Crystallographic characterization of divalent organosamarium compound
\((C_5H_5)_2\text{Sm(THF)}_2\)\(^*\)

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The single pot reaction between SmX\(_2\) (X = Cl, I) and 'BuLi in THF at -40°C, followed by the addition of C\(_6\)H\(_6\)/Na\(^+\) results in a dark red solution. Leasing the concentrated reaction mixture at -25°C for two days in a deep freezer results in the formation of the crystals of the compound, \((C_5H_5)_2\text{Sm(THF)}_2\). The compound is insoluble in any solvent and it has been characterized by conventional methods. The crystals are monoclinic with space group \(C2/c\), and \(a = 13.416(1)\, \text{Å}, b = 9.644(1)\, \text{Å}, c = 14.129(2)\, \text{Å}, \beta = 109.873(9)\, ^\circ\) and \(z = 4\) for \(\rho_{	ext{calc}} = 1.64 \, \text{g cm}^{-3}\). Least squares refinement on the basis of 1804 observed reflections has led to a final R value of 0.037 and \(R_w = 0.054\).

The organometallic chemistry of the most reactive divalent lanthanide metal ion, Sm(II), with \(\text{Sm}^{II}/\text{Sm}^{III}\) couple of -1.15 V\(^1\), has been extensively studied\(^2\) since 1981. The organometallic compounds of the other two chemically accessible divalent lanthanides Eu(II) and Yb(II) were familiar since 1964 and 1966 respectively, because of the solubility of \((C_5H_5)_2\text{Eu}, (C_5H_5)_2\text{Yb}\) and other monosubstituted cyclopentadienyl derivatives\(^3\). A number of methods have been developed subsequently for the preparation of Eu(II) and Yb(II) organometallic compounds\(^4,5\). The Sm(II) analogue \((C_5H_5)_2\text{Sm(THF)}_2\) was first obtained by the reduction of \((C_5H_5)_2\text{Sm}\) with potassium and naphthalene in THF\(^6\). The organometallic chemistry of Sm(II) gained momentum with the preparation of the soluble complex with permethylated cyclopentadiene \((C_5\text{Me}_5)\), first by using metal vapourization technique\(^7\) and then by solution method\(^8\). Subsequently, Evans et al.\(^9\) have obtained the unsolvated arené soluble complex, \((C_5\text{Me}_5)_2\text{Sm}\).

As part of our interest in divalent organolanthanides, we have investigated the solubility of bis-(pentamethylcyclopentadienyl)samarium(II) in a solvent other than tetrahydrofuran, i.e., dimethoxyethane(DME)\(^10\). Further, we have reported a new soluble Sm(II) organometallic compound with a stabilizing and solubilizing ring bridged dicyclopentadienide\(^11\). In continuation of our efforts to obtain heteroleptic organolanthanides, we accidentally obtained the title compound in crystalline form. The synthetic strategy, structural parameters of \((C_5H_5)_2\text{Sm(THF)}_2\) (I) and a comparative account of divalent organolanthanide complexes are described in this note.

**Experimental**

The complex described in this note and other reagents used are extremely air and moisture sensitive. Therefore, all operations were performed under rigorously purified argon by Schlenk and vacuum-line techniques. Pre-dried THF was distilled from sodium bezophenone ketyl immediately before use. THF-d\(_6\) was dried by refluxing over sodium metal for several hours. Anhydrous SmCl\(_2\) was prepared by reducing SmCl\(_3\) in THF with Li and naphthalene\(^12\), and the solution of SmL\(_2\) in THF was prepared by the reaction between excess metal (Auer-Remy) and 1,2-diiodoethane\(^13\). Elemental analyses were carried out with a Perkin-Elmer CHN-analyzer 2400. Metal analysis involved complexometric titration using dithizone\(^14\). Infrared spectra were recorded in paraffin mulls between CsI plates on a Perkin-Elmer 560B (200-4000 cm\(^{-1}\)) spectrometer. \(^{1}H\) NMR spectra were recorded for samples in sealed 5 mm tubes on a Brucker WP80 SY instrument.

**Reactions**

To a suspension of 1.1 g (5 mmol) of red SmCl\(_2\) in 30 ml THF or to a 30 ml of solution of SmL\(_2\)(THF)\(_2\) (2.74 g, 5 mmol), 2.94 ml of 1.7M solution of 'BuLi (3.2 g, 5 mmol) in pentane was added slowly at -40°C. A violet solution was obtained. Then at the same temperature 0.79 g (5 mmol) of NaC\(_5\text{Me}_5\), containing an adventitious amount of NaC\(_5\text{H}_5\), in 20 ml of THF was added in one experiment. In another experiment a solution of 0.44 g (5 mmol) of NaC\(_5\text{H}_5\) in 20 ml of THF was added slowly. In both the cases the colour of the solutions changed to dark red. The reaction mixture was stirred for another 3 hours, concentrated to 20 ml by removing the solvents under vacuum and then filtered through a fine frit. The

Dedicated to Dr. P. Lingamah, Professor of Chemistry, Kakatiya University on his 60\(^{th}\) Birthday and retirement from the service in November 2001.
concentrated solution was left in a deep freezer at about -25°C. Purple crystals were found after 2 days, which were filtered (0.26 g, 14%) and used for CHM analyses and recording IR spectra. Analytical results: Found (\%) - C, 50.42, H, 6.25, Sm, 35.13, calculated for C_{18}H_{26}O_{2}Sm (\%) - C, 50.9, H, 6.17, Sm, 35.4. IR (Nujol/polychlorofluoroethylene oil, cm\(^{-1}\)) 3080, 1475, 1347, 1308, 1263, 1070, 1008, 775, 740 assignable to \(\nu(C-H)\) and \(\delta(C-H)\) of Cp and 2980, 2880, 1375, 725 and 565 attributable to coordinated THF.

X-ray crystallography of (C\(_5\)H\(_5\))\(_2\)Sm(THF)\(_2\)

A single crystal measuring 0.49 \times 0.27 \times 0.23 mm was selected from the suspension taken in a device reported by Veith and Barninghausen\(^7\). It was fastened to a glass fiber with grease and placed in the cold nitrogen stream in the X-ray diffractometer, Enraf-Nonius CAD4.

The data were collected by the \(\omega\)-20 scan technique with Mo-K\(_\alpha\) radiation (\(\lambda\), 71.073 pm). The parameters are given in Table 1. The final lattice parameters were determined from least squares refinement of intensities in the limits 0 \(\leq h \leq 15, 0 \leq k \leq 11, -16 \leq l \leq 16); from 20 values of 25 computer centered reflections in the range of 1 \(\leq 2\theta \leq 53^\circ\), measured at 110 K. Initial investigation showed the crystal system to be monoclinic with space group Cc, and C2/c from the systematic absent reflections. The successive refinements confirm the C2/c space group. Three reflections were checked every hour and the maximum fluctuation was found to be -1.7%. The crystal orientation was checked after each 200 intensity measurements by scanning three orientation check reflections. In case of angular change greater than 0.1° an array of 25 reflections was re-centered. The intensities were corrected for Lorentz and polarization effects. No absorption correction was made (\(\mu = 32.37\) cm\(^{-1}\)).

The positional parameters of the samarium atom were calculated from the Patterson map. A difference Fourier map based on the metal atom phase revealed
the positions of all non-hydrogen atoms. Least squares refinement with isotropic thermal parameters led to $R = \Sigma ||F_o|-|F_c||/\Sigma |F_o| = 0.037$. The hydrogen atom positions were calculated ($d_C-H = 0.95$ pm) and added to the structure model with constant temperature factor ($U_{iso-H} = 0.08 \text{ Å}^2$). After all atoms in the structure have been positioned, the empirical absorption corrections were made (minimum and maximum correction factors were 0.666 and 1.736). The final difference Fourier showed a maximum electron density of 1.05 e/Å$^3$ near the heavy metal.

All calculations were performed with the programme SHELX-76. Atomic scattering factors for Sm were taken from ref. 29, and anomalous dispersion terms from ref. 30 (The data have been deposited at the Fachinformationzentrum Energie, Physik, Mathematik GmbH, D-7514, number CSD 53204). Additional data pertaining to the crystal structure determination are summarized in Table 1. Selected interatomic distances and angles are listed in Table 2.

### Results and discussion

Namy et al., have reported the synthetic applications of the insoluble (C$_6$H$_5$)$_2$Sm(THF)$_2$ in Barbier type reactions between alkyl halides and aldehydes/ketones. The reactions of the soluble complex (C$_6$Me$_3$)$_2$Sm(THF)$_2$ were investigated extensively which resulted in interesting products, (C$_6$Me$_3$)$_2$Sm$^+$, (C$_6$Me$_3$)$_2$SmI$_2$(N$_2$)$^-$(1) and [[(C$_6$Me$_3$)$_2$Sm(THF)] [Co(CO)$_3$]]. Because of the insolubility of the complex, (C$_6$H$_5$)$_2$Sm(THF)$_2$, it was characterized by elemental analysis, magnetic susceptibility and IR spectral data only. Deacon et al. have obtained the soluble derivative of Sm(II) with cyclopentadienyl by reduction of (C$_6$H$_5$)$_2$Sm with potassium in presence of benzophenone in THF. They reported the DME soluble species as K$_2$[(C$_6$H$_5$)$_2$Sm]$_3$.

In one of our attempts to prepare heteroleptic Sm(II) and Yb(II) derivatives, containing a pentahapto ligand, C$_6$H$_5$/C$_6$Me$_3$ and an alkyl group, we observed the formation of compound, I in crystalline form. Earlier, we have reported the preparation of (C$_6$H$_5$)$_2$YbCl(THF)$_2$. The reaction of (C$_6$H$_5$)$_2$YbCl(THF)$_2$ with RLi did not give any characterizable product. Then we have tried another route for the preparation of the organolanthanides.

SmX$_2$ + BuLi $\rightarrow$ 40°C THF $\rightarrow$ 40°C NaC$_5$H$_5$ I + Y ... (1)

On addition of BuLi to the suspension of red SmI$_2$, a violet solution was obtained, which turned red on addition of NaC$_5$H$_5$ in THF. From the concentrated reaction mixture, after removal of alkali metal halides, red crystals were obtained which analyzed for the formula C$_6$H$_5$O$_2$Sm. The other substance Y could not be characterized. Further, the IR spectrum of the product was the same as reported for (C$_6$H$_5$)$_2$Sm(THF)$_2$. The formation of the compound was attributed to the presence of an adventitious quantity of NaC$_5$H$_5$ or BuLi, and the compound I was crystallized from the solution as its solubility is very low. Then similar reactions were repeated with NaC$_5$H$_5$. The same colour changes were observed. The solid obtained exhibited similar IR spectrum and analytical data were also identical. Then we have tried to obtain the $^1$H NMR spectrum of the complex as follows. A few drops of the reaction mixture was dried completely in a Schlenk flask to which an NMR tube was fused, and THF-d$_8$ was added to the flask. The solid dissolved completely. The solubility of the title compound in the present investigation may be attributed to the presence of a slight excess of BuLi and/or NaC$_5$H$_5$, which solubilize the Sm(II) complex by forming an ion pair as reported by Deacon et al.

The principal signals in the spectrum [δ, ppm] are 5.5 (C$_5$H$_5$), 3.5 and 1.6 (THF $H's$) and another signal at -18.6 was observed, which may be due to the Bu-protons (a satisfactory analysis could not be obtained for the species in the solution).

**Molecular structure of (C$_6$H$_5$)$_2$Sm(THF)$_2$**

The ORTEP diagram of the crystal structure of the complex (C$_6$H$_5$)$_2$Sm(THF)$_2$ is given in Fig. 1. The crystal data, atomic positional parameters, anisotropic
Table 3—Structural data of divalent organolanthanides, \((\text{C}_n\text{R}_3)_2\text{M.D}_n\) (D = donor molecules, \(n = 2\) or 1)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Average M–C distance, Å</th>
<th>M–D distance, Å</th>
<th>Cp–M–Cp angle (deg)</th>
<th>D–M–D angle (deg)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}<em>6\text{H}</em>{5})_2\text{Yb(DME)})</td>
<td>2.72</td>
<td>2.45(3) O 2.50(3) O</td>
<td>129</td>
<td>67.2(9)</td>
<td>22</td>
</tr>
<tr>
<td>([\text{MeC}<em>6\text{H}</em>{5}]\text{Yb(THF)}) (\mu -\text{MeC}<em>6\text{H}</em>{5})</td>
<td>2.76, 2.87, 2.91</td>
<td>2.53(2) O</td>
<td>–</td>
<td>–</td>
<td>23</td>
</tr>
<tr>
<td>((\text{C}<em>6\text{Me}</em>{3})\text{Yb(NC}_4\text{H}_2))</td>
<td>2.74</td>
<td>2.586(7) N 2.544(6) N</td>
<td>136.3(3)</td>
<td>82.5(2)</td>
<td>24</td>
</tr>
<tr>
<td>([\text{C}<em>8\text{H}</em>{8}\text{CH}_3\text{H}_2\text{Yb(THF)}]_2)</td>
<td>2.706</td>
<td>2.42(1) O 2.41(1) O</td>
<td>127(1)</td>
<td>82.4(5)</td>
<td>14</td>
</tr>
<tr>
<td>((\text{C}<em>6\text{Me}</em>{3})\text{Eu})</td>
<td>2.79(1)</td>
<td>–</td>
<td>140.3</td>
<td>–</td>
<td>12</td>
</tr>
<tr>
<td>((\text{C}<em>6\text{Me}</em>{3})\text{Sm})</td>
<td>2.79</td>
<td>–</td>
<td>140.1</td>
<td>–</td>
<td>11.12</td>
</tr>
<tr>
<td>((\text{C}<em>8\text{H}</em>{8})\text{Sm(THF)}_2)</td>
<td>2.86</td>
<td>2.61(2) O 2.65(2) O</td>
<td>136.7</td>
<td>82.6(4)</td>
<td>2.10</td>
</tr>
<tr>
<td>([\text{C}<em>6\text{Me}</em>{3}]\text{Sm(μ-I)(THF)}_2)</td>
<td>2.81(2)</td>
<td>2.62(2) O 2.66(2) O</td>
<td>–</td>
<td>73.5(6)</td>
<td>10</td>
</tr>
<tr>
<td>((\text{C}<em>6\text{Me}</em>{3})\text{SmCl(DME),DME})</td>
<td>2.79</td>
<td>2.52(1) O 2.61(2) O</td>
<td>140.0</td>
<td>62.8(4)</td>
<td>13</td>
</tr>
<tr>
<td>((\text{C}<em>8\text{H}</em>{8})\text{Sm(THF)}_2) ([\text{C}<em>6\text{Me}</em>{3}]\text{Sm^*}][\text{I(N)}_2])</td>
<td>2.69(2)</td>
<td>2.407(4) O</td>
<td>129.8(1)</td>
<td>82.0(2)</td>
<td>5</td>
</tr>
<tr>
<td>((\text{C}<em>6\text{Me}</em>{3})\text{Sm^*}][\text{I(N)}_2])</td>
<td>2.73(2)</td>
<td>2.3 N 2.4 N</td>
<td>129.8(1)</td>
<td>82.0(2)</td>
<td>5</td>
</tr>
</tbody>
</table>

#(1–Sm–1), @ Sm in +3 oxidation state, $ Present work

The smallest (ring centroid)–Sm–(ring centroid) angle of 120° was reported for the Sm(III) complex in \((\text{C}_6\text{Me}_{3})\text{Sm}\). The observed angle in the compound I, 129.8(1)°, is the smallest angle observed to date for a Sm(II) complex. The angle in other pentamethylcyclopentadienyl complexes is in the range of 136.7°-140.1°. This smallest Cp–Sm–Cp angle indicates less steric interactions between the \(\text{C}_8\text{H}_{8}\) rings as compared to the \(\text{C}_6\text{Me}_{3}\) rings. The smallest (ring centroid)–Yb–(ring centroid) angle, 127(1)°, was found in the case of ring bridged complex \([\text{C}_8\text{H}_{8}\text{CH}_3\text{H}_2\text{Yb(THF)}]_2\). While in the case of an open Cp\(_2\) complex with a chelating solvent molecule (DME) the rings are slightly far apart, 129°, in \((\text{C}_8\text{H}_{8})\text{Yb(DME)}_2\). The O-Sm-O angle, 82.0(2)° is in the same order as observed in similar complexes with monodentate THF\(_2\) and pyridine\(_2\) coordinated to Sm(II) and Yb(II).

The average Sm–C(ring) distance in I, 2.69 Å, is the shortest observed to date between ring carbon atoms and Sm(II) [2.79-2.86 Å], and is close to that reported in cyclopentadienyl\(_2\) and ring bridged...
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References