Crystal Structure of [Sm(OPMePh$_2$)$_4$I$_2$]I. A Cationic Octahedral Complex of Samarium(III)

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Abstract

The crystal structure of [Sm(OPMePh$_2$)$_4$I$_2$]I, **1**, was determined by X-ray diffraction and refined anisotropically to a final R value of 0.067 from 3040 reflections with $I > 3.0\sigma(I)$. The space group was $P2/a$ and $Z = 2$. The unit cell dimensions were: a = 17.777(6), b = 13.559(2), c = 11.656(4) Å, $\alpha = \gamma$ = 90.0 and β = 97.25(3)°. The cation geometry was octahedral with the Sm(III) bonded to two mutually *trans* I$^-$ ions and four OPMePh$_2$ groups. A third non-bonded I$^-$ was present elsewhere in the cell. The Sm–I and Sm–O distances were 3.077(1) and 2.27(1) Å respectively. Two of the Sm–O–P angles were 172.1(6)° and the other two were 162.0(6)°.

Introduction

The number of lanthanide metal compounds with coordination number ≤6 that have been structurally characterized by X-ray diffraction is small and, in particular, we are unaware of any prior example of a cationic complex that belongs to this group [1]. Herein, we describe the X-ray crystal structure of one such compound: [Sm(OPMePh$_2$)$_4$I$_2$]I, **1**, a cationic, six-coordinate, octahedral complex of Sm(III). The cationic nature of **1** is intriguing since, given the tendency for lanthanide ions to exhibit high coordination numbers [1], the coordination of the third I$^-$ ion to the Sm(III) cation in **1** to yield a seven-coordinate complex would not have been unreasonable. That this did not occur even for a large, early lanthanide metal ion and a strongly coordinating halide anion must be due to steric crowding around the Sm(III) center. The structure of **1** presents several interesting features including two sets of Sm–O–P angles differing by 10°. In addition, in conjunction with our structural elucidation of SmI$_2$ derivatives [2], it is now possible to compare the terminal metal–halogen bond distances for a lanthanide metal in two different oxidation states.

Experimental

Synthesis of 1

SmI$_2$ [3] was treated with excess isopropanol in THF and stirred overnight. The solution slowly turned colorless and a white precipitate was formed. Following filtration to remove this precipitate, an excess of OPMePh$_2$ was added to the filtrate. On standing, crystals of **1** were deposited.

Structure Determination of 1

A crystal of **1** was sealed in a capillary and mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 15°$) during

TABLE I. Crystal Data for [Sm(OPMePh$_2$)$_4$I$_2$]I

Formula	SmI$_3$C$_{52}$H$_{52}$P$_4$O$_4$
M_r	1364.28
a	17.777(6) Å
b	13.559(2) Å
c	11.656(4) Å
α	90.0°
β	97.25(3)°
γ	90.0°
V	2787.2(14) Å^3
F(000)	1330
μ Mo Kα	22.56 cm^{-1}
λ Mo Kα	0.71069 Å
D_c	1.625 g cm^{-3}
Z	2
Observed reflections	3040
R	6.7%
Space group	$P2/a$

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normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$ Å). Data (6116 points) were collected at room temperature using a variable scan rate, a $\theta - 2\theta$ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 116°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections and the intensities of these reflections showing less than 8% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz polarization and background effects. After removal of redundant and space group forbidden data, 3040 reflections were considered observed $[I > 3.0\sigma(I)]$. The structure was solved using a Patterson synthesis to locate the heavy atom. Successive least-squares/difference Fourier cycles allowed location of the remainder of the non-hydrogen atoms.

Refinement of scale factor, positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence [4]. Methyl hydrogen positional parameters were determined from a difference Fourier synthesis. Ring bound hydrogen positions were calculated assuming normal geometry and a C–H distance of 0.97 Å. These hydrogen positional parameters and their isotropic thermal parameters of $U = 0.03$ Å^2 were included in the final cycles of refinement but were held fixed. The final cycle of refinement [function minimized $\Sigma(|F_o| - |F_c|)^2$] led to a final agreement factor, $R = 6.7\%$ $[R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) \times 100]$. Anomalous dispersion corrections were made for Sm and I. Scattering factors for I, C, P, O and H were taken from Cromer and Mann [5]. Those for Sm were from the International Tables [6]. In the final cycles of refinement a weight scheme equal to $1/\sigma F$ was introduced.

The refinement of Sm, I, P, O, and two of the phenyl rings progressed in satisfactory fashion. However the refinement of ring C21–C26 and of atoms C35 and C34 of ring C31–C36 progressed in less satisfactory fashion. The atom positions for ring C21–C26 clearly indicated disorder, but the disorder could not be resolved in terms of partial occupancy positions. Similarly the movement of ring C31–C36 was evident in the thermal parameters but attempts to resolve the disorder in terms of several partially populated positions did not lead to a reasonable result.

The bond distances and bond angles are given in Table II; the positional parameters are given in Table III.

TABLE II. Selected Bond Angles (°) and Distances (Å) for $[Sm(OPMePh_2)_4I_2]I$

Sm1–I1	3.077(1)	I1–Sm1–O1	89.8(2)
Sm1–O1	2.27(1)	I1–Sm1–O2	89.6(2)
Sm1–O2	2.28(1)	Sm1–O1–P1	162.0(6)
O1–P1	1.50(1)	O1–P1–C10	113.1(8)
P1–C10	1.77(2)	O1–P1–C11	109.5(6)
P1–C11	1.81(2)	O1–P1–C31	111.2(7)
P1–C31	1.79(2)	C10–P1–C11	109.4(9)
O2–P2	1.49(1)	C10–P1–C31	107.0(9)
P2–C1	1.76(2)	C11–P1–C31	106.5(7)
P2–C21	1.79(2)	O1–Sm1–O2	89.9(4)
P2–C3	1.78(1)	Sm1–O2–P2	172.1(6)
C11–C12	1.39(2)	O2–P2–C1	112.9(7)
C12–C13	1.36(3)	O2–P2–C21	107.7(8)
C13–C14	1.40(3)	O2–P2–C3	109.5(6)
C14–C15	1.38(5)	C1–P2–C21	108.2(9)
C15–C16	1.44(3)	C1–P2–C3	108.5(7)
C16–C11	1.32(3)	C21–P2–C3	110.0(8)
C31–C32	1.37(2)	P1–C11–C12	120(1)
C32–C33	1.37(4)	C11–C12–C13	121(2)
C33–C34	1.22(6)	C12–C13–C14	118(2)
C34–C35	1.08(9)	C13–C14–C15	123(2)
C35–C36	1.67(6)	C14–C15–C16	114(2)
C36–C31	1.34(3)	C15–C16–C11	122(2)
C3–C4	1.35(2)	C16–C11–C12	121(2)
C4–C5	1.42(3)	C16–C11–P1	120(1)
C5–C6	1.33(3)	P1–C31–C32	118(1)
C6–C7	1.31(4)	C31–C32–C33	121(2)
C7–C8	1.42(3)	C32–C33–C34	107(4)
C8–C3	1.37(2)	C33–C34–C35	155(6)
		C34–C35–C36	102(4)
		C35–C36–C31	114(2)
		C36–C31–C32	121(2)
		C36–C31–P1	122(1)
		P2–C3–C4	123(1)
		C3–C4–C5	118(2)
		C4–C5–C6	123(2)
		C5–C6–C7	118(2)
		C6–C7–C8	122(2)
		C7–C8–C3	119(2)
		C8–C3–C4	119(1)
		C8–C3–P2	124(1)

Results and Discussion

The Sm(III) ion in **1** was on a center of symmetry and was bonded to two mutually *trans* I^- ions (Sm–I, 3.077(1) Å) and to four $OPMePh_2$ groups (Sm–O, 2.27(1) Å average), Table II and Fig. 1. The +1 charge on the complex was balanced by the presence of a non-bonded I^- ion elsewhere in the cell. In Fig. 1, C1 and C10 represent the methyl groups and C3, C21, C11 and C31 the ipso carbons of the phenyl groups. The rest of the phenyl carbons have been omitted for clarity.

The cation geometry was octahedral with the *trans* I–Sm–I and O–Sm–O angles constrained by symmetry to be 180°. The *cis* I–Sm–O and O–Sm–O angles were very close to 90°. A remarkable structural feature of **1** was the widely divergent Sm–O–P angles of 172.1(6)° and 162.0(6)°. The latter was the smallest M–O–P angle observed for phosphine

TABLE III. Positional Parameters for [Sm(OPMePh$_2$)$_4$I$_2$]I

Atom	*x*	*y*	*z*
Sm1	0.5000	0.0000	0.0000
I1	0.6604(1)	0.0294(1)	0.1291(1)
I2	0.7500	0.6040(1)	0.5000
O1	0.4901(6)	−0.1446(7)	0.0958(9)
O2	0.5506(5)	−0.0824(7)	−0.1426(8)
P1	0.5078(2)	−0.2303(2)	0.1760(3)
P2	0.5932(2)	−0.1373(3)	−0.2242(3)
C1	0.6785(9)	−0.1889(12)	−0.1560(15)
C3	0.5355(7)	−0.2343(11)	−0.2904(11)
C4	0.5621(10)	−0.3031(14)	−0.3585(15)
C5	0.5120(13)	−0.3790(15)	−0.4040(17)
C6	0.4396(12)	−0.3839(19)	−0.3856(23)
C7	0.4147(10)	−0.3165(19)	−0.3196(20)
C8	0.4610(9)	−0.2374(14)	−0.2717(16)
C10	0.5605(14)	−0.1966(14)	0.3088(14)
C11	0.4205(9)	−0.2889(10)	0.2032(14)
C12	0.4235(11)	−0.3698(14)	0.2765(15)
C13	0.3590(13)	−0.4090(14)	0.3079(17)
C14	0.2897(14)	−0.3742(15)	0.2521(25)
C15	0.2841(12)	−0.3016(25)	0.1686(36)
C16	0.3548(12)	−0.2535(15)	0.1550(29)
C21	0.6164(11)	−0.0521(18)	−0.3319(15)
C22	0.6348(21)	0.0333(22)	−0.3134(29)
C23	0.6373(30)	0.0839(32)	−0.4238(55)
C24	0.6418(20)	0.0907(32)	−0.4859(30)
C25	0.6867(18)	−0.0480(50)	−0.5034(33)
C26	0.5970(28)	−0.0503(44)	−0.4361(38)
C31	0.5617(8)	−0.3222(10)	0.1123(14)
C32	0.5333(12)	−0.3568(14)	0.0047(17)
C33	0.5721(19)	−0.4251(19)	−0.0512(27)
C34	0.6299(18)	−0.4452(31)	0.0126(74)
C35	0.6699(16)	−0.4392(35)	0.0903(62)
C36	0.6285(12)	−0.3537(16)	0.1648(23)
H1	0.7050	−0.1451	−0.1018
H2	0.6616	−0.2345	−0.1170
H3	0.7026	−0.1996	−0.2142
H4	0.6154	−0.3005	−0.3765
H5	0.5356	−0.4301	−0.4541
H6	0.4113	−0.4414	−0.4123
H7	0.3604	−0.3174	−0.3032
H8	0.4397	−0.1847	−0.2260
H101	0.5360	−0.2475	0.3531
H102	0.5146	−0.1648	0.3660
H103	0.5745	−0.1436	0.3442
H12	0.4737	−0.4000	0.3047
H13	0.3616	−0.4650	0.3643
H14	0.2471	−0.4019	0.2907
H15	0.2335	−0.2878	0.1172
H16	0.3562	−0.1964	0.0996
H22	0.6474	0.0530	−0.2175
H23	0.6618	0.1816	−0.3648
H24	0.7088	0.1177	−0.5228
H25	0.6373	−0.0081	−0.6057
H26	0.5491	−0.0918	−0.4551
H32	0.4813	−0.3298	−0.0359
H33	0.5609	−0.4518	−0.1328
H34	0.6655	−0.5082	−0.0103
H35	0.7241	−0.4527	0.1499
H36	0.6487	−0.3266	0.2506

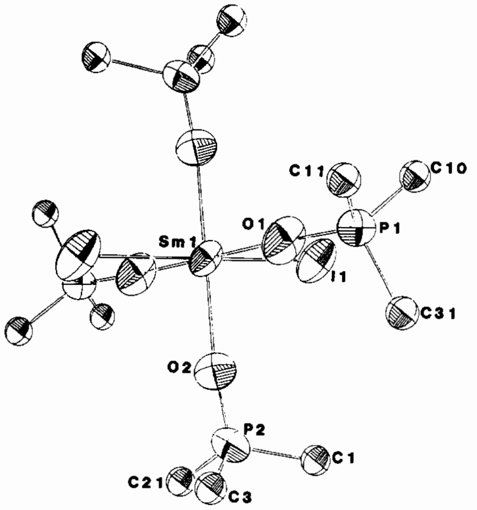

Fig. 1. ORTEP drawing of the Sm(III) cation in I.

oxide derivatives of the lanthanide metals with the exception of the severely sterically congested molecule, *trans*-[Sm(C$_5$Me$_5$)$_2$(OPPh$_3$)]$_2$(μ-OCH=CHO) which had Sm–O–P angles of 163.0(5)° and 158.7(5)° [7].

It is interesting to compare the Sm(III)–I distance in 1 with the Sm(II)–I distances in the compounds, SmI$_2$(NCCMe$_3$)$_2$, 2 [2] and SmI$_2$[O(CH$_2$CH$_2$OMe)$_2$]$_2$, 3 [2]. In the absence of any steric congestion, the Sm–I bond distance should be determined purely on the basis of the ionic radii of the respective ions. The Sm(II)–I distances in 2 and 3 were very similar (3.225(1) and 3.260(1) Å for 2 and 3.265(1)° for 3) even though the coordination number of Sm(II) in the two compounds were different (6 and 8, respectively) and the I$^-$ ions were bridging in 2* and terminally bonded in 3. Also, apart from the coordinated I$^-$ ions, the other ligating atoms were N in 2 and O in 3. The Sm(III)–I distance of 3.077(1) Å in 1 is *ca.* 0.15–0.19 Å shorter than those in 2 and 3 and compares favorably with a 0.14–0.15 Å difference in ionic radii of Sm(II) and Sm(III) [9].

Supplementary Material

The cell packing diagram, and tables of thermal parameters and structure factors may be obtained from the Editor-in-Chief.

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*In the sterically crowded molecule, [Sm(C$_5$Me$_5$)(THF)$_2$(μ-I)]$_2$, the Sm(II)–I bridge bond distances are significantly longer (3.356(2) and 3.459(2) Å) [8].

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