

Synthesis and Characterization of Ethylthioethylcyclopentadienyl Organolanthanide Complexes: $\text{Cp}_2^{\text{Th}}\text{LnCl}$ ($\text{Ln}=\text{Gd}, \text{Dy}$), $\text{Cp}_2\text{LnCp}^{\text{Th}}$ ($\text{Ln}=\text{Yb}, \text{Sm}, \text{Dy}, \text{Y}$) and $\text{Cp}^{\text{Th}}\text{ErCl}_2\cdot 2\text{THF}^\dagger$

ZHU, Ming^a(朱铭) ZHANG, Li-Bei^a(张丽蓓) CHEN, Ying-Hua^a(陈应华)
 ZHOU, Xi-Geng^{*a,b}(周锡庚) CAI, Rui-Fang^a(蔡瑞芳) WENG, Lin-Hong^a(翁林红)

^a Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China

^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Six new ethylthioethylcyclopentadienyl-containing organolanthanide complexes $\text{Cp}_2^{\text{Th}}\text{LnCl}$ [$\text{Ln}=\text{Gd}$ (**1**), Dy (**2**)] and $\text{Cp}_2\text{LnCp}^{\text{Th}}$ [$\text{Cp}=\text{C}_5\text{H}_5$, $\text{Ln}=\text{Yb}$ (**3**), Sm (**4**), Dy (**5**), Y (**6**)] were synthesized by the reaction of ethylthioethylcyclopentadienyl (Cp^{Th}) sodium salt with LnCl_3 or Cp_2LnCl in THF. Complexes **1**—**6** were characterized by elemental analyses, infrared and mass spectroscopies. The molecular structures of complexes **1**—**3** were also determined by the X-ray single crystal diffraction. The results show that the side-chain sulfur atom on the ethylthioethylcyclopentadienyl ring can form intramolecular chelating coordination to the central lanthanide ion, improving the stability of organolanthanide complexes and reducing the number of coordinated THF molecules.

Keywords organolanthanide, substituted cyclopentadienyl, crystal structure, synthesis

Introduction

Functional substituted cyclopentadienyl organolanthanide complexes continue to attract considerable attention because these donor-functionalized side chains can increase the stability of highly reactive organolanthanide complexes by forming the additional intramolecular chelating coordination with the central metal, and for early lanthanide complexes, the enhanced stability offers the opportunity to explore the reactivity of the remaining ligands.¹⁻⁴ In addition, the intramolecular coordination may pose these complexes great difference in reactivities, structures and physical properties from the non-functionalized counterparts.^{5,6} Investigation are primarily focused on the synthesis of complexes with substituted cyclopentadienyl ligands containing strong donor atoms such as nitrogen⁷⁻¹⁵ and oxygen^{3,8,16-20} in their chains, whereas very few substituted cyclopentadienyl complexes with the sulfur-containing substituent have been reported to date.²¹ Considering that the strong intramolecular coordination should lead to the missing ability of the lanthanides to coordinate with other substrates, the weakly binding donor sulfur atom may favor ensuring the catalytic activity of the complexes, since sulfur is easily displaced by an incoming substrate compared to the strong donor

atoms of oxygen and nitrogen. Recently, Schumann and co-workers reported the properties of organolanthanide complexes with ethylthioethyl-substituted cyclopentadienyl ligand.²¹ To further understand the influence of the intramolecular coordination formed by the sulfur atom in the side chain on the structures and the properties of cyclopentadienyl organolanthanide complexes, we report here the synthesis and characterization of some new ethylthioethylcyclopentadienyl lanthanide derivatives $\text{Cp}_2^{\text{Th}}\text{LnCl}$ [$\text{Ln}=\text{Gd}$ (**1**), Dy (**2**)], and $\text{Cp}_2\text{LnCp}^{\text{Th}}$ [$\text{Ln}=\text{Yb}$ (**3**), Sm (**4**), Dy (**5**), Y (**6**)].

Experimental

All manipulations were carried out under nitrogen with rigorous exclusion of air and moisture using standard Schlenk techniques. All solvents were refluxed and distilled over sodium benzophenone ketyl prior to use. Anhydrous LnCl_3 ²² and Cp_2LnCl ²³ were prepared by the literature procedures. $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_3$ was purchased and used without further purification. $\text{Cp}^{\text{Th}}\text{H}$ was prepared by the reaction of CpNa with $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_3$ in THF at $-30\text{ }^\circ\text{C}$. $\text{Cp}^{\text{Th}}\text{Na}$ was prepared by the reaction of $\text{Cp}^{\text{Th}}\text{H}$ with Na in THF at ambient temperature.

Elemental analyses for carbon and hydrogen were

* E-mail: xgzhou@fudan.edu.cn; Tel.: +86-21-65643769; Fax: +86-21-65641740

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performed on a Rapid CHN-O analyzer. Metal analyses for lanthanides were accomplished using the literature method.²⁴ Melting points were determined in sealed nitrogen-filled capillaries and uncorrected. Infrared spectra were obtained on a NICOLET FT-IR 360 spectrometer with samples prepared as Nujol mulls. Mass spectra were recorded on a Philips HP5989A instrument operating in the EI mode at 70 eV.

Synthesis of Cp₂ThGdCl (1)

To a suspension of GdCl₃ (0.580 g, 2.20 mmol) in THF (30 mL) was added ethylthioethylcyclopentadienylsodium (0.240 mol/L, in THF, 9.2 mL) at room temperature. The mixture was stirred at room temperature for 24 h and then centrifuged. The solution was decanted from undissolved NaCl and concentrated by reduced pressure to *ca.* 4 mL. Crystallization by diffusion of hexane into the THF solution afforded colorless crystals of **1** (0.687 g, 62.6 %). m.p. 87 °C. IR (KBr) ν : 3176 (m), 3047 (m), 2955 (s), 2918 (s), 2851 (s), 2725 (m), 1465 (s), 1440 (m), 1381 (s), 1373 (s), 1268 (m), 1258 (m), 1153 (m), 1046 (m), 1027 (m), 768 (m), 717 (m) cm⁻¹; MS (EI) m/z (%): 499 (M⁺, 5), 464 (M⁺-Cl, 3), 435 (M⁺-Cl-Et, 1), 425 (M⁺-CHSEt, 1), 390 (M⁺-Cl-CHSEt, 2), 154 (CpThH, 34). Anal. calcd for C₁₈H₂₆ClGdS₂: C 43.32, H 5.25, Gd 31.51; found C 43.03, H 5.36, Gd 30.96.

Synthesis of Cp₂ThDyCl (2)

A solution of CpThNa (0.240 mol/L, 11.0 mL) in THF was added to a stirred suspension of DyCl₃ (0.874 g, 3.25 mmol) in THF (25 mL). The mixture was stirred at room temperature for 24 h and then centrifuged. The solution was decanted from undissolved NaCl, concentrated to *ca.* 5 mL and cooled to -18 °C to provide 1.16 g of **2** (yield 71%) as yellow crystals. m.p. 86 °C. IR (KBr) ν : 3166 (m), 3051 (s), 2958 (s), 2855 (s), 2727 (m), 1588 (m), 1465 (s), 1377 (s), 1301 (m), 1268 (m), 1051 (m), 1028 (m), 773 (m), 721 (s) cm⁻¹; MS (EI) m/z (%): 505 (M⁺, 8), 470 (M⁺-Cl, 2), 441 (M⁺-Cl-Et, 1), 431 (M⁺-CHSEt, 2), 352 (M⁺-CpTh, 21), 154 (CpThH, 30). Anal. calcd for C₁₈H₂₆ClDyS₂: C 42.86, H 5.20, Dy 33.16; found C 42.54, H 5.15, Dy 32.68.

Synthesis of Cp₂YbCpTh (3)

A solution of CpThNa (0.250 mol/L, 7.2 mL) in THF was added to a solution of Cp₂YbCl (0.610 g, 1.8 mmol) in THF (25 mL). The reaction mixture was stirred at room temperature for 24 h and then centrifuged. The dark-green solution was decanted from undissolved NaCl, concentrated to *ca.* 4 mL and cooled to -18 °C to provide 0.493 g (yield 60%) of green crystalline **3**. IR (KBr) ν : 3076 (s), 2951 (s), 2926 (s), 2717 (m), 1618 (m), 1459 (s), 1416 (m), 1376 (s), 1262 (m), 1127 (m), 1061 (m), 1020 (m), 1012 (m), 968 (m), 916 (m), 890 (m), 838 (m), 801 (m), 767 (s), 722 (s), 663 (m) cm⁻¹. Anal. calcd for C₁₉H₂₃SYb: C 50.00, H 5.08, Yb 37.91; found C 49.83, H 5.01, Yb 37.53.

Synthesis of Cp₂SmCpTh (4)

Using the procedure described for **3**, the reaction of CpThNa (1.24 mmol) and Cp₂SmCl (THF) (0.481 g, 1.24 mmol) in THF afforded 0.333 g of yellow crystals of **4** (yield 62%). IR (KBr) ν : 3078 (s), 2950 (s), 2720 (m), 1618 (m), 1460 (s), 1376 (s), 1260 (m), 1125 (m), 1060 (m), 1020 (m), 1012 (m), 970 (m), 890 (m), 800 (m), 770 (s), 721 (s), 663 (m) cm⁻¹; MS (EI) m/z (%): 433 (M⁺, 2), 372 (M⁺-SEt, 77), 368 (M⁺-Cp, 38), 303 (M⁺-2Cp, 18), 280 (M⁺-CpTh, 3), 215 (M⁺-CpTh-Cp, 13), 154 (CpThH, 22), 65 (CpH, 82). Anal. calcd for C₁₉H₂₃SSm: C 52.61, H 5.34, Sm 34.66; found C 52.42, H 5.20, Sm 34.50.

Synthesis of Cp₂DyCpTh (5)

Using the procedure described for **3**, the reaction of CpThNa (2.69 mmol) and Cp₂DyCl (0.437 g, 2.69 mmol) in THF afforded 0.756 g of yellow crystals of **5** (yield 63%). IR (KBr) ν : 2984 (s), 2926 (s), 2725 (m), 1621 (m), 1459 (s), 1377 (s), 1264 (m), 1132 (m), 1014 (m), 967 (m), 916 (m), 888 (m), 838 (m), 798 (m), 763 (m), 721 (s), 663 (m) cm⁻¹; MS (EI) m/z (%): 445 (M⁺, 4), 384 (M⁺-SEt, 5), 380 (M⁺-Cp, 76), 315 (M⁺-2Cp, 13), 292 (M⁺-CpTh, 8), 227 (M⁺-CpTh-Cp, 11), 154 (CpThH, 13), 65 (CpH, 21). Anal. calcd for C₁₉H₂₃DyS: C 51.18, H 5.20, Dy 36.44; found C 50.94, H 5.12, Dy 36.10.

Synthesis of Cp₂YCpTh (6)

Using the procedure described for **3**, the reaction of CpThNa (1.40 mmol) and Cp₂YCl (0.356 g, 1.40 mmol) in THF afforded 0.365 g of white crystals of **6** (yield 70%). IR (KBr) ν : 3072 (m), 2976 (s), 2925 (s), 2852 (s), 2716 (m), 1593 (m), 1457 (s), 1419 (m), 1376 (s), 1261 (m), 1132 (m), 1094 (m), 1010 (m), 970 (m), 916 (m), 862 (m), 838 (m), 801 (m), 759 (m), 722 (s), 663 (m) cm⁻¹; MS (EI) m/z (%): 372 (M⁺, 2), 311 (M⁺-SEt, 1), 307 (M⁺-Cp, 100), 242 (M⁺-2Cp, 3), 219 (M⁺-CpTh, 20), 154 (CpThH, 15), 65 (CpH, 19). Anal. calcd for C₁₉H₂₃SY: C 61.30, H 6.23, Y 23.88; found C 60.65, H 6.08, Y 23.52.

X-ray crystal structure determination of complexes 1—3

Suitable single crystals of complexes **1—3** were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART CCD diffractometer using graphite-monochromated Mo K α ($\lambda = 0.071073$ nm) radiation.²⁵ The structures were solved by direct methods using SHELXS-97²⁶ and were refined on F^2 using all observed reflections with SHELXL-97.²⁷ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in idealized positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in refinement. SADABS was used to perform area detector scaling and absorption corrections for the data.²⁸ All calculations were performed using the Bruker Smart

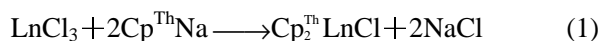
program. Crystal data and details of collection and refinement are summarized in Table 1.

Results and discussion

Synthesis of $\text{Cp}_2^{\text{Th}}\text{LnCl}$ [$\text{Ln}=\text{Gd}$ (1), Dy (2)]

Treatment of LnCl_3 with two equivalents of $\text{Cp}^{\text{Th}}\text{Na}$ in THF results in the formation of solvent-free bis(ethylthioethylcyclopentadienyl)lanthanide chlorides $\text{Cp}_2^{\text{Th}}\text{LnCl}$ [$\text{Ln}=\text{Gd}$ (1), Dy (2)] [Eq. (1)]. Complexes **1** and **2** are soluble in THF, toluene, and less soluble in hydrocarbons. They are relatively stable towards air and moisture as compared with their unsubstituted counter-

parts.



$\text{Ln}=\text{Gd}$ (1), Dy (2)

Complexes **1** and **2** are characterized by elemental analysis, IR, mass spectroscopies and X-ray diffraction. The IR spectra of **1** and **2** show the characteristic absorptions of the $\eta^5\text{-Cp}^{\text{Th}}$ group at about 3050, 1460, 1010, 770 cm^{-1} and the C-S-C stretch near 1260 cm^{-1} . The EI-MS spectra of **1** and **2** show the molecular ions as the peaks of the highest mass.

Table 1 Crystal data and structure refinements for complexes **1**–**3**

Compound	1	2	3
Empirical formula	$\text{C}_{18}\text{H}_{26}\text{ClGdS}_2$	$\text{C}_{18}\text{H}_{26}\text{ClDyS}_2$	$\text{C}_{19}\text{H}_{23}\text{SYb}$
Formula weight	499.21	504.46	456.47
Temperature/K	293(2)	293(2)	293(2)
Wavelength/nm	0.071073	0.071073	0.071073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$	Cc
Lattice parameters			
a/nm	1.1615(5)	1.157(3)	1.3097(5)
b/nm	0.8077(3)	0.8118(19)	1.0042(4)
c/nm	2.1319(8)	2.125(5)	1.3227(5)
$\beta/^\circ$	95.739(5)	96.17(3)	105.483(5)
V/nm^3	1.9902(13)	1.985(8)	1.6764(11)
Z	4	4	4
$D_{\text{calc}}/(\text{g}\cdot\text{cm}^{-3})$	1.666	1.688	1.809
μ/mm^{-1}	36.71	4.104	5.694
$F(000)$	988	996	892
Crystal size/ mm^3	$0.60 \times 0.25 \times 0.15$	$0.1 \times 0.15 \times 0.2$	$0.40 \times 0.25 \times 0.30$
θ range/ $^\circ$	1.76–25.01	1.77–25.01	2.59–25.00
hkl range	$-13 \leq h \leq 13,$ $-9 \leq k \leq 9,$ $-25 \leq l \leq 21$	$-13 \leq h \leq 10,$ $-9 \leq k \leq 8,$ $-25 \leq l \leq 25$	$-8 \leq h \leq 15,$ $-11 \leq k \leq 11,$ $-15 \leq l \leq 14$
Reflections collected	8041	8041	4112
Unique reflections	3504 ($R_{\text{int}}=0.0209$)	3497 ($R_{\text{int}}=0.0436$)	1990 ($R_{\text{int}}=0.0390$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3504/0/200	3497/0/201	1990/2/190
Goodness-of-fit on F^2	1.409	1.085	1.036
Final R indices [$I > 2\sigma(I)$]	$R_1=0.0402,$ $wR_2=0.0769$	$R_1=0.0361,$ $wR_2=0.0781$	$R_1=0.0349,$ $wR_2=0.0709$
R indices (all data)	$R_1=0.0415,$ $wR_2=0.0773$	$R_1=0.0466,$ $wR_2=0.0819$	$R_1=0.0411,$ $wR_2=0.0729$
Largest peak and hole/ $(\text{e}\cdot\text{\AA}^{-3})$	0.724, -1.203	0.912, -0.719	0.966, -0.767

The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. Selected bond distances and angles are listed in Tables 2 and 3, respectively. Both complexes are solvent-free monomers in which each metal is coordinated by two ethylthioethylcyclopentadienyl rings, one chloride atom and two donor sulfur atoms of the ethylthioethyl substituents. Assuming the centroid of the η^5 -bonded $C_5H_4CH_2CH_2SCH_2CH_3$ ring as the ligand center, the coordination geometry around the lanthanide ion is a distorted trigonal bipyramid with the $C_5H_4CH_2CH_2SCH_2CH_3$ ring in an eclipsed conformation with respect to the central metal. The coordination number of the central metal is nine.

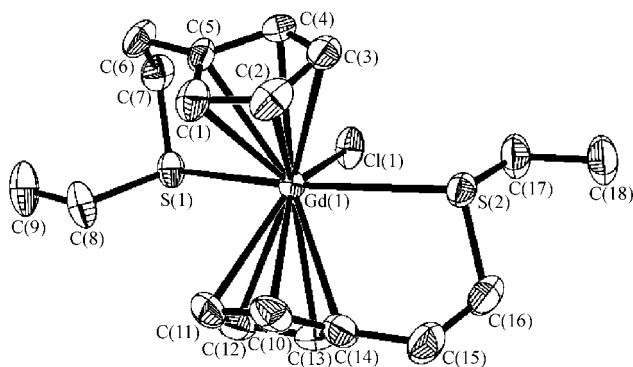


Figure 1 Molecular structure of $Cp_2^{Gd}Cl$ (**1**).

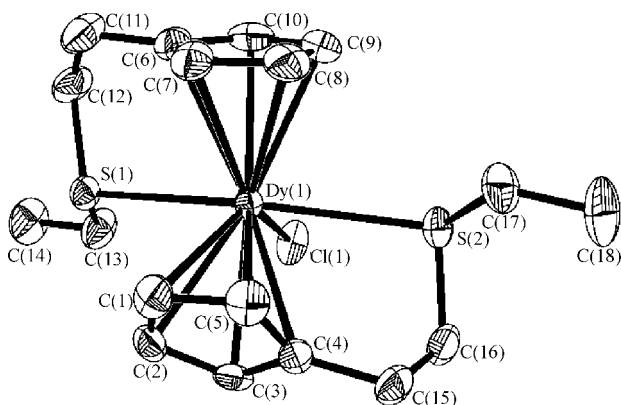


Figure 2 Molecular structure of $Cp_2^{Dy}Cl$ (**2**).

In complex **1**, the Gd—C distances range from 0.2650(7) to 0.2743(6) nm and are in normal ranges observed for gadolinium metallocenes.^{29,30} The average Gd—C(η^5) distance of 0.2699(7) nm is compatible with those found in related compounds: $[(C_5H_5)_2Gd(\mu-\eta^2-ONCMe_2)]_2$ (0.268(2) nm)²⁹ and $[(C_5H_5)_2GdCl]_4$ (0.267(4) nm).³⁰ The Gd—Cl bond length of 0.2624(2) nm is in good consistency with the terminal Gd—Cl bond lengths in $CpGdCl_2 \cdot 3THF$,³¹ but is shorter than the known Gd—Cl (bridging) distances in $[(C_5H_4SiMe_2-Bu^t)_2Gd(\mu-Cl)]_2$ (average 0.2708 nm)³² and $[(C_5H_5)_2Gd-Cl]_4$ (average 0.2745 nm).³⁰ This shortening of 0.0084—

0.0121 nm is quite normal going from bridging to non-bridging.³³ The average Gd—S distance of 0.2963(2) nm is close to the values observed in $(EtSCH_2CH_2-C_5H_4)_2YCl$ (0.2957(1) and 0.2938(1) nm), but is slightly longer than that found in $(C_5Me_5)(EtSCH_2CH_2-C_5H_4)LuCl$ (0.2794(3) nm),²¹ considering the different ionic radii of the central metals.³⁴ The substituted cyclopentadienyl rings are planar within the estimated *S.D.*

Table 2 Selected bond lengths (nm) and angles (°) for complex **1**

Gd(1)—Cl(1)	0.2624(2)	Gd(1)—C(1)	0.2687(6)
Gd(1)—C(2)	0.2650(7)	Gd(1)—C(3)	0.2692(7)
Gd(1)—C(4)	0.2718(7)	Gd(1)—C(5)	0.2743(6)
Gd(1)—C(10)	0.2709(7)	Gd(1)—C(11)	0.2662(8)
Gd(1)—C(12)	0.2680(8)	Gd(1)—C(13)	0.2713(7)
Gd(1)—C(14)	0.2739(8)	Gd(1)—S(1)	0.2953(2)
Gd(1)—S(2)	0.2972(2)		
Cl(1)—Gd(1)—S(1)	74.2(6)	Cl(1)—Gd(1)—S(2)	82.6(5)
S(1)—Gd(1)—S(2)	156.6(5)	Gd(1)—S(1)—C(7)	99.5(2)
C(16)—S(2)—Gd(1)	103.8(3)	C(6)—C(7)—S(1)	112.3(5)
C(15)—C(16)—S(2)	109.1(6)	C(5)—C(6)—C(7)	113.8(6)
C(14)—C(15)—C(16)	113.9(7)		

Table 3 Selected bond lengths (nm) and angles (°) for complex **2**

Dy(1)—Cl(1)	0.2601(5)	Dy(1)—C(1)	0.2627(8)
Dy(1)—C(2)	0.2665(8)	Dy(1)—C(3)	0.2687(7)
Dy(1)—C(4)	0.2707(8)	Dy(1)—C(5)	0.2642(7)
Dy(1)—C(6)	0.2720(8)	Dy(1)—C(7)	0.2687(8)
Dy(1)—C(8)	0.2653(9)	Dy(1)—C(9)	0.2665(9)
Dy(1)—C(10)	0.2677(8)	Dy(1)—S(1)	0.2959(6)
Dy(1)—S(2)	0.2944(5)		
Cl(1)—Dy(1)—S(1)	82.1(6)	Cl(1)—Dy(1)—S(2)	73.79(12)
S(1)—Dy(1)—S(2)	155.8(6)	Dy(1)—S(1)—C(12)	103.2(3)
C(16)—S(2)—Dy(1)	99.4(3)	C(11)—C(12)—S(1)	109.6(6)
C(15)—C(16)—S(2)	112.1(5)	C(6)—C(11)—C(12)	113.7(6)
C(4)—C(15)—C(16)	113.3(4)		

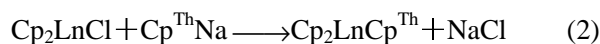
The structural parameters of complex **2** (Table 3) are very similar to those found in complex **1**, with no unusual distances or angles. The Dy—C(Cp) distances range from 0.2627(8) to 0.2720(8) nm, and the average value of 0.2673(9) nm is close to those found in other Cp_2Dy -containing complexes, such as $[Cp_2Dy(OCMe=CHMe)]_2$ (0.2668(6) nm)³⁵ and $[MeCpDy(\eta^2-PzMe_2)(\mu-OSiMe_2PzMe_2)]_2$ (0.2684(16) nm).³⁶ The Dy—S and Dy—Cl distances are close to the corresponding dis-

tances in complex **1**, respectively, when the difference in the metal ionic radii is considered.³⁴

Since the combination of the "hard" lanthanide ion and the "soft" donor sulfur atom is unstable and the bound thioether readily undergoes decomplexation in solution, thioether complexes of lanthanide elements are very rare. These results indicate that the cyclopentadienyl group linked to the thioether moiety can assist in stabilization of the Ln←:S donor bond, inhibiting decomplexation of the more weakly bound thioether in the donor solvents such as THF.

Synthesis of Cp₂LnCpTh [Ln=Yb (**3**), Sm (**4**), Dy (**5**), Y (**6**)]

Nonbridged mixed cyclopentadienyl lanthanide complexes are rare due to the tendency of redistribution to homoleptic cyclopentadienyl complexes in crystallization. To obtain additional data on the other ethylthioethylcyclopentadienyl-containing organolanthanide complexes, the synthesis of mixed-ring complexes Cp₂LnCpTh [Ln=Yb (**3**), Sm (**4**), Dy (**5**), Y (**6**)] by the reactions of bis(cyclopentadienyl)lanthanide chloride with one equivalent of CpThNa in THF was also carried out [Eq. (2)].



Ln=Yb (**3**), Sm (**4**), Dy (**5**), Y (**6**)

Complexes **3–6** are sensitive to air and moisture. The elemental analyses, IR and mass spectra obtained are in agreement with their molecular formulae. The mass spectra of complexes **4–6** show the molecular ions and the typical fragments [M⁺—SEt], [M⁺—Cp], [M⁺—2Cp], [M⁺—CpTh], [CpThH] and [CpH].

Figure 3 shows the molecular structure of Cp₂YbCpTh (**3**). The Yb³⁺ ion is coordinated by two cyclopentadienyl groups, one ethylthioethylcyclopentadienyl group and one sulfur atom from the side-chain. The coordination number is ten. Selected bond distances and bond angles are listed in Table 4. The average Yb—C(Cp)

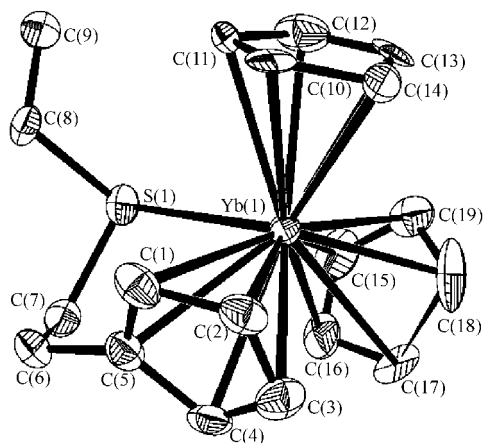


Figure 3 Molecular structure of Cp₂YbCpTh (**3**).

Table 4 Selected bond lengths (nm) and angles (°) for complex **3**

Yb(1)—C(1)	0.2678 (14)	Yb(1)—C(2)	0.2609(16)
Yb(1)—C(3)	0.2631(14)	Yb(1)—C(4)	0.2700(12)
Yb(1)—C(5)	0.2691(12)	Yb(1)—C(10)	0.2760(6)
Yb(1)—C(11)	0.2677(16)	Yb(1)—C(12)	0.2660(5)
Yb(1)—C(13)	0.2722(6)	Yb(1)—C(14)	0.2648(19)
Yb(1)—C(15)	0.2703(0)	Yb(1)—C(16)	0.2594(1)
Yb(1)—C(17)	0.2673(15)	Yb(1)—C(18)	0.2613(2)
Yb(1)—C(19)	0.2698(18)	Yb(1)—S(1)	0.2885(4)
S(1)—C(8)	0.1817(14)	S(1)—C(7)	0.1821(14)
Yb(1)-S(1)-C(7)	101.1(5)	Yb(1)-S(1)-C(8)	115.8(5)
C(8)-S(1)-C(7)	99.7(7)	C(9)-C(8)-S(1)	111.7(10)
C(6)-C(7)-S(1)	111.0(9)		

distance of 0.2659 nm is slightly shorter than the average Yb—C(CpTh) distance of 0.2693 nm due to the differences in ring substitution. These values are comparable to those found in Cp₃Yb-containing compounds, such as Cp₃Yb(NCEt) (0.2677 nm).³⁷ The Yb—S distance of 0.2885(4) nm is close to the values observed in complexes **1** and **2**, when the difference in the metal ionic radii is considered.³⁴

References

- Janiak, C. G.; Schumann, H. *Adv. Organomet. Chem.* **1991**, 33, 291.
- Schumann, H.; Meese-Marktscheffel, E. J. A. L. *Chem. Rev.* **1995**, 95, 865.
- Zhang, L. B.; Zhou, X. G.; Cai, R. F.; Weng, L. H. *J. Organomet. Chem.* **2000**, 612, 176.
- Schumann, H.; Heim, A.; Demtschuk, J.; Mühle, S. *Organometallics* **2003**, 22, 118.
- Ephritikhine, M. *Chem. Rev.* **1997**, 97, 2193.
- Zhou, X. G.; Zhu, M. *J. Organomet. Chem.* **2002**, 647, 28.
- Jutzi, P.; Dahihhaus, J.; Kristen, M. O. *J. Organomet. Chem.* **1993**, 450, C1.
- Herrmann, W. A.; Anwander, R.; Munck, F. C.; Scherer, W. *Chem. Ber.* **1993**, 126, 331.
- Anwander, R.; Herrmann, W. A.; Scherer, W.; Munck, F. C. *J. Organomet. Chem.* **1993**, 462, 163.
- Schumann, H.; Erbstein, F.; Herrmann, K.; Demtschuk, J.; Weimann, R. *J. Organomet. Chem.* **1998**, 562, 255.
- Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J.; Molander, G. A. *Organometallics* **1998**, 17, 5324.
- Schumann, H.; Erbstein, F.; Karasiak, D. F.; Fedushkin, I. L.; Demtschuk, J.; Girgsdies, F. *Z. Anorg. Allg. Chem.* **1999**, 625, 781.
- Schumann, H.; Erbstein, F.; Demtschuk, J.; Weimann, R. *Z. Anorg. Allg. Chem.* **1999**, 625, 1457.
- Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J.; Mühle, S. *Z. Anorg. Allg. Chem.* **2000**, 626, 2161.
- Fedushkin, I. L.; Dechert, S.; Schumann, H. *Organometal-*

- lics* **2000**, 19, 4066.
- 16 Deng, D. L.; Li, B.; Qian, C. T. *Polyhedron* **1990**, 12, 1453.
- 17 Deng, D. L.; Qian, C. T.; Wu, G.; Zheng, P. J. *J. Chem. Soc., Chem. Commun.* **1990**, 880.
- 18 Qian, C.; Zhu, D.; Li, D. *J. Organomet. Chem.* **1992**, 430, 175.
- 19 Laske, D. A.; Duchateau, R.; Teuben, J. H.; Spek, A. L. *J. Organomet. Chem.* **1993**, 462, 149.
- 20 Qian, C.; Zou, G.; Sun, J. *J. Organomet. Chem.* **1998**, 566, 21.
- 21 Schumann, H.; Hermann, K.; Demtschuk, J.; Mühle, S. H. *Z. Anorg. Allg. Chem.* **1999**, 625, 1107.
- 22 Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, 24, 387.
- 23 Deacon, G. B.; Fallon, G. D.; MacKinnon, P. I.; Newnham, R. H.; Pain, G. N.; Tuong, T. D.; Wilkinson, D. L. *J. Organomet. Chem.* **1984**, 277, C21.
- 24 Qian, C. T.; Ye, C. Q.; Lu, H. Z.; Li, Y. Q.; Zhou, J. L.; Ge, Y. W.; Tsutsui, M. *J. Organomet. Chem.* **1983**, 247, 161.
- 25 SMART and SAINT, *Data Collection and Processing Software for SMART System*; Siemens Analytical X-ray Instruments, Inc., Madison, WI, **1995**.
- 26 Sheldrick, G. M., *SHELXS-97, Program for Crystal Structure Determination*, Universität Göttingen, Göttingen, Germany, **1997**.
- 27 Sheldrick, G. M., *SHELXL-97, Program for Crystal Structure Determination*, Universität Göttingen, Göttingen, Germany, **1997**.
- 28 Sheldrick, G. M., *SADABS, A Program for Empirical Absorption Correction*, Göttingen, Germany, **1998**.
- 29 Wu, Z. Z.; Zhou, X. G.; Zhang, W.; Xu, Z.; You, X. Z.; Huang, X. Y. *J. Chem. Soc., Chem. Commun.* **1994**, 813.
- 30 Lamberts, W.; Hessner, B.; Lucken, H. *Inorg. Chim. Acta* **1987**, 139, 215.
- 31 Wu, Z. Z.; Xu, Z.; You, X. Z.; Zhou, X. G.; Shi, L. *J. Coord. Chem.* **1992**, 26, 329.
- 32 Zhou, X. G.; Zhang, L. X.; Zhang, C. M.; Zhang, J.; Zhu, M.; Cai, R. F.; Huang, Z. E.; Huang, Z. X.; Wu, Q. J. *J. Organomet. Chem.* **2002**, 655, 120.
- 33 Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, 4, 554.
- 34 Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.
- 35 Wu, Z. Z.; Xu, Z.; You, X. Z.; Zhou, X. G.; Huang, X. Y. *J. Organomet. Chem.* **1994**, 483, 107.
- 36 Zhou, X. G.; Ma, W. W.; Huang, Z. E.; Cai, R. F.; You, X. Z.; Huang, X. Y. *J. Organomet. Chem.* **1997**, 545, 309.
- 37 Spirlet, M. R.; Rebizant, J.; Apostolidis, C.; Kanellakopoulos, B. *Inorg. Chim. Acta* **1987**, 139, 211.

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