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Synthesis and crystal structure of $[(\text{Me}_4\text{C}_2\text{Cp}_2\text{SmCl} \cdot \text{MgCl}_2 \cdot 3\text{THF})\text{THF}]_2$

Chaode Sun, Gecheng Wei, Zhongsheng Jin and Wenqi Chen

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022 (China)

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Abstract

$[(\text{Me}_4\text{C}_2\text{Cp}_2\text{SmCl} \cdot \text{MgCl}_2 \cdot 3\text{THF})\text{THF}]_2$ was prepared by the reaction of $\text{Me}_4\text{C}_2\text{Cp}_2\text{MgCl}_2 \cdot 4\text{THF}$ (Cp = C_5H_4 , THF = tetrahydrofuran) with SmCl_3 in THF. The crystals belong to triclinic space group $P\bar{1}$ with a 12.149(3), b 13.187(4), c 13.810(5) Å, α 117.23(2), β 94.07(2), γ 62.86(2)°, $V = 1723.9(1.0)$ Å³. In the molecular structure of the title compound there is a symmetrical centre and a quadrilateral formed by Sm, Mg, Cl₁, Cl₂ atoms. Two centroids of the cyclopentadienyls, bridged by a tetramethylethano group form with three bridging chlorine atoms (Cl₁, Cl₂, Cl_{1a}) a pseudo-trigonal bipyramid around Sm. Three oxygen atoms of THF and three chlorine atoms (Cl₁, Cl₂, Cl₃) constitute a distorted octahedron around Mg.

1. Introduction

In order to prevent the disproportionation of bis(cyclopentadienyl) lighter lanthanide chlorides the bridged bis(cyclopentadienyl) group is customarily used as a ligand [1–3]. However, a few crystal structures of lanthanide compounds bearing bridged bis(cyclopentadienyl) ligand such as $(\text{Me}_2\text{SiCp}_2\text{NdCl}_2)_2\text{Cl}^- \text{Li}^+$ (thf)₂ [4], $\text{Me}_2\text{SiCp}_2\text{NdCH}(\text{SiMe}_3)_2$ [4], $(\text{CH}_2)_3\text{Cp}_2\text{Yb}(\text{thf})_2$ [5], $(\text{Me}_4\text{C}_2\text{Cp}_2\text{YbCl}_2)^- (\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF})^+$ [6], $\text{Me}_4\text{C}_2\text{Cp}_2\text{SmC}_5\text{H}_5$ [7] and $[\text{IME}_4\text{C}_2\text{Cp}_2\text{SmCl} \cdot \text{THF}]_2$ [8] have been reported. Here we report the synthesis and crystal structure of a new type of tetramethylethano-bridged bis(cyclopentadienyl)samarium chloride.

2. Experimental section

2.1. Preparation of the crystal

Solid SmCl_3 (0.9 g, 3.5 mmol) in a glass bottle was heated over a naked flame under reduced pressure for several minutes, the glass bottle cooled by filling it with nitrogen, and THF (40 ml) was added. The resulting solution was left to stand overnight. To the SmCl_3 solution was added $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4\text{MgCl})_2 \cdot (\text{THF})_4$ (2.87

g, 5.25 mmol) and the mixture was allowed to react with stirring for two days. THF was removed and toluene (20 ml) was added to the residue with stirring for half an hour. The toluene solution was centrifuged to remove undissolved solids and the resulting clear solution was evaporated to dryness. The residue was dissolved in THF and to the resulting solution was added a suitable amount of hexane which was then left to stand overnight. At room temperature a yellow fragment of crystal was obtained in ca. 50% yield.

2.2. Determination of crystal structure

A single crystal of dimensions $0.24 \times 0.44 \times 0.55$ mm was selected for structure analysis. Diffraction data were collected on a Nicolet R3m/E four-circle diffractometer using a graphite monochromator, Mo K α radiation (0.71069 Å), ω scan mode, scan speed of 7°/min and scan width of 1.2°. A total of 6566 reflections was measured within the range of $3 < 2\theta < 54^\circ$, of which 3529 reflections with $I > 3\sigma(I)$ were considered observed. Intensities were corrected for Lp factors and absorption effect. The crystal data are listed in Table 1.

The coordinates of samarium atom derived from Patterson analysis and other non-hydrogen atoms were found by difference Fourier maps. The atomic coordinates and anisotropic temperature factors for all non-hydrogen atoms were refined by block-matrix least-squares. The coordinates of hydrogen atoms were cal-

Correspondence to: Dr. W. Chen.

TABLE 1. Crystal data

[(Me ₄ C ₂ Cp ₂ SmCl·MgCl ₂ ·3THF)THF] ₂	M.W. 1563.5
triclinic	Space group $P\bar{1}$
<i>a</i> 12.149(3) Å	<i>b</i> 13.187(4) Å
<i>c</i> 13.810(5) Å	α 117.23(2)°
β 94.07(2)°	γ 62.86(2)°
<i>V</i> 1723.9(1.02) Å ³	<i>Z</i> = 1
<i>F</i> (000) = 802	<i>D_c</i> 1.51 g/cm ³
μ 20.2 cm ⁻¹ (Mo K α , λ = 0.71069 Å)	

culated according to theoretical models. Further refinements led to final $R = 0.0771$, $R_w = 0.0798$ ($w = [\sigma^2(F_o) + gF_o^2]^{-1}$). The calculations were performed on an Eclipse S/140 computer using SHELXTL programs.

Atomic coordinates and isotropic thermal parameters, selected bond lengths and bond angles are given in Tables 2, 3 and 4, respectively.

3. Results and discussion

Figure 1a gives a view of the title complex. There is a symmetrical centre in the molecule of [(Me₄C₂Cp₂SmCl·MgCl₂·3THF)THF]₂. Two centroids of cyclopentadienyl rings and three chlorine atoms (Cl₁, Cl₂, Cl_{1a}) (Fig. 2a) form a distorted trigonal bipyramid around Sm. The coordination number of Sm is 9. Three THF oxygen atoms, two chlorine atoms (Cl₁ and Cl₂) and one chlorine atom form an octahedron around Mg. The coordination number of Mg is 6. The average value of Sm–C(η^5 -Cp₁) is 2.66(9) Å, Sm–C(η^5 -Cp₂) 2.68(5) Å; Sm–Cp₁ (centroid) 2.38 Å, Sm–Cp₂ (centroid) 2.40 Å. Angle Cp₁–Sm–Cp₂ is 117.4° (Sm coordination number is 9). In (Me₄C₂Cp₂YbCl₂)⁻(Mg₂Cl₃·6THF)⁺ [6] angle Cp₁–Yb–Cp₂ is 121.0° (Yb coordination number 8). In Me₄C₂Cp₂SmC₅H₅(THF) [7] angle Cp₁–Sm–Cp₂ is 111.5° (Sm coordination number 10). Angle Cp₁–Sm–Cp₂ in the title compound is intermediate between those of Cp₁–Yb–Cp₂ and Cp₁–Sm–Cp₂(Me₄C₂Cp₂SmC₅H₅). This is explained by the hypothesis that the size of the angle Cp₁–Ln–Cp₂ is related to the coordination number of Ln atom, which increases as angle Cp₁–Ln–Cp₂ decreases. The coordination number of [(Me₄C₂Cp₂SmCl·THF)₂] is equal to that in the title compound and angle Cp₁–Sm–Cp₂ [(Me₄C₂Cp₂SmCl·THF)₂] is 115.4°, near to that for Cp₁–Sm–Cp₂ (title compound).

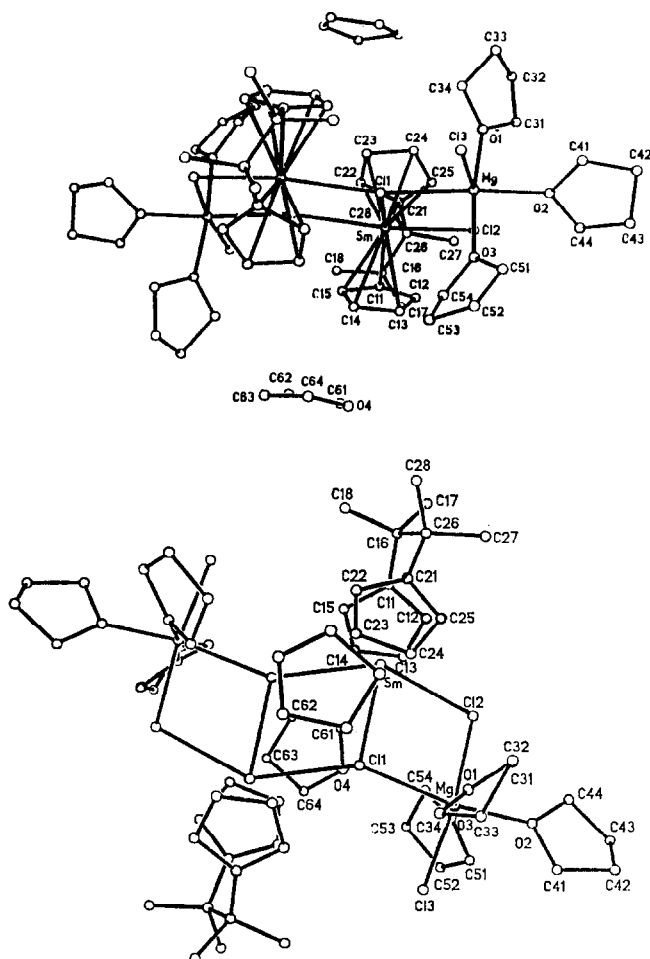
Angles C₁₁–C₁₆–C₂₆ and C₂₁–C₂₆–C₁₆ are 114.0(15)° and 110.6(12)°, respectively. In Me₄C₂Cp₂SmC₅H₅(THF) angles C₁₁–C₁₆–C₂₆ and C₂₁–C₂₆–C₁₆ are 111.8° and 110.3°, and in (Me₄C₂Cp₂YbCl₂)⁻(Mg₂Cl₃·6THF)⁺ (THF) these two angles are 114.6°. The conformation of the Cp rings (Fig. 1b) in the title

TABLE 2. Atomic coordinates ($\times 10^4$) and thermal parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Sm	4767(1)	6556(1)	-485(1)	26(1)
Cl(1)	3743(4)	6135(2)	998(2)	36(2)
Cl(2)	2883(4)	8977(2)	1108(2)	35(2)
Cl(3)	1134(4)	7777(3)	3240(2)	45(2)
Mg	1846(5)	8509(3)	2254(3)	33(3)
O(1)	679(11)	8210(7)	1085(7)	33(5)
O(2)	486(10)	10444(7)	3057(7)	38(4)
O(3)	2893(11)	9052(8)	3458(7)	47(5)
O(4)	7793(19)	7221(13)	3943(17)	132(13)
C(11)	6429(16)	6964(9)	-1254(9)	39(6)
C(12)	5747(16)	8093(10)	-238(10)	40(8)
C(13)	6068(17)	7759(11)	619(10)	39(8)
C(14)	6906(17)	6443(12)	137(11)	45(9)
C(15)	7121(15)	5952(10)	-993(11)	39(8)
C(16)	6395(18)	6887(11)	-2401(9)	49(9)
C(17)	6859(15)	7821(10)	-2360(10)	42(7)
C(18)	7428(18)	5506(11)	-3214(10)	45(9)
C(21)	4424(15)	6690(10)	-2374(8)	33(7)
C(22)	4770(15)	5379(10)	-2683(8)	27(7)
C(23)	3911(18)	5295(12)	-2231(9)	43(9)
C(24)	2840(18)	6596(12)	-1592(10)	40(9)
C(25)	3219(16)	7426(11)	-1707(10)	40(8)
C(26)	5088(17)	7231(10)	-2745(8)	46(8)
C(27)	4241(21)	8714(10)	-2255(11)	58(9)
C(28)	5214(20)	6670(14)	-4008(10)	57(10)
C(31)	-2(15)	9057(9)	612(10)	36(6)
C(32)	-764(20)	8531(14)	-111(12)	61(12)
C(33)	-1046(17)	7822(14)	397(12)	40(10)
C(34)	238(18)	7273(13)	736(11)	36(10)
C(41)	-748(16)	10895(11)	3634(11)	45(7)
C(42)	-1543(16)	12347(11)	4074(11)	43(7)
C(43)	-486(18)	12678(11)	4274(11)	60(9)
C(44)	596(18)	11569(11)	3299(11)	42(9)
C(51)	2407(23)	9777(20)	4628(12)	71(14)
C(52)	3428(23)	9374(21)	5164(15)	99(15)
C(53)	4639(22)	8458(19)	4314(14)	72(13)
C(54)	4211(19)	8636(13)	3325(11)	59(10)
C(61)	8265(33)	6998(21)	2971(17)	146(23)
C(62)	9118(28)	5573(26)	2314(17)	141(20)
C(63)	9175(27)	5008(21)	3050(24)	107(19)
C(64)	8157(29)	6134(22)	4001(22)	107(21)

TABLE 3. Bond lengths (Å)

Sm–Cl(1)	2.842(4)	Sm–Cl(2)	2.809(2)
Sm–C(11)	2.705(20)	Sm–C(12)	2.675(20)
Sm–C(13)	2.660(19)	Sm–C(14)	2.638(20)
Sm–C(15)	2.647(19)	Sm–C(21)	2.685(13)
Sm–C(22)	2.703(11)	Sm–C(23)	2.685(17)
Sm–C(24)	2.696(19)	Sm–C(25)	2.657(16)
Sm–Cl(1a)	2.896(3)	Cl(1)–Mg	2.672(4)
Cl(1)–Sma	2.896(3)	Cl(2)–Mg	2.520(8)
Cl(3)–Mg	2.382(8)	Mg–O(1)	2.091(12)
Mg–O(2)	2.072(7)	Mg–O(3)	2.083(12)
C(16)–C(17)	1.551(29)	C(16)–C(18)	1.548(15)
C(16)–C(26)	1.545(27)	C(21)–C(26)	1.531(28)
C(26)–C(27)	1.547(15)	C(26)–C(28)	1.538(17)
C(11)–C(16)	1.538(19)		

Fig. 1. Structure of [(Me₄C₂Cp₂SmCl · MgCl₂ · 3THF)THF]₂.

compound is different from that of nonbridged Cp rings. The bridged Cp rings have an almost eclipsed conformation. The tetramethylethylene adopts a distorted staggered conformation with the torsion angles:

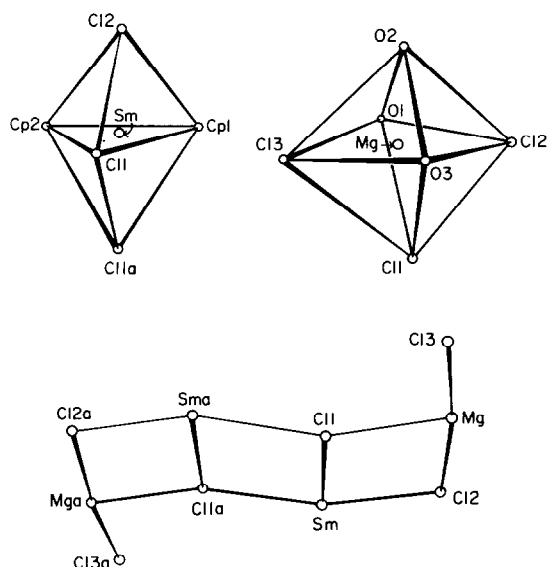


Fig. 2. Perspective drawing of atom space arrangement.

$C(11)-C(16)-C(26)-C(21) = -38.6(1.2)^\circ$, $C(17)-C(16)-C(26)-C(27) = -37.0(1.6)^\circ$, $C(18)-C(16)-C(26)-C(28) = -38.0(2.1)^\circ$, these three angles are almost equal. The average lengths of the $C(16)-C(17)$ and $C(26)-C(27)$ bonds is $1.549(22)$ Å; the average value of $C(16)-C(18)$ and $C(26)-C(28)$ is $1.543(16)$ Å. Both bond lengths are almost the same, which is not the case in $(Me_4C_2Cp_2YbCl_2)^-(Mg_2Cl_3 \cdot 6THF)^+(THF)$ [6].

In $[(Me_4C_2Cp_2SmCl \cdot MgCl_2 \cdot 3THF)THF]_2$ there are three kinds of chlorine atoms. The Cl₁ atom links to Sm, Sm_a and Mg with μ_3 -Cl; the Cl₂ links to Sm and Mg with μ_2 -Cl; the Cl₃ links to Mg with μ_1 -Cl. There are three kinds of Sm-Cl distances, $Sm-Cl_1(\mu_3) = 2.842(4)$ Å, $Sm-Cl_2(\mu_2) = 2.809(2)$ Å, $Sm-Cl_{1a}(\mu_3)$

TABLE 4. Bond angles (°)

Cl(1)-Sm-Cl(2)	72.2(1)	Cl(2)-Sm-Cl(1a)	142.8(1)
Cl(1)-Sm-Cl(1a)	71.3(1)	Sm-Cl(1)-Sm _a	108.7(1)
Sm-Cl(1)-Mg	101.3(2)	Sm-Cl(2)-Mg	106.1(1)
Mg-Cl(1)-Sm _a	150.0(2)	Cl(1)-Mg-Cl(3)	92.3(2)
Cl(1)-Mg-Cl(2)	79.7(2)	Cl(1)-Mg-O(1)	91.6(2)
Cl(2)-Mg-Cl(3)	171.8(2)	Cl(3)-Mg-O(1)	92.7(4)
Cl(2)-Mg-O(1)	89.5(4)	Cl(2)-Mg-O(2)	90.2(4)
Cl(1)-Mg-O(2)	169.8(5)	O(1)-Mg-O(2)	87.4(4)
Cl(3)-Mg-O(2)	97.9(4)	Cl(2)-Mg-O(3)	87.6(5)
Cl(1)-Mg-O(3)	94.3(3)	O(1)-Mg-O(3)	172.7(4)
Cl(3)-Mg-O(3)	91.1(4)	Mg-O(1)-C(31)	125.4(9)
O(2)-Mg-O(3)	86.0(4)	C(11)-C(16)-C(17)	106.4(13)
C(11)-C(16)-C(18)	105.9(11)	C(11)-C(16)-C(26)	114.0(15)
C(17)-C(16)-C(26)	110.9(12)	C(18)-C(16)-C(26)	113.5(12)
C(16)-C(26)-C(21)	110.6(12)	C(16)-C(26)-C(27)	112.0(14)
C(21)-C(26)-C(27)	108.8(14)	C(16)-C(26)-C(28)	110.4(14)
C(21)-C(26)-C(28)	109.1(15)		

TABLE 5. Atom plane equations and dihedral angles of $(\text{Me}_4\text{C}_2\text{Cp}_2\text{SmCl} \cdot \text{MgCl}_2 \cdot 3\text{THF})\text{THF}]_2$

Plane	Equation, atoms and deviation of atoms	Dihedral angles
1	$9.214x + 2.502y + 8.005z = 5.7130$ Sm Cl ₁ Cl ₂ Mg -0.0684 0.0701 0.0769 -0.0786	
2	$9.298x + 3.724y + 7.474z = 6.5111$ Cl ₁ Sm Cl _{1a} Sm _a 0.000 0.000 0.000 0.000	5.8
3	$9.214x + 2.502y + 8.005z = 6.0037$ Sm _a Cl _{1a} Cl _{2a} Mg _a 0.0684 -0.0701 -0.0769 0.0786	0.0 5.8

= 2.896(3) Å. Sm-Cl₁(μ^3) and Sm-Cl_{1a}(μ_3) distances are greater than that of Sm-Cl₂(μ_2).

In title complex there are three different kinds of Mg-Cl bond lengths: Mg-Cl₃(μ_1) = 2.362(6) Å, Mg-Cl₂(μ_2) = 2.520(8) Å, Mg-Cl₁(μ_3) = 2.672(4) Å. Length of the Mg-Cl₂(μ_2) bond is similar to the corresponding Mg-Cl(μ_2) bond in $(\text{Me}_4\text{C}_2\text{Cp}_2\text{YbCl}_2)^- (\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF})^+\text{THF}$ [6]. The three Mg-O(THF) bond lengths (Mg-O(1) 2.091(12), Mg-O(2) 2.072(7), Mg-O(3) 2.083(12) Å) are almost equal. The average length of

Mg-O bonds is 2.08(2) Å. From Fig. 2b and Table 5 it can be seen that Sm, Cl and Mg form three planar quadrilaterals. Sm_a, Cl₁, Cl_{1a}, Sm form a parallelogram. The nip angle between the planes formed by Mg₁, Cl₁, Cl₂, Mg (or Mg_a, Cl_{1a}, Cl_{2a}, Sm_a) and Sm_a, Cl₁, Cl_{1a}, Sm is 5.8°. The three quadrilaterals adopt a chair conformation. The Sm-Sm_a distance is 4.66(3) Å and for Mg-Sm 4.26(4) Å.

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