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The formation and molecular structure of $(\eta^5\text{-}C_5H_5)_3Sm \cdot OC_4H_8$

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Abstract

Reaction of 1/2 mole ratio of $(\eta^5\text{-}C_5H_5)SmCl_2 \cdot 3THF$ and $NaC{\equiv}CCH_2OCH_2CH{=}CH_2$ in THF solution resulted in the formation of $(\eta^5\text{-}C_5H_5)_3Sm \cdot OC_4H_8$; the complex crystallizes in monoclinic space group $P2_1/n$ with unit cell constants $a = 8.254(5)$, $b = 24.63(1)$, $c = 8.339(3)$ Å, $\beta = 101.33(5)°$ and $D_c = 1.67$ g/cm^3 for $Z = 4$. Refinement has led to a final R value of 0.041 based on 2106 independent observed reflections. The THF molecule is coordinated to the samarium atom at a Sm–O distance of 2.522(6) Å. The Sm–C(cyclopentadienyl) bond lengths range from 2.70(1) to 2.80(1) Å and average 2.742(1) Å. A comparison of some significant structural parameters along the isostructural series $(\eta^5\text{-}C_5H_5)_3Ln \cdot THF$ (Ln = La, Pr, Nd, Gd, Dy, Lu and Sm) with the ionic radii of Ln^{3+} was made.

Key words: Samarium; Cyclopentadienyl; Crystal structure

1. Introduction

Although some dicyclopentadienyl lanthanide alkynyl complexes, Cp_2Ln(alkynyl), have been reported [1–3], only one monocyclopentadienyl lanthanide bisalkynyl complex of the type $CpLn(alkynyl)_2$, namely $CpHo(C \equiv CPh)_2$ [4] has been synthesized and characterized. With the original intention of broadening the scope of research on $CpLn(alkynyl)_2$ type complexes, we attempted to synthesize $CpSm(C{\equiv}CCH_2OCH_2CH{=}CH_2)_2$. As a result, a fine crystal of $Cp_3Sm \cdot THF$, instead of $CpSm(C{\equiv}CCH_2OCH_2CH{=}CH_2)_2$ was obtained. Considering the series $Cp_3Ln \cdot THF$, the synthesis and structure of $Cp_3Sm \cdot THF$ have not been reported. We therefore investigated the structure of the title complex and compared some significant structural parameters of the isostructural series $Cp_3Ln \cdot THF$ (Ln = La [5], Pr [6], Nd [6,7], Gd [8], Dy [9], Lu [10] and Sm).

2. Results and discussion

The crystal of $Cp_3Sm \cdot OC_4H_8$ is monoclinic, space group $P2_1/n$ with unit cell constants $a = 8.254(5)$, $b = 24.63(1)$, $c = 8.339(3)$ Å, $\beta = 101.33(5)°$ and $D_c = 1.67$ g/cm^3 for $Z = 4$. The final values of the positional and thermal parameters are listed in Table 1, bond lengths and angles are in Table 2.

In some of our previous work [11–17], we reported that the organolanthanide complexes with both Cp and other ligands are comparatively unstable when heated, disproportionating, owing to rearrangement of ligands at different temperatures. We also found that complexes of the type $CpLnL_2$ (L = ligand) are less thermally stable than those of the type Cp_2LnL. The final disproportionation products of both $CpLnL_2$ and Cp_2LnL type complexes are Cp_3Ln and LnL_3. Rogers *et al.* [8] also pointed out that the formation of $Cp_3Gd \cdot THF$ is the result of the disproportionation reaction of $CpGdCl_2$ in THF solution. The same situation has been encountered in the reaction of 1/2 mole ratio of $(\eta^5\text{-}C_5H_5)SmCl_2 \cdot 3THF$ and $NaC{\equiv}CCH_2OCH_2CH{=}$

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CH_2 in THF with $Cp_3Sm \cdot OC_4H_8$ being the only identified product. Since after the initial filtration a pure solution was obtained, it seems likely that the formation of the title complex is the result of the disproportionation reaction shown below:

$$3CpSmCl_2 \cdot 3THF + 6NaC{\equiv}CCH_2OCH_2CH{=}CH_2 \xrightarrow{THF} \{3[CpSm(C{\equiv}CCH_2OCH_2CH{=}CH_2)_2]\} + 6NaCl$$

$$\{3[CpSm(C{\equiv}CCH_2OCH_2CH{=}CH_2)_2]\} \xrightarrow{THF} (\eta^5\text{-}C_5H_5)_3Sm \cdot OC_4H_8 + 2Sm(C{\equiv}CCH_2OCH_2CH{=}CH_2)_3$$

The molecule (Fig. 1) has a coordination sphere of three η^5-cyclopentadienyl ligands and one tetrahydrofuran ligand. The geometry around the samarium atom in this structure can be described as slightly distorted tetrahedral, with the centres of the three cyclopentadienyl rings and the oxygen atom of tetrahydrofuran forming the apices of the tetrahedron. In overall geometry, $(\eta^5\text{-}C_5H_5)_3Sm \cdot OC_4H_8$ bears a remarkable resemblance to $Cp_3La \cdot OC_4H_8$ [5], $Cp_3Pr \cdot OC_4H_8$[6], $Cp_3Nd \cdot OC_4H_8$ [6,7], $Cp_3Gd \cdot OC_4H_8$[8], $Cp_3Dy \cdot OC_4H_8$[9] and $Cp_3Lu \cdot OC_4H_8$ [10].

The fact that there are 15 lanthanide elements which have such a close mutual resemblance means that we can compare the influence of ionic radius on coordination geometry and crystal structures. Table 3 compares some significant structural parameters along the isostructural series $Cp_3Ln \cdot OC_4H_8$. The Sm–O distance of 2.522(6) Å appears short compared with the Nd–O length of 2.56(1) Å, but long in relation to the Gd–O length of 2.494(7) Å. The bond length Ln–O in the isostructural series $Cp_3\text{-}Ln \cdot OC_4H_8$, from La to Gd therefore presents a decreasing trend as the ionic radius of Ln^{3+} decreases. The three cyclopentadienyl ligands are coordinated to the samarium atom in an η^5-fashion with an average Sm–C length of 2.742(1) Å. The range extends from 2.70(1) to 2.80(1) Å. As can be seen (Table 3) the length of Ln–C, in general, decreases as the crystal radius of Ln^{3+} decreases.

Baker and Raymond [18] previously pointed out that $Cp_3Ln\text{-}X$ compounds are structurally similar to those formulated as $Cp_3U\text{-}X$. Thus, the centroid–U–centroid angles in $Cp_3U(C \equiv CPh)$ [19] average 117°, while the centroid–U–C(σ) angles are nearly 100°. In the title complex the corresponding average angles are 117.19° and 99.8°.

3. Experimental section

All manipulations were routinely performed under argon using Schlenk tubes with solvents and reactants purified and dehydrated by standard methods. Melting points were determined in sealed argon-filled capillaries. IR spectra was recorded on a Perkin-Elmer 983(G) spectrometer, and elemental analysis was carried out with a Yanaco MT-2 analyzer.

3.1. *Formation of $Cp_3Sm \cdot THF$*

To the suspension of 0.226 g (5.79 mmol) $NaNH_2$ in 30 ml THF was added dropwise 0.556 g (5.79 mmol) allylpropargyl ether, prepared by a literature method [21]. After the reaction was stirred for 10 h, a solution of $CpSmCl_2 \cdot 3THF$, prepared by a literature method

TABLE 1. Positional and thermal parameters

Atom	x	y	z	B_{eq}
Sm(1)	0.07864(6)	0.35570(2)	0.44590(5)	2.34(2)
O(1)	−0.1109(8)	0.4183(3)	0.2559(7)	3.3(3)
C(1)	−0.284(1)	0.4259(6)	0.262(1)	5.1(6)
C(2)	−0.371(2)	0.436(1)	0.091(2)	11.0(1)
C(3)	−0.252(2)	0.4516(8)	0.004(2)	9.0(1)
C(4)	−0.090(1)	0.4316(6)	0.091(1)	5.0(6)
C(11)	0.379(1)	0.3373(6)	0.367(2)	6.6(8)
C(12)	0.302(2)	0.378(1)	0.250(1)	8.0(1)
C(13)	0.299(2)	0.4254(8)	0.338(3)	7.6(9)
C(14)	0.372(2)	0.4158(7)	0.496(2)	6.1(7)
C(15)	0.414(1)	0.3643(7)	0.511(2)	5.4(6)
C(21)	−0.140(2)	0.2943(5)	0.229(2)	8.1(8)
C(22)	0.015(2)	0.2771(6)	0.212(2)	7.0(8)
C(23)	0.083(2)	0.2497(5)	0.350(1)	5.2(6)
C(24)	−0.022(2)	0.2509(5)	0.455(1)	5.0(6)
C(25)	−0.164(2)	0.2779(5)	0.382(2)	5.8(6)
C(31)	0.137(3)	0.4088(9)	0.742(2)	7.0(1)
C(32)	0.002(3)	0.4275(7)	0.674(2)	8.0(1)
C(33)	−0.119(1)	0.386(2)	0.662(2)	12.0(1)
C(34)	−0.020(5)	0.342(1)	0.736(3)	11.0(2)
C(35)	0.120(4)	0.359(1)	0.775(2)	10.0(1)
H(1)	−0.3274	0.3942	0.3031	6.1
H(2)	−0.2974	0.4561	0.3288	6.1
H(3)	−0.4246	0.4040	0.0453	12.8
H(4)	−0.4500	0.4642	0.0885	12.8
H(5)	−0.2771	0.4363	−0.1028	10.4
H(6)	−0.2500	0.4900	−0.0041	10.4
H(7)	−0.0087	0.4590	0.0945	6.0
H(8)	−0.0588	0.4003	0.0384	6.0
H(9)	0.4224	0.3032	0.3428	7.9
H(10)	0.2832	0.3747	0.1341	9.6
H(11)	0.2728	0.4603	0.2915	9.1
H(12)	0.4033	0.4428	0.5781	7.4
H(13)	0.4814	0.3496	0.6069	6.5
H(14)	−0.2226	0.3082	0.1439	9.7
H(15)	0.0552	0.2767	0.1125	8.4
H(16)	0.1792	0.2277	0.3619	6.2
H(17)	−0.0105	0.2295	0.5510	6.0
H(18)	−0.2663	0.2781	0.4187	7.0
H(19)	0.2324	0.4298	0.7826	8.8
H(20)	−0.0202	0.4650	0.6549	9.5
H(21)	−0.2358	0.3898	0.6419	13.8
H(22)	−0.0605	0.3094	0.7731	13.1
H(23)	0.2045	0.3389	0.8446	11.5

TABLE 2. Selected bond lengths (Å) and bond angles (°)

Sm(1)–O(1)	2.522(6)	C(1)–C(2)	1.48(2)
Sm(1)–C(11)	2.72(1)	C(2)–C(3)	1.38(2)
Sm(1)–C(12)	2.75(1)	C(3)–C(4)	1.47(2)
Sm(1)–C(13)	2.78(1)	C(11)–C(15)	1.36(2)
Sm(1)–C(14)	2.80(1)	C(11)–C(12)	1.45(2)
Sm(1)–C(15)	2.72(1)	C(12)–C(13)	1.39(2)
Sm(1)–C(21)	2.74(1)	C(13)–C(14)	1.36(2)
Sm(1)–C(22)	2.73(1)	C(14)–C(15)	1.31(2)
Sm(1)–C(23)	2.73(1)	C(21)–C(22)	1.38(2)
Sm(1)–C(24)	2.72(1)	C(21)–C(25)	1.39(2)
Sm(1)–C(25)	2.75(1)	C(22)–C(23)	1.35(2)
Sm(1)–C(31)	2.75(1)	C(23)–C(24)	1.35(2)
Sm(1)–C(32)	2.76(1)	C(24)–C(25)	1.38(2)
Sm(1)–C(33)	2.76(1)	C(31)–C(32)	1.23(2)
Sm(1)–C(34)	2.72(1)	C(31)–C(35)	1.27(3)
Sm(1)–C(35)	2.70(1)	C(32)–C(33)	1.42(3)
O(1)–C(1)	1.45(1)	C(33)–C(34)	1.42(3)
O(1)–C(4)	1.46(1)	C(34)–C(35)	1.21(3)
Sm(1)–Cent1	2.498	Sm(1)–Cent2	2.470
Sm(1)–Cent3	2.500		

Cent1–Sm1–Cent2	119.22	O(1)–Sm1–Cent1	101.12
Cent1–Sm1–Cent3	113.38	O(1)–Sm1–Cent2	96.3
Cent2–Sm1–Cent3	118.97	O(1)–Sm1–Cent3	101.92
C(1)–O(1)–C(4)	107.4(7)	C(1)–O(1)–Sm(1)	123.5(6)
C(4)–O(1)–Sm(1)	123.9(6)	O(1)–C(1)–C(2)	106(1)
C(3)–C(2)–C(1)	107(1)	C(2)–C(3)–C(4)	108(1)
O(1)–C(4)–C(3)	106.2(9)	C(13)–C(12)–C(11)	106(1)
C(15)–C(11)–C(12)	104(1)	C(14)–C(13)–C(12)	108(1)
C(15)–C(14)–C(13)	109(2)	C(14)–C(15)–C(11)	113(1)
C(22)–C(21)–C(25)	108(1)	C(23)–C(22)–C(21)	107(1)
C(24)–C(23)–C(22)	109(1)	C(23)–C(24)–C(25)	109(1)
C(24)–C(25)–C(21)	106(1)	C(32)–C(31)–C(35)	110(2)
C(31)–C(32)–C(33)	109(2)	C(32)–C(33)–C(34)	100(1)
C(33)–C(34)–C(35)	107(2)	C(34)–C(35)–C(31)	114(2)

Cent1 is the centroid of the C(11)–C(15) ring, Cent2 of the C(21)–C(25) ring and Cent3 of the C(31)–C(35) ring.

[20], 1.452 g, 2.89 mmol in THF was transferred to the thus formed sodium alkynylide, $NaC{\equiv}CCH_2OCH_2\text{-}CH{=}CH_2$, and the reaction mixture stirred at room temperature for another 10 h. The orange mixture was then centrifuged and the solution concentrated to about 10 ml. The orange crystal formed upon cooling. Yield 32% (0.42 g, based on $CpSmCl_2 \cdot 3THF$), melting point 212°C (colour darkening from 167°C), IR(cm^{-1}) ν(Sm–η^5-C_5H_5) 776, 1014, 1462, 3089, ν(Sm–OC_4H_8) 928, 1075. Found: C, 53.89; H, 5.57. Calc. for $C_{19}H_{23}OSm$ ($Cp_3Sm \cdot THF$): C, 54.61; H, 5.54%.

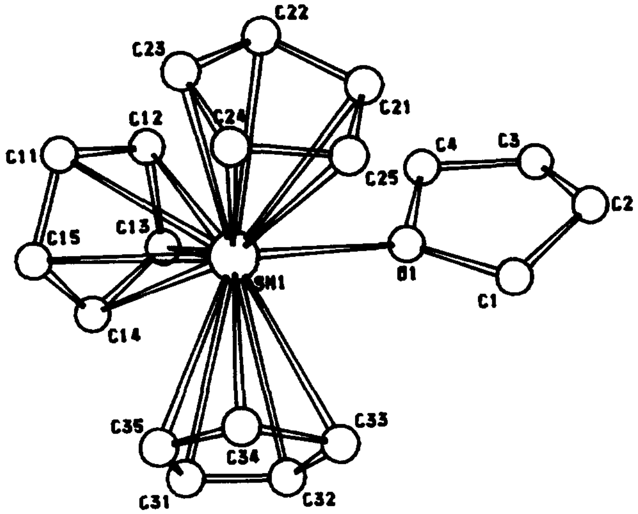

Fig. 1. Crystal structure of $(\eta^5\text{-}C_5H_5)_3Sm \cdot OC_4H_8$.

3.2. *Crystallography of $Cp_3Sm \cdot THF$*

A single crystal of the title complex with dimensions 0.6 × 0.3 × 0.15 mm was sealed in a thin-walled glass capillary under argon. Unit cell parameters and 3282 intensities were measured on a Rigaku AFC-5R diffractometer with Mo Kα radiation (λ = 0.71069 Å) in the range of $3° < 2\theta < 50°$ by $2\theta/\omega$ scanning. Corrections for Lp and absorption with empirical scanning technique were applied and 2106 independent reflections with $I > 3\sigma(I)$ were used in the structure determination. The heavy atom Sm was located by directed methods and other nonhydrogen atoms were obtained from successive difference Fourier synthesis. The convergence of the last stage of full-matrix least-squares refinement with nonhydrogen atoms anisotropically re-

TABLE 3. Significant structural parameters in the isostructural series $Cp_3Ln \cdot THF$

Compound		Ln^{3+} ionic radii (Å) [22]	Ln–O (Å)	Ln–Cent1 (Å)	Ln–Cent2 (Å)	Ln–Cent3 (Å)	Ln–C(av) (Å)
$Cp_3La \cdot THF$	[5]	1.36	2.57(1)	2.5	2.575	2.576	2.84(4)
$Cp_3Pr \cdot THF$	[6]	1.32	2.555(9)	2.54	2.55	2.51	2.80(2)
$Cp_3Nd \cdot THF$	[6]	1.30	2.54(1)	2.51	2.51	2.51	2.78(2)
$Cp_3Nd \cdot THF$	[7]	1.30	2.56(1)	2.52	2.55	2.54	2.79(4)
$Cp_3Sm \cdot THF$ [a]		1.27	2.522(6)	2.498	2.470	2.500	2.742(1)
$Cp_3Gd \cdot THF$	[8]	1.25	2.494(7)	2.47	2.49	2.49	2.74(3)
$Cp_3Dy \cdot THF$	[9]	1.20	2.522(5)	2.4772	2.5158	2.5071	2.74(8)
$Cp_3Lu \cdot THF$	[10]	1.17	2.39(2)	2.40	2.42	2.43	2.69(4)

[a] Present work.

fined and hydrogen atoms isotropically joined only in Fc calculations reached to $R = 0.041$, $R_w = 0.052$, ($w = 1/\sigma^2$(Fi)), $\Delta\max/\sigma = 0.11$ with the residual peaks in the final difference Fourier map $\Delta\rho_{\max} = -1.030$ to 0.807 e/Å^3. All calculations were performed on a MicroVAX-II computer with Rigaku/MSC TEXSAN V2.1 package.

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