

Synthesis and thermal stability of binuclear biscyclopentadienyl lanthanide thiolates, X-ray crystal structure of $[(C_5H_5)_2Yb(\mu-SCH_2CH_2CH_2CH_3)]_2$

Zhong-Zhi Wu^a, Zu-En Huang^{a,*}, Rui-Fang Cai^a, Xi-Geng Zhou^b, Zheng Xu^b,
Xiao-Zeng You^b, Xiao-Yun Huang^c

^a Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China

^b The State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, Jiangsu, People's Republic of China

^c The State Key Laboratory of Structural Chemistry, Fuzhou 350002, Fujian, People's Republic of China

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Abstract

The trivalent lanthanide metallocenes Cp_3Ln ($Cp = C_5H_5$, $Ln = Dy$ or Yb) react with thiols, HSR ($R = CH_2CH_2CH_3$ or $CH_2CH_2CH_2CH_3$) to give the dimeric complexes $[Cp_2Ln(\mu-SR)]_2$ ($R = CH_2CH_2CH_3$; $Ln = Dy$ (1) or Yb (2)) ($R = CH_2CH_2CH_2CH_3$; $Ln = Dy$ (3) or Yb (4)) in tetrahydrofuran at room temperature. They have been characterized by elemental analysis and mass spectroscopy or 1H NMR spectra, indicating that they are dimers bridged through the sulphide atoms of thiolate ligands. Crystals of 4 are monoclinic, of space group $P2_1/a$ with $a = 8.928(3)$, $b = 17.620(7)$ and $c = 9.208(4)$ Å, $\beta = 103.94(3)^\circ$, $V = 1405.8(9)$ Å³, $Z = 2$ and $D_c = 1.85$ g cm³. The structure was refined by the full-matrix least-squares method to a conventional R factor of 0.039, for 1868 data with $I > 3\sigma(I)$. The Yb_2S_2 unit is planar, and the geometry about the ytterbium atom is pseudotetrahedral although the geometry is pyramid at sulfur so that the *n*-butyl groups are *anti* relative to the Yb_2S_2 ring. The average $Y-C(Cp)$ and $Yb-S$ bond distances are 2.59(1) and 2.708(3) Å respectively. It was found that these complexes are thermally unstable and tend to decompose into Cp_3Ln species upon heating.

Keywords: Dysprosium; Ytterbium; Cyclopentadienyl; Thiolate; Crystal structure

1. Introduction

The chemistry of cyclopentadienyl lanthanide alkoxides have been extensively investigated [1]. The organolanthanide thiolates, however, are rarely described, although several cyclopentadienyl-like derivatives such as $(Me_5C_5)_2Yb(SC_6H_5)(NH_3)$ prepared from $(Me_5C_5)_2Yb(NH_3)$ and R_2S_2 [2], $[(Me_3CC_5H_4)_2Ce(\mu-SCHMe_2)]_2$ prepared from $(Me_3CC_5H_4)_3Ce$ and $HSCMe_2$ [3], $(Me_5C_5)Lu(SCMe_3)_2Li(THF)_2$ prepared from the thiol and $(Me_5C_5)_2LuMe_2Li(THF)_2$ [4], $[(^tBuC_5H_4)_2Ln(\mu-SR)]_2$ prepared from $[(^tBuC_5H_4)_2Ln(\mu-Me)]_2$ ($Ln = Y$ or Lu) and R_2S_2 ($R = Ph$, nBu , tBu or CH_2Ph) [5], and $[(C_5H_5)Sm(\mu-SAr)(THF)]_2$ ($THF =$ tetrahydrofuran) prepared by the reaction of Sm with C_5H_6 and $ArSSAr$ [6] have been isolated. There-

fore the chemistry of organolanthanide thiolates obviously remains to be explored. In order to characterize the $Ln-S$ bond and to investigate the thermal reactivity of organolanthanide thiolates, we herein reported the synthesis, mass spectra and thermal stability of four new binuclear organolanthanide thiolates $[Cp_2Ln(\mu-SR)]_2$ ($Ln = Dy$ or Yb ; $R = CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$) as well as the X-ray crystal structure of $[Cp_2Yb(\mu-SCH_2CH_2CH_2CH_3)]_2$.

2. Experimental section

2.1. Materials and measurements

The title complexes are extremely air and moisture sensitive. Therefore both the synthesis and the subsequent manipulations of the complexes were conducted

* Corresponding author.

under purified argon with rigorous exclusion of air and water using Schlenk or glovebox techniques. THF solvent was refluxed and distilled over the sodium ketyl of benzophenone under argon immediately before use. *n*-Hexane was distilled over finely divided LiAlH₄ prior to use. Anhydrous LnCl₃ [7] and the lanthanide metallocenes Cp₃Ln [8,9] (Ln = Dy or Yb) were prepared according to the literature methods. The *n*-propanethiol and *n*-butanethiol are analytical pure grade and used without further purification.

Carbon and hydrogen analyses were performed on a Perkin–Elmer 240C microanalyzer. The analysis for the lanthanide metals was accomplished using a literature procedure with disodium EDTA [10]. Mass spectroscopy (MS) was carried out on a VG ZAB-HS, Finigan MAT 312 or a JMS-D3000 mass spectrometer with electron impact mode. The crystal samples were introduced by the direct inlet techniques. Mass data are based on ¹²C, ³²S, ¹H, ¹⁶⁴Dy and ¹⁷⁴Yb. The ¹H NMR data (δ (ppm)) were obtained on a Bruker MSL-300 MHz spectrometer with Me₄Si as internal reference.

2.2. Synthesis of 1–4

To a THF solution (20 ml) of Cp₃Dy (0.269 g, 0.75 mmol), 0.068 ml (0.75 mmol) of *n*-propyl thiol was added with stirring. After stirring for 24 h at room temperature, the reaction solution was concentrated by reduced pressure to about 5 ml. Then, 20 ml of *n*-hexane was added to it and a pale-yellow solid was deposited, which was purified by recrystallization from THF–*n*-hexane to afford the product as pale-yellow powder.

According to a similar procedure, the yellow product of **3** and red products of **2** and **4** could be readily obtained with good yields. The crystals of **4** suitable for X-ray analysis were grown by slowly cooling the hot oversaturated THF solution to the room temperature.

1: yield, 68.3%. Anal. Found: C, 42.11; H, 4.82; Dy, 44.54. C₂₆H₃₄S₂Dy₂ Calc.; C, 42.45; H, 4.66; Dy, 44.18%. MS: *m/e* [fragment, relative intensity (%)] 622 [M – SR – R + 2, 1.5], 557 [M – Cp – SR – R + 2, 6.3], 358 [M' – 1, 22.4], 293 [M' – Cp – 1, 100.0], 228 [M' – 2Cp – 1, 26.6], 164 [Dy, 9.6], 66 [HCp, 2.4]. (M = [Cp₂Dy(SCH₂CH₂CH₃)₂]; M' = Cp₃Dy; R = CH₂CH₂CH₃ or CH₂CH₂CH₂CH₃.)

2: yield, 78.3%. Anal. Found: C, 41.03; H, 4.65; Yb, 45.85. C₂₆H₃₄S₂Yb₂ Calc.; C, 41.27; H, 4.53; Yb, 45.73%. ¹H NMR (C₄D₈O, 297 K): δ 58.3 (6H, CH₃), 87.42 (4H, CH₂), 112.41 (4H, CH₂S), –51.73 (20H, C₅H₅) ppm. MS: *m/e* [fragment, relative intensity (%)] 756 [M – 2 = A, 6.8], 691 [A – Cp, 100.0], 681 [A – SR, 13.6], 635 [M – Cp – R – CH₃, 4.4], 626 [A – 2Cp, 13.7], 616 [A – Cp – SR, 7.8], 583 [A – 2Cp – R, 16.7], 575 [A – Cp – SR – R, 6.6], 556 [M – 2Cp – R – CH₂CH₃, 3.7], 540 [A – 2Cp – 2R, 6.1], 518 [A –

3Cp – R, 10.7], 510 [A – 2Cp – SR – R, 14.3], 491 [M – 3Cp – R – CH₂CH₃, 1.5], 475 [A – 3Cp – 2R, 15.3], 453 [A – 4Cp – R, 5.8], 445 [A – 3Cp – SR – R, 10.5], 426 [Yb₂S₂CH₂, 1.3], 410 [Yb₂S₂, 10.9], 394 [Yb₂SCH₂, 1.7], 379 [M/2, 7.3], 378 [Yb₂S, 11.9], 369 [M', 4.8], 336 [M/2 – R, 1.7], 312 [M/2 – Cp – 2, 3.1], 304 [Cp₂Yb 53.7], 269 [M/2 – Cp – R, 4.0], 249 [M/2 – 2Cp, 6.1], 239 [CpYb, 71.1] 207 [YbSH, 7.1], 174 [Yb, 3.4], 129 [C₁₂H₉, 11.6], 76 [HSR, 1.4], 66 [HCp, 7.1]. (M = [Cp₂Yb(SCH₂CH₂CH₃)₂]; M/2 = Cp₂YbSCH₂CH₂CH₃; M' = Cp₃Yb.)

3: yield, 74.6%. Anal. Found: C, 43.86; H, 5.25; Dy, 42.76. C₂₄H₃₄S₂Dy₂ Calc.; C, 44.03; H, 5.01; Dy, 42.55%. MS: *m/e* [fragment, relative intensity (%)] 359 [M', 9.5], 294 [M' – Cp, 100.0], 229 [M' – 2Cp, 31.3], 164 [Dy, 24.7], 66 [HCp, 7.0], 65 [Cp, 15.6]. (M' = Cp₃Dy.)

4: yield, 74.6%. Anal. Found: C, 42.53; H, 4.64; Yb, 44.52. C₂₈H₃₈S₂Yb₂ Calc.; C, 42.85; H, 4.88; Yb, 44.10%. ¹H NMR (C₄D₈O, 297 K): δ 36.22 (6H, CH₃), 60.64 (4H, CH₂), 86.75 (4H, CH₂), 112.42 (4H, CH₂S), –50.83 (20H, C₅H₅) ppm. MS: *m/e* [fragment, relative intensity (%)] 786 [M, 2.5], 721 [M – Cp, 41.9], 697 [M – SR, 20.6], 650 [M – Cp – R – Me + H, 8.2], 632 [M – Cp – SR, 1.9], 627 [M – 2Cp – CH₂CH₃, 2.8], 599 [M – 2Cp – R, 5.9], 585 [M – 2Cp – R – Me + H, 4.2], 575 [M – Cp – SR – R, 2.7], 558 [M – 2Cp – R – CH₂CH₂CH₃ + 2H, 3.9], 542 [M – 2Cp – 2R, 3.4], 534 [M – 3Cp – R, 3.4], 510 [M – 2Cp – SR – R, 8.3], 493 [M – 3Cp – R – CH₂CH₂CH₃ + 2H, 2.7], 477 [M – 3Cp – 2R, 6.7], 445 [M – 3Cp – SR – R, 5.2] 428 [Yb₂S₂CH₂ + 2H, 1.6], 412 [Yb₂S₂, 4.8], 380 [Yb₂S, 1.7], 393 [M/2, 5.3], 369 [M', 9.2], 336 [M/2 – R, 1.0], 328 [M/2 – Cp, 1.1], 304 [Cp₂Yb, 47.2], 271 [M/2 – Cp – R, 1.4], 263 [M/2 – 2Cp, 1.5], 239 [CpYb, 57.3], 207 [YbSH, 1.0], 174 [Yb, 15.1], 130 [C₁₀H₁₀, 3.5], 90 [HSR, 12.7], 65 [Cp, 100.0]. (M = [Cp₂Yb(SCH₂CH₂CH₂CH₃)₂]; M/2 = Cp₂YbSCH₂CH₂CH₂CH₃; M' = Cp₃Yb; R = CH₂CH₂CH₂CH₃.)

2.3. Thermal decomposition reaction of 1 and 3

The saturated THF solution of **1** was refluxed for about 10 min under argon and then cooled to room temperature to give a pale-yellow crystal product suitable for X-ray diffraction study. Anal. Found: C, 52.77; H, 5.53; Dy, 37.95. (C₅H₅)₃Dy(OC₄H₈) Calc.; C, 53.09; H, 5.40; Dy, 37.80%. MS: *m/e* [fragment, relative intensity (%)] 359 [Cp₃Dy, 7.4].

According to a similar procedure, Cp₃Dy(THF) can also be obtained by cooling the boiling oversaturated THF solution of **3**. The crystal structure of Cp₃Dy(THF) has been confirmed by X-ray analysis. Complexes **2** and **4** did not give Cp₃Yb(THF) under same conditions.

2.4. X-ray crystal structure determination of $[\text{Cp}_2\text{Yb}(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2]$

The crystals of **4** suitable for X-ray analysis were sealed under argon in the Lindemann capillaries. Accurate cell dimensions and the crystal orientation matrix were determined by a least-squares treatment of the setting angles of 20 reflections with $10.38^\circ \leq \theta \leq 16.71^\circ$. Data were collected on a Rigaku-AFC5R diffractometer using graphite-monochromated Mo K α radiation. Intensities of three standard reflections measured every 250 reflections showed no decay. Data were corrected for Lorentz, polarization and empirical absorption effects. Relevant crystal and data collection parameters for the present study are given in Table 1.

The position of ytterbium atom was located by the direct method. The structure was developed and refined by least-squares techniques, initially with isotropic and then with anisotropic thermal parameters. The hydrogen atoms were added at the calculated position using a C–H bond length of 0.95 Å and ideal bond angles and were included in the structure factor calculation. Scattering factors were taken from [11]. All calculations were performed on a MICRO VAX 3100 computer using the MSC/Rigaku TEXSAN program. Atomic coordinates are given in Table 2.

3. Results and discussion

3.1. Synthesis and mass spectroscopy characterization

The very versatile method of liberating cyclopentadiene from a Cp_3Ln moiety by the action of protonic acids stronger than C_5H_6 have been adopted [3,12–21] $[\text{Cp}_2\text{Ln}(\mu\text{-SR})_2]$ ($\text{Ln} = \text{Dy}$ or Yb ; $\text{R} = \text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) complexes were synthesized by re-

Table 1
Crystal, data collection and refinement parameters of **4**

Formula	$\text{C}_{28}\text{H}_{38}\text{S}_2\text{Yb}_2$
Formula weight	784.81
Crystal size (mm)	$0.70 \times 0.10 \times 0.40$
Crystal color and shape	Red block
Crystal system	Monoclinic
Space group	$P2_1/a$
Lattice parameters	
a (Å)	8.928(3)
b (Å)	17.620(7)
c (Å)	9.208(4)
β (°)	103.94(3)
V (Å ³)	1405.8(9)
Z	2
D_c (g cm ³)	1.85
$F(000)$	756
Radiation (Å)	Mo K α ($\lambda = 0.71069$ Å)
μ (cm ⁻¹)	67.5
Scan type	ω - 2θ
hkl range	0–11, 0–21, –11–11
$2\theta_{\text{max}}$ (°)	50.0
Scan width (°)	$1.628 + 0.35 \tan \theta$
Scan speed (° min ⁻¹)	16.00
Number of reflections measured	2740
Number of independent reflections	2570
Number of observed reflections ($I > 3\sigma(I)$)	1868
Number of parameters refined	145
R	0.039
R_w	0.049
Goodness of fit	1.41
Weight scheme ω	$1/\sigma^2(F_o)$
Maximum shift/error	< 0.05
ρ_{max} (electron Å ⁻³)	1.08

action of Cp_3Ln with the equimolar thiols in THF at room temperature. The reaction equation is

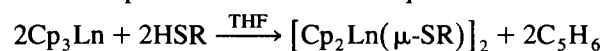


Table 2
Atomic coordinates and B_{eq} for $[\text{Cp}_2\text{Yb}(\mu\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2]$

Atom	x	y	z	B_{eq}
Yb	0.54799(4)	0.42658(2)	0.85374(5)	2.88(2)
S	0.6213(3)	0.4458(1)	1.1553(3)	3.7(1)
C(1)	0.824(1)	0.4529(8)	1.257(1)	5.9(6)
C(2)	0.897(2)	0.384(1)	1.342(2)	10(1)
C(3)	0.928(3)	0.324(1)	1.256(3)	12(1)
C(4)	1.006(3)	0.254(1)	1.343(2)	11(1)
C(11)	0.478(2)	0.2871(7)	0.894(2)	6.5(7)
C(12)	0.364(2)	0.3260(8)	0.927(2)	6.0(6)
C(13)	0.277(1)	0.3600(6)	0.800(2)	5.9(6)
C(14)	0.345(2)	0.3394(8)	0.683(2)	6.6(6)
C(15)	0.475(2)	0.2945(7)	0.748(2)	6.7(7)
C(21)	0.893(1)	0.4248(8)	0.857(2)	5.8(6)
C(22)	0.796(1)	0.5032(9)	0.854(1)	5.7(6)
C(23)	0.696(1)	0.516(1)	0.712(2)	6.5(7)
C(24)	0.681(2)	0.449(1)	0.636(1)	6.4(7)
C(25)	0.770(2)	0.3966(8)	0.726(2)	5.7(6)

The $[\text{Cp}_2\text{Ln}(\mu\text{-SR})_2]$ -type complexes can usually be obtained from a hydrocarbon solvent such as hexane, benzene or toluene [3,5]. The synthesis of the title complexes has revealed that the $[\text{Cp}_2\text{Ln}(\mu\text{-SR})_2]$ -type complexes can also be obtained from the coordination solvents, e.g. THF by selecting appropriate thiolate ligands and lanthanide metals.

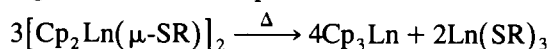
Four new complexes have been characterized by elemental analysis and mass or ^1H NMR spectra. The analytical data for all the complexes conformed to their formula. They have no melting points and decomposition occurs at above 250°C . these complexes are all extremely air and moisture sensitive and the samples of complexes changed into white powder in about 0.5 min as exposed in air (22°C ; relative humidity, 35%). The corresponding alkoxides, however, could stably exist in air for 24 h. The complexes 1–4 rapidly decomposed into free cyclopentadiene, thiols and white powder (lanthanide hydroxides in water). However, the corresponding alkoxides are stable in water for at least several hours.

The 300 MHz ^1H NMR spectra in $\text{C}_4\text{D}_8\text{O}$ of 2 and 4 have been determined. Although the proton signals of the ligands shift significantly upfield or downfield owing to the paramagnetism of the complexes, four resonances appearing at 112.41, 87.41, 58.63 and -51.73 ppm in an area ratio of 4:4:6:20 for 2 and five resonances at 112.42, 86.75, 60.64, 36.22 and -50.83 ppm in an area ratio of 4:4:4:6:20 for 4 can readily be attributed to $\text{SCH}_2\text{CH}_2\text{CH}_3$ and C_5H_5 protons in 2 and to $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and C_5H_5 protons in 4 respectively. The mass spectra of 2 and 4 clearly display their molecular ions which are characterized by the ready loss of Cp group from the molecular ions with the $[\text{M-Cp}]^+$ ion as the base or a strong peak in the spectra. The presence of peaks corresponding to $[\text{Yb}_2\text{S}_2]^+$ and $[\text{Yb}_2\text{S}]^+$ in the mass spectra evidently indicates the sulfur-bridged structure of the complexes. Two complexes have similar mass spectra cleavage patterns, which are also similar to those reported for the corresponding alkoxides [1]. Nevertheless, the direct loss of SR ligand from the molecular ions is apparently readier than the loss of the R group. This phenomenon was also found in the spectra of alkoxides [1]. This result suggests that the bridging unit $[\text{Yb}_2(\mu\text{-SR})_2]^+$ is easily dissociated into $[\text{Yb}(\mu\text{-SR})\text{YbSR}]$ species in the vapor phase, thus leading to the ready loss of the terminal SR ligand. The mass spectra of 1 and 3 do not show their molecular ions. For 1, only some fragments derived from the dimers were observed in the spectra.

3.2. Studies on the thermal stability of 1–4

For the purpose of studying the thermal stability of 1–4, their mass spectra have been recorded at different

vaporization temperatures. It is interesting to note that the spectra of 1 and 3 only exhibit fragments corresponding to $[\text{Cp}_3\text{Dy}]^+$ and its fragments at above 200°C . In the spectra of 2 and 4, not only are the peaks of $[\text{Cp}_2\text{Yb}(\text{SR})]^+$ and its fragments observed in both spectra, but also the peaks corresponding to $[\text{Cp}_3\text{Yb}]^+$ and its fragments can be seen at the same time. According to our previous studies [12–16,18,21–24], we predict that these complexes are thermally unstable and may undergo the following disproportionation reaction during the course of evaporation:



The complexes 1 and 3 were refluxed in THF to give a decomposition product $\text{Cp}_3\text{Dy}(\text{THF})$, which has been characterized by elemental analysis, MS and X-ray analysis [25]. The decomposition of analogous Yb complexes is not observed under the same conditions. This result demonstrates that the Yb complexes are thermally stable than the Dy complexes. The reason for this can be ascribed to the greater steric saturation around the smaller metal center and the stronger attraction of the Yb–SR bond compared with the Dy–SR bond [26,27]. In addition, it was found that the corresponding alkoxides are much more stable than thiolates and do not decompose into Cp_3Ln species by refluxing in THF solution [1].

3.3. Description and discussion of crystal structure of 4

The molecular structure of 4 is shown in Fig. 1. The complex is centrosymmetrical; the Yb_2S_2 unit is planar and the geometry at the ytterbium atom can be described as pseudotetrahedron. The geometry at sulfur in the *n*-butylthiolate ligand is pyramid, since the angles about sulfur sum to 330° , and the *n*-butyl groups are of *anti* configuration relative to the Yb_2S_2 ring. This is the usual geometry found in the sulfur-bridged complexes

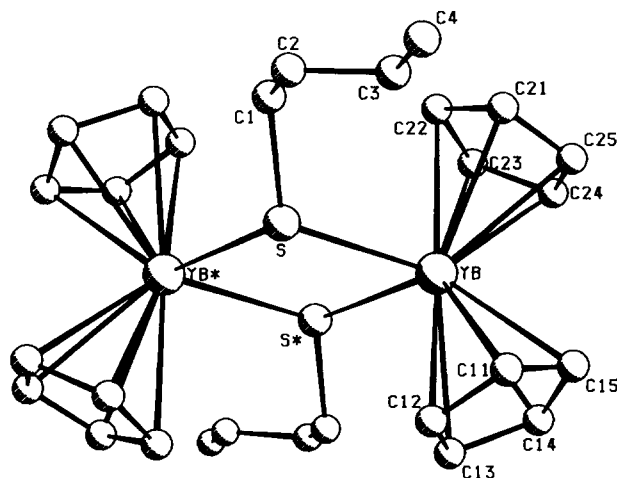


Fig. 1.

Table 3
Selected bond distances (Å) of $[\text{Cp}_2\text{Yb}(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2]$

Yb–S	2.716(3)	C(1)–C(2)	1.50(2)
Yb–S*	2.699(3)	C(2)–C(3)	1.39(2)
Yb–C(11)	2.58(1)	C(3)–C(4)	1.55(2)
Yb–C(12)	2.61(1)	C(11)–C(12)	1.32(2)
Yb–C(13)	2.63(1)	C(12)–C(13)	1.37(2)
Yb–C(14)	2.59(1)	C(13)–C(14)	1.41(2)
Yb–C(15)	2.55(1)	C(14)–C(15)	1.41(2)
Yb–C(21)	2.59(1)	C(15)–C(11)	1.34(2)
Yb–C(22)	2.59(1)	C(21)–C(22)	1.43(2)
Yb–C(23)	2.60(1)	C(22)–C(23)	1.41(2)
Yb–C(24)	2.59(1)	C(23)–C(24)	1.37(2)
Yb–C(25)	2.59(1)	C(24)–C(25)	1.36(2)
Yb–Yb*	3.974(1)	S–C(1)	1.83(1)
Cp(1)–Yb*	2.315(1)	Cp(2)–Yb	2.312(1)

* Cp represents the centroid of the cyclopentadienyl ring.

[3–6,28]. On the contrary, for $[\text{Cp}_2\text{Yb}(\mu\text{-OR})_2]$ -type complexes, the geometry at oxygen atom is completely planar.

The bond distances and angles of **4** are listed in Tables 3 and 4. The Yb–C(Cp) distances range from 2.55(1) to 2.63(1) Å, and average 2.60(1) Å. This average is average slightly shorter than those found in the structurally similar alkoxides complexes $[\text{Cp}_2\text{Yb}(\mu\text{-OCH}_2\text{CH}=\text{CHCH}_3)_2]$ (2.643 Å) [29] and $[\text{Cp}_2\text{Yb}(\mu\text{-O}(\text{Me})\text{C}=\text{CHCH}_3)_2]$ (2.629 Å) [1]. The reason for this can be attributed to the following. In the bridging unit Yb_2O_2 of alkoxides, the Yb–Yb separations (3.5324(15) Å [29] and 3.490(2) Å [1]) are shorter than that (3.974(1) Å) of the title structure. Therefore the steric repulsion between two bent Cp_2Yb units in the title structure should be smaller than that existing in the corresponding alkoxides, thus leading to the shortening of the Yb–C bond of **4**.

Two Yb–S distances are not equal; the individual distances are 2.699(3) and 2.716(3) Å, with the average being 2.707(3) Å. This average distance is compatible with those found in related sulfur-bridged complexes ($(\text{C}_5\text{Me}_5)_2\text{Lu}(\mu\text{-S}^t\text{Bu})_2\text{Li}(\text{THF})_2$, 2.716(7) Å [4]; $(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{Ce}(\mu\text{-SCHMe}_2)_2$, 2.882(6) Å [3]) when the difference in metallic ionic radii was considered [30]. However, the Yb–S distance in **4** is 0.033 Å longer than that (2.674(5) Å) of the monomeric complex $\text{Cp}_2\text{Yb}(\text{SC}_6\text{H}_5)(\text{NH}_3)$ [2]. Evidently, this variation

Table 4
Selected bond angles (°) for $[\text{Cp}_2\text{Yb}(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2]$

Yb–S–Yb	94.43(8)	C(11)–C(12)–C(13)	110(1)
S–Yb–S*	85.57(8)	C(12)–C(13)–C(14)	106(1)
Yb–S–C(1)	119.7(4)	C(13)–C(14)–C(15)	107(1)
Yb*–S–C(1)	115.9(4)	C(14)–C(15)–C(11)	107(1)
S–C(1)–C(2)	118(1)	C(15)–C(11)–C(12)	110(1)
C(1)–C(2)–C(3)	116(2)	C(21)–C(22)–C(23)	107(1)
C(2)–C(3)–C(4)	116(2)	C(22)–C(23)–C(24)	107(1)
C(23)–C(24)–C(25)	108(1)	C(24)–C(25)–C(21)	112(1)
C(25)–C(21)–C(22)	106(1)	Cp(1)–Yb–Cp(2)	128.3

is typical of bridging to monomeric complexes and is in agreement with the results reported for organolanthanide halides [31] and alkoxides [1,17].

The S–C bond length (1.83(1) Å) is normal for an sp^3 sulfur–carbon single bond and is similar to the distances reported in other complexes containing SR groups [3,4]. The C(1)–C(2) and C(3)–C(4) bond distances are 1.50(2) and 1.55(2) Å respectively, which are quite reasonable for a carbon–carbon single bond. However, the C(2)–C(3) bond (1.39(2) Å) is obviously shorter than a usual single C–C bond, probably owing to the thermal disorder of C(2) and C(3) atoms. The ^1H NMR spectra of the hydrolysate $\text{HSCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ of **4** shows the single-bond nature of the C(2)–C(3) bond.

In the bridging unit Yb_2S_2 , the angles of Yb–S–Yb and S–Yb–S are 94.43(8)° and 85.57(8)° respectively, which are very different from the corresponding values in another bridging complex $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{Ce}(\mu\text{-SCHMe}_2)_2]$ [3]. This deviation in angles, however, is not observed in the analogous alkoxides [1]. Two Cp rings of Cp_2Yb unit are completely planar, which form a dihedral angle of 51.26°. The Cp(centroid)–Yb–Cp(centroid) angle (128.34°) and Cp(centroid)–Yb distances (2.315 and 2.412 Å) are unexceptional, which are comparable with those found in related alkoxides [1].

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References

- [1] Z.-Z. Wu, Z. Xu, X.-Z. You, X.-G. Zhou and X.-Y. Huang, *J. Organomet. Chem.*, **483** (1994) 107, and references cited therein.
- [2] A. Zalkin, T.J. Henly and R.A. Anderson, *Acta Crystallogr., Sect. C* **43** (1987) 233.
- [3] S.D. Stults, R.A. Anderson and A. Zalkin, *Organometallics*, **9** (1990) 1623.
- [4] (a) H. Schumann, I. Albrecht and E. Hahn, *Angew. Chem., Int. Edn. Engl.*, **24** (1985) 985; (b) H. Schumann, M. Gallagher, E. Hahn, C. Janiak, C. Kolax, J. Loebel, S. Nickel and E. Palamidis, *Polyhedron*, **7** (1988) 2307.
- [5] I.P. Beletskaya, A.Z. Voskoboynikov, A.K. Shestakova, A.I. Yanovsky, G.K. Fukin, L.N. Zacharov, Y.T. Struchkov and H. Schumann, *J. Organomet. Chem.*, **468** (1994) 121.
- [6] K. Mashima, Y. Nakayama, N. Kanehisa, Y. Kai and A. Nakamura, *J. Chem. Soc., Chem. Commun.*, (1993) 1847.
- [7] M.D. Tayler and C.P. Carter, *J. Inorg. Nucl. Chem.*, **24** (1962) 387.
- [8] Z.-Z. Wu, Z. Xu, X.-Z. You, X.-G. Zhou and H.-Q. Wang, *Polyhedron*, **12** (1993) 795.
- [9] G. Wilkinson and M. Birmingham, *J. Am. Chem. Soc.*, **78** (1956) 42.
- [10] C. Ye and Y. Li, *Youji Huaxue*, (1981) 210.

- [11] *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974.
- [12] Z.-W. Ye and Z.-Z. Wu, *Synth. React. Inorg. Met.-Org. Chem.*, **19** (1989) 157.
- [13] Z.-Z. Wu, Z.-W. Ye and Z.-N. Zhou, *Polyhedron*, **8** (1989) 2109.
- [14] Z.-Z. Wu and Z.-W. Ye, *Polyhedron*, **9** (1990) 2143.
- [15] Z.-Z. Wu and Z.-W. Ye, *Polyhedron*, **10** (1991) 27.
- [16] H.-Z. Ma and Z.-W. Ye, *J. Organomet. Chem.*, **126** (1986) 405.
- [17] Z.-Z. Wu, Z. Xu, X.-Z. You, X.-G. Zhou and Z.-S. Jin, *Polyhedron*, **11** (1992) 2673.
- [18] X.-G. Zhou, Z.-Z. Wu and Z.-S. Jin, *J. Organomet. Chem.*, **431** (1992) 289.
- [19] Z.-Z. Wu, Z. Xu, X.-Z. You, X.-G. Zhou and Z.-S. Jin, *J. Chem. Soc., Chem. Commun.*, (1993) 1494.
- [20] Z.-Z. Wu, X.-G. Zhou, W. Zhang, Z. Xu, X.-Z. You and X.-Y. Huang, *J. Chem. Soc., Chem. Commun.*, (1994) 813.
- [21] Z.-Z. Wu, Z. Xu and X.-Z. You, *Gaodeng Xuexiao Huaxue Xuebao*, **14** (1993) 9.
- [22] Z.-Z. Wu, F.-M. Zhao, X.-J. Song and Z.-N. Zhou, *Youji Huaxue*, **11** (1991) 187.
- [23] Z.-Z. Wu, Z. Xu and X.-Z. You, *Synth. React. Inorg. Met.-Org. Chem.*, **23** (1993) 1155.
- [24] Z.-Z. Wu, Z. Xu, X.-Z. You, X.-G. Zhou and L. Shi, *J. Coord. Chem.*, **26** (1992) 329.
- [25] Z.-Z. Wu, Z. Xu, X.-Z. You, X.-G. Zhou, X.-Y. Huang and J.-T. Chen, *Polyhedron*, **13** (1994) 397.
- [26] R.D. Fischer and L. Xing-Fu, *J. Less-Common Met.*, **112** (1985) 404.
- [27] W.J. Evans, *Polyhedron*, **6** (1986) 803.
- [28] I.G. Dance, *Polyhedron*, **5** (1986) 1037.
- [29] G. Massarweh and R.D. Fischer, *J. Organomet. Chem.*, **459** (1993) 79.
- [30] R.C. Weast (ed.), *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 66th edn., 1985–1986.
- [31] W.J. Evans, T.T. Peterson, M.D. Raush, W.E. Hunter and J.L. Atwood, *Organometallics*, **4** (1985) 554.