

[26] Deng, D.; Qian, C.; Song, F.; Wang, Z. *Sci. Chin. (Ser. B)* **1994**, *24*, 120−128.