

Synthesis and crystal structure of an organolanthanide fluoride, $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Sm}(\mu\text{-F})\}_2$

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Abstract

Treatment of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmI}(\text{THF})$ with stoichiometric amounts of AgSbF_6 in dry diethyl ether, or reaction of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Sm}$ with one equivalent of Me_3NHF in dry 1,2-dimethoxyethane afforded the dimeric complex $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Sm}(\mu\text{-F})\}_2$ in good yield, which represents the first structurally characterized example of a fluoride-bridged organosamarium complex. It crystallizes in space group $P2_1/n$ with $a = 12.215(1)\text{Å}$, $b = 16.028(1)\text{Å}$, $c = 15.677(1)\text{Å}$, $\beta = 99.78(1)^\circ$, $V = 3025(2)\text{Å}^3$, and $Z = 2$ for $D_{\text{calcd}} = 1.292\text{gcm}^{-3}$. Least squares refinement of the structural model based on 5471 reflections ($|F| > 6.0\sigma|F|$) converged to $R_F = 0.040$. The average $\text{Sm}(1)\text{-F}$ distance is $2.302(3)\text{Å}$. © 1997 Elsevier Science S.A.

Keywords: Lanthanide; Cyclopentadienyl; X-ray diffraction; Trimethylsilyl; Fluorine; Samarium

1. Introduction

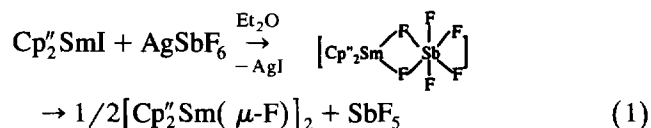
Trivalent lanthanide chlorides are the most important starting materials for the syntheses of all kinds of organolanthanide complexes [1,2]. Lanthanide trifluorides, however, are very unreactive towards organoalkali reagents due to their very poor solubility even in highly polar organic solvents, so that they are not common starting materials. In fact, none of organolanthanide fluorides had been prepared from LnF_3 . To date only a few of such fluorides are known, including structurally characterized examples such as $\text{Cp}_2^*\text{Yb}(\mu\text{-F})\text{YbCp}_2^*$ [3], $\text{Cp}_6^*\text{Yb}_4\text{F}_4$ [4], $\text{Cp}_6^*\text{Yb}_5\text{F}_9$ [5], $\text{Cp}_2^*\text{YbF}(\text{OEt}_2)$ and $\text{Cp}_2^*\text{YbF}(\text{THF})$ [5]. All of them were prepared from the corresponding divalent organolanthanide complexes $\text{Cp}_2^0\text{Ln}(\text{L})$ ($\text{Cp}^0 = \text{Cp}^*$ (C_5Me_5), Cp' ($\text{CH}_3\text{C}_5\text{H}_4$); $\text{Ln} = \text{Yb, Eu, Sm}$; $\text{L} = \text{THF, Et}_2\text{O}$). Since only three elements (Sm, Eu and Yb) of the lanthanide series can form stable divalent organometallic complexes, the above methodology is therefore severely limited and may not be applied to the remaining 12 lanthanide elements. We report here a convenient synthesis of organolanthanide fluoride from

its trivalent organolanthanide complexes as well as the first structurally characterized organosamarium fluoride, $[\text{Cp}_2''\text{Sm}(\mu\text{-F})]_2$ ($\text{Cp}'' = (\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$) (**1**) which also represents the first example of a dimeric organolanthanide complex with a doubly bridging Ln_2F_2 unit.

2. Results and discussion

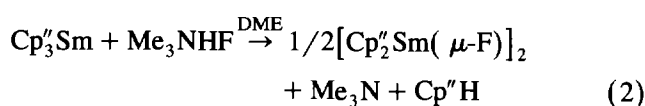
2.1. Synthesis of $[\text{Cp}_2''\text{Sm}(\mu\text{-F})]_2$ (**1**)

Cationic organometallic complexes of d-block transition metals have been shown to play a key role in many industrially important catalytic reactions [6–8]. We wished to prepare the cationic complex, $[\text{Cp}_2''\text{Sm}(\text{solvent})_x][\text{SbF}_6]$ by treatment of stoichiometric amounts of the yellow $\text{Cp}_2''\text{SmI}(\text{THF})$ with AgSbF_6 in dry diethyl ether at room temperature. Unfortunately, we did not isolate the desirable ionic compound, but obtained the unsolvated dimer, **1**, as yellow crystals instead in good yield. Compound **1** was formed presumably via the fluoride abstraction of the possible intermediate $\text{Cp}_2''\text{SmSbF}_6$ according to Eq. (1).



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This transformation may be best interpreted in terms of bond dissociation energy, Sm–F (135 kcal mol⁻¹) vs. Sb–F (96 kcal mol⁻¹) [9]. The stronger Sm–F bond formation should be the driving force of this fluoride abstraction reaction. In contrast, the tetrafluoroborate (BF₄⁻) and hexafluorophosphate (PF₆⁻) anions are stable to the cationic organolanthanide complexes. No fluoride abstraction product was mentioned in the synthesis of compounds [Cp₂Ce(NCMe)_x][BF₄]_x (*x* = 2 [10]; *x* = 0 [11]) and [Cp₂^{*}Yb(DME)][PF₆]₂ [12]. **1** can also be synthesized in good yield by the reaction of Cp₃Sm with one equivalent of Me₃NHF in dry 1,2-dimethoxyethane (DME) as shown in Eq. (2). This is a more economic route than the previous one.



2.2. Crystal structure of **1**

Single crystal X-ray analysis reveals that **1** is a centrosymmetric fluoride-bridged dimer with pseudo-tetrahedral geometry around the Sm center (Fig. 1) (considering the centroid of a cyclopentadienyl ring as occupying one coordination site), similar to those previously reported for dimeric organolanthanide complexes such as [Cp₂Sm(μ-OH)]₂ (**2**) [13], [Cp₂Sm(μ-C≡CCMe₃)]₂ (**3**) [14], [Cp₂Pr(μ-Cl)]₂ [15] and [(Bu₂C₅H₃)₂Ce(μ-Cl)]₂ [16]. The average Sm–C distance of 2.721(6) Å in **1** is identical to the 2.72(3) Å average in **2**, the 2.72(4) Å average in **3** and the 2.72(3) Å average in formally nine-coordinate [Cp₂Sm(THF)(μ-Cl)]₂ (**4**) [17]. The Sm–Cent(1) (the centroid of the C(1) to C(5) ring) and Sm–Cent(2) (the centroid of the C(6) to C(10) ring) distances in **1**, 2.447 Å and 2.432 Å respectively, are

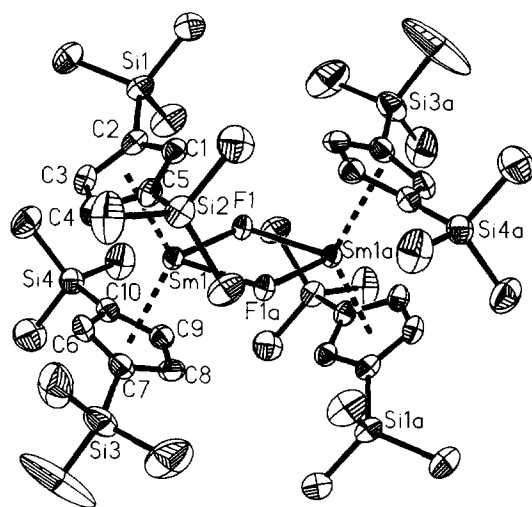


Fig. 1. Perspective view of the molecular structure of **1**. All hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 35% probability level.

similar to the reported values of 2.46 Å and 2.44 Å respectively in **2**, and 2.458 Å and 2.437 Å respectively in **3**. The value 129.6° for the Cent(1)–Sm–Cent(2) angle in **1** is comparable to 129.5° in **2** and 126.4° in **3**.

There is no organosamarium–fluoride bond distance reported in the literature to date (the structure of [(η⁵-C₅H₄Bu¹)₂Sm(μ-F)]₃ was very recently reported [24]). The value found for **1**, 2.302(3) Å, is very close to the value of 2.300 Å which would be expected by adding the difference, 0.094 Å, between Shannon's ionic radii [18] of Sm³⁺ (1.079 Å) and Yb³⁺ (0.985 Å) to a doubly bridging Yb–F bond distance of an eight-coordinate complex, for instance, 2.206(5) Å in Cp₆^{*}Yb₅F₉ [5]. This measured value is also very similar to the value of 2.309 Å derived from subtracting the 0.45 Å difference in Pauling's crystal radii [19] of chloride (1.81 Å) and fluoride (1.36 Å) ion from a doubly bridging Sm–Cl bond distance, 2.759(3) Å, in **4**. The F(1)–Sm(1)–F(1A) angle in **1** is 70.9(1)° as compared to the 76.6(6)° in **2** and the 73.8(1)° in **3**.

3. Conclusion

We have developed new methods to prepare organolanthanide fluorides. The advantage of this methodology is to use readily available trivalent organolanthanide complexes as starting materials, rather than divalent complexes.

4. Experimental section

4.1. General procedure

All experiments were performed under an atmosphere of dry dinitrogen using standard Schlenk or cannula techniques, or in a glovebox. All solvents were freshly distilled from sodium benzophenone ketyl prior to use. Cp₃Sm [20] and Cp₂SmI(THF) [21] were prepared according to the literature methods. Other chemicals were purchased from Aldrich Chemical Company and used as-received. Infrared spectra were obtained on a Perkin–Elmer 1600 Fourier transform spectrometer. Mass spectra were recorded on an HP5989A spectrometer.

4.2. Preparation of [Cp₂Sm(μ-F)]₂

4.2.1. Method A

To a stirring solution of 0.216 g (0.28 mmol) of Cp₂SmI(THF) in 20 ml of Et₂O was slowly added 0.096 g (0.28 mmol) of AgSbF₆ in 20 ml of Et₂O at room temperature and the reaction mixture was stirred overnight. The yellow precipitate (AgI) was filtered off

and the resulting clear yellow solution was then reduced in volume under vacuum to about 20 ml, followed by cooling down to -30°C to give shiny yellow crystals which were suitable for X-ray diffraction (0.10 g, 61%). IR (KBr, cm^{-1}): 3082w, 2955s, 2898m, 1437m, 1318m, 1247s, 1077s, 921s, 832vs, 782s, 753s, 691m. MS (^{152}Sm , EI): m/z (%) 1163 (2) $[\text{M} - \text{CH}_3]^+$, 969 (4) $[\text{M} - \text{Cp}^*]^+$, 589 (2) $[\text{Cp}_2^*\text{SmF}]^+$, 570 (100) $[\text{Cp}_2^*\text{Sm}]^+$, 361 (18) $[\text{Cp}^*\text{Sm}]^+$. Anal. Calcd. for $\text{C}_{44}\text{H}_{84}\text{F}_2\text{Si}_8\text{Sm}_2$: C, 44.91; H, 7.20; Sm, 25.56. Found: C, 44.45; H, 7.19; Sm, 25.33.

4.2.2. Method B

A 100 ml Schlenk flask was charged with 0.56 g (0.71 mmol) of Cp_2^*Sm , 0.056 g (0.71 mmol) of dry Me_3NHF (prepared from Me_3N and HF in aqueous solution, followed by recrystallization from acetone) and 30 ml of DME. The mixture was stirred under reflux condition for 5 h, and then reduced in volume under vacuum to about 15 ml. The clear warm solution was cooled down to room temperature to yield shiny yellow crystals (0.27 g, 65%). The spectroscopic data of the crystals are the same as above; the unit cell parameters were also the same.

4.3. X-ray structure determination

The crystal data are summarized in Table 1, and selected bond distances and angles are given in Table 2. A single crystal was sealed under N_2 and immersed in Paraton-N oil in a thin-walled glass capillary. Data were collected on an MSC/Rigaku RAXIS-IIC imaging plate using $\text{Mo K}\alpha$ radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. Absorption correction was applied by correlation of

Table 1
Crystallographic data

Formula	$\text{C}_{44}\text{H}_{84}\text{F}_2\text{Si}_8\text{Sm}_2$
Fw	1176.6
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	12.215(1)
b (Å)	16.028(1)
c (Å)	15.677(1)
β (deg)	99.78(1)
V (Å ³)	3025(2)
Z	2
d_{calcd} (g cm^{-3})	1.292
$\lambda(\text{Mo K}\alpha)$ (Å)	0.71073
μ (mm^{-1})	2.112
Temperature (K)	298
R , R_w^a	0.040, 0.054
No. of independent reflections	6214
No. of observed reflections ($F > 6.0\sigma(F)$)	5471
Data-to-parameter ratio	21.5:1

^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)–F(1)	2.304(3)	Sm(1)–F(1a)	2.299(2)
Sm(1)–C(1)	2.739(5)	Sm(1)–C(2)	2.750(5)
Sm(1)–C(3)	2.695(4)	Sm(1)–C(4)	2.700(5)
Sm(1)–C(5)	2.760(4)	Sm(1)–C(6)	2.716(5)
Sm(1)–C(7)	2.730(5)	Sm(1)–C(8)	2.696(6)
Sm(1)–C(9)	2.697(5)	Sm(1)–C(10)	2.731(4)
Sm(1)–Cent(1)	2.447	Sm(1)–Cent(2)	2.432
F(1)–Sm(1)–F(1a)	70.9(1)	Sm(1)–F(1)–Sm(1a)	109.1(1)
F(1)–Sm(1)–Cent(1)	113.2	F(1a)–Sm(1)–Cent(2)	107.0
F(1)–Sm(1)–Cent(2)	107.2	F(1a)–Sm(1)–Cent(1)	113.7
Cent(1)–Sm(1)–Cent(2)	129.6		

symmetry-equivalent reflections using the ABCOR program [22]. The structure was solved by direct methods and refined using the Siemens SHELXTL PLUS program package (PC version) [23].

5. Supporting information

Tables of crystallographic data collection information, atomic coordinates, bond distances and angles, anisotropic thermal parameters and an atom-numbering scheme (11 pages) are available. Ordering information is given on any current masthead page.

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