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Synthesis and structure of a compound with an ytterbium–tin bond, $(Ph_3Sn)_2Yb(THF)_4$

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Abstract

The distannylytterbium complex $(Ph_3Sn)_2Yb(THF)_4$ was obtained by reaction of naphthaleneytterbium with Ph_4Sn. According to X-ray data this molecule has a distorted octahedral structure. The Yb atom is bonded with four oxygen atoms of THF molecules which are on the equatorial plane and with two Sn atoms of Ph_3Sn groups in axial positions. The Sn–Yb distances are equal 3.305(1) Å, the SnYbSn angle is 164.5(1)°. Crystals are monoclinic with space group $C2/c$ and unit cell dimensions a 16.190(3), b 15.903(3), c 19.066(4) Å, β 98.91(3)°, Z 4, D_c 1.59 g cm^{-3}. The same complex was obtained in low yield in the reaction of napththaleneytterbium with Ph_6Sn_2. Tetraphenylgermane does not react with $C_{10}H_8Yb(THF)_x$.

Introduction

Only a few compounds which probably have a direct lanthanoid–metal bond have been reported [1–3]. None has been verified by rigorous X-ray studies *. Among the complexes containing a lanthanoid–group 14 element bond the silylsamarium compound $[Cp_2Sm(SiMe_3)_2]Li \cdot (DME)_3$ [5] with Sm–Si bond has been the subject of X-ray study, and so has the germane–ytterbium complex $(Ph_3GeH)_2Yb(THF)_4$ [6] in which the presence of tricenter bond $Ge \overset{H}{\cdots\cdots} Yb$ is possible. The interatomic distances Sm–Si and Yb–Ge in these complexes approximate the sum of the covalent radii of the corresponding elements. In the other cases the presence of Ln–M bonds was inferred from indirect data and consequently these suppositions are not definitely confirmed.

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* When this paper was in preparation we received information about the synthesis and X-ray study of a compound with a Lu–Ru bond [4].

In this paper we report the synthesis and the first X-ray diffraction study of a complex with a lanthanoid–tin bond *.

Results and discussion

Naphthaleneytterbium $C_{10}H_8Yb(THF)_3$, which we recently synthesized, is highly reactive in many processes [8], including transmetallations with organomercurials [9,10]. Continuing investigation in this area we have found that naphthaleneytterbium in THF medium does not react with tetraphenylgermane but reacts easily with tetraphenyltin to give two new complexes besides free naphthalene. One of them is isolated from ether–THF solution as dark-ruby, almost black diamagnetic crystals decomposing on heating to 110–115 °C. Judging from the products of its hydrolysis and bromination, as well as from IR spectroscopy, this compound has Yb–Sn and Yb–Ph groupings. Now we try to solve their structure by X-ray analysis.

The second complex, bis(triphenylstannyl)tetrakis(tetrahydrofuran)ytterbium (I), is isolated in 25% yield from ether solution as yellow diamagnetic crystals. Compound I is unstable in air, readily soluble in THF, DME and aromatic solvents. On heating to 127–132° C, I melts and decomposes. The IR spectra of I show the absorption bands of coordinated THF (1020, 860 cm^{-1}) and Ph_3Sn groups (1420 (doublet), 1060 (doublet), 725, 695, 450 (doublet) cm^{-1}).

The same complex but in lower yield is formed in the reaction of naphthaleneytterbium with hexaphenyldistannane.

$$\left.\begin{array}{l} Ph_4Sn + C_{10}H_8Yb(THF)_2 \\ Ph_6Sn_2 + C_{10}H_8Yb(THF)_2 \end{array}\right] \longrightarrow \underset{(I)}{(Ph_3Sn)_2Yb(THF)_4}$$

An X-ray diffraction study has shown that I has a distorted octahedral structure (Fig. 1): the Yb atom is bonded with four oxygen atoms of THF molecules, situated in the equatorial plane, and two tin atoms of Ph_3Sn groups in axial positions. In a crystal the molecule is situated on a 2-fold crystallographic axis which passes through the Yb, O(1) and O(2) atoms. The SnYbSn(a) and O(3)YbO(3a) angles are 164.5(1) and 172.9(7)°, respectively. The Sn and O atoms appear to deviate by 0.3 Å from the middle plane of the YbSnSn(a)O(3)O(3a) fragment. The SnYbO(1) angle of 97.7(1)° is slightly larger but the O(1)YbO(3) angle of 86.5(4)° is smaller than the ideal value 90°, while the SnYbO(3) and SnYbO(3a) angles (91.4(3) and 89.5(3)°) are close to this value. The Yb–Sn bond lengths are 3.305(1) Å. It should be noted that this value is ~ 0.15 Å longer than Yb · · · Ge interatomic distances in $(Ph_3GeH)_2Yb(THF)_4$ (3.140(2) and 3.152(2) Å). This difference is close to the difference between covalent tetrahedral radii of Sn and Ge reported by Pauling (0.18 Å) [11].

The THF molecules are not planar: greatest deviation of atoms from the middle plane is 0.2 Å, greatest bend angle of the molecule along the C · · · C line is 12.3°. The Yb–O(1,2,3) bond lengths (2.38(2), 2.38(2) and 2.42(2) Å) are a little shorter than the Yb–O(THF) bond lengths in $(Ph_3GeH)_2Yb(THF)_4$ (2.399–2.475 Å), but

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* Preliminary communication [7].

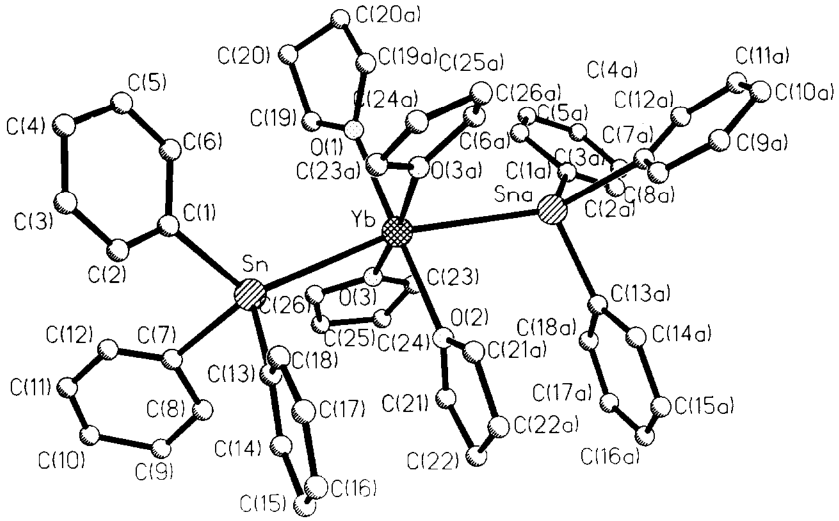

Fig. 1. The molecular structure of $(Ph_3Sn)_2Yb(THF)_4$.

Table 1

Atomic coordinates ($\times 10^4$) in the structure of I and their anisotropic thermal factors (Å^2 $\times 10^3$)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Yb	0	1442(1)	1/4	33(1)	33(1)	34(1)	0	6(1)	0
Sn	2047(1)	1722(1)	2800(1)	32(1)	30(1)	30(1)	−2(1)	7(1)	0(1)
O(1)	0	−53(13)	1/4	48(13)	39(12)	96(18)	0	18(12)	0
O(2)	0	2941(12)	1/4	57(13)	19(10)	104(19)	0	1(13)	0
O(3)	3(9)	1348(10)	1233(7)	37(8)	70(10)	41(8)	−2(7)	−2(6)	−11(7)
C(1)	2859(12)	940(12)	3605(10)	41(11)	37(11)	39(11)	15(8)	13(9)	11(8)
C(2)	3574(13)	1217(16)	3969(12)	39(12)	74(16)	51(13)	−1(11)	12(10)	19(12)
C(3)	4044(17)	741(20)	4493(16)	56(16)	104(23)	78(19)	6(15)	22(14)	30(17)
C(4)	3814(18)	−55(19)	4660(14)	74(18)	93(22)	66(17)	41(16)	30(15)	38(16)
C(5)	3038(19)	−349(15)	4261(13)	104(22)	51(14)	56(15)	43(14)	38(15)	31(12)
C(6)	2570(14)	115(13)	3746(10)	68(14)	44(12)	35(11)	8(10)	16(10)	3(9)
C(7)	2962(20)	1835(12)	2027(14)	152(28)	16(10)	83(18)	6(13)	90(19)	−4(10)
C(8)	2676(14)	2334(15)	1403(12)	58(14)	61(14)	55(14)	33(12)	22(11)	28(11)
C(9)	3198(17)	2438(17)	892(12)	82(18)	87(19)	46(14)	35(15)	32(13)	39(13)
C(10)	3989(18)	1981(17)	996(14)	92(20)	71(17)	69(17)	−25(15)	63(16)	−13(14)
C(11)	4150(13)	1517(14)	1545(12)	40(12)	46(12)	64(14)	3(10)	14(10)	4(11)
C(12)	3644(10)	1451(12)	2060(8)	28(9)	42(10)	22(8)	7(8)	6(7)	3(7)
C(13)	2313(11)	2940(11)	3295(9)	39(10)	31(10)	34(10)	14(8)	12(8)	9(8)
C(14)	2381(13)	3642(13)	2909(10)	52(13)	43(12)	38(11)	4(10)	16(9)	5(9)
C(15)	2461(18)	4482(13)	3221(14)	113(22)	27(11)	78(17)	−2(12)	71(17)	1(11)
C(16)	2490(14)	4560(13)	3940(12)	60(14)	34(11)	62(14)	−11(10)	21(11)	−16(10)
C(17)	2449(14)	3870(13)	4352(10)	57(13)	47(12)	31(10)	15(10)	4(9)	−1(9)
C(18)	2391(12)	3085(12)	4049(9)	46(11)	43(11)	25(9)	−7(9)	0(8)	−1(8)
C(19)	276(56)	−609(21)	2034(38)	660(14)	31(19)	420(91)	6(42)	441(103)	−5(33)
C(20)	316(22)	−1476(19)	2297(32)	81(27)	48(17)	300(68)	8(15)	−8(34)	−21(27)
C(21)	14(27)	3454(20)	1897(23)	131(33)	62(21)	164(39)	−9(20)	41(30)	27(22)
C(22)	28(35)	4331(18)	2108(41)	137(33)	35(16)	522(142)	31(22)	176(62)	49(33)
C(23)	−658(22)	1416(26)	699(14)	112(25)	190(37)	49(16)	96(26)	37(17)	55(20)
C(24)	−357(30)	1444(35)	11(20)	153(40)	258(58)	89(25)	72(40)	77(28)	89(32)
C(25)	508(18)	1280(26)	166(15)	54(17)	187(38)	54(17)	−6(20)	14(14)	23(20)
C(26)	674(19)	1155(35)	869(18)	52(18)	352(66)	85(23)	−40(27)	23(17)	−135(33)

Table 2

The bond lengths *d* (Å) in I

Yb–Sn	3.305(1)	C(7)–C(12)	1.254(35)
Yb–O(1)	2.378(21)	C(8)–C(9)	1.395(37)
Yb–O(2)	2.384(19)	C(9)–C(10)	1.457(39)
Yb–O(3)	2.422(14)	C(10)–C(11)	1.275(35)
Sn–C(1)	2.238(18)	C(11)–C(12)	1.377(30)
Sn–C(7)	2.254(32)	C(13)–C(14)	1.352(27)
Sn–C(13)	2.168(18)	C(13)–C(18)	1.442(25)
O(1)–C(19)	1.376(68)	C(14)–C(15)	1.460(30)
O(2)–C(21)	1.412(43)	C(15)–C(16)	1.369(35)
O(3)–C(23)	1.361(32)	C(16)–C(17)	1.357(30)
O(3)–C(26)	1.410(39)	C(17)–C(18)	1.373(28)
C(1)–C(2)	1.330(28)	C(19)–C(20)	1.464(54)
C(1)–C(6)	1.431(29)	C(20–C(20a)	1.376(104)
C(2)–C(3)	1.382(36)	C(21)–C(22)	1.451(48)
C(3)–C(4)	1.372(44)	C(22)–C(22a)	1.511(156)
C(4)–C(5)	1.442(38)	C(23)–C(24)	1.468(52)
C(5)–C(6)	1.361(31)	C(24)–C(25)	1.410(56)
C(7)–C(8)	1.446(33)	C(25)–C(26)	1.340(45)

Table 3

The bond angles *ω* (°) in I

Sn–Yb–O(1)	97.7(1)	C(4)–C(5)–C(6)	123.2(24)
Sn–Yb–O(2)	82.3(1)	C(1)–C(6)–C(5)	118.0(20)
Sn–Yb–O(3)	91.4(3)	Sn–C(7)–C(8)	115.0(20)
O(1)–Yb–O(3)	86.5(4)	Sn–C(7)–C(12)	126.2(17)
O()–Yb–O(3)	93.5(4)	C(8)–C(7)–C(12)	118.5(26)
Sn–Yb–Sn(a)	164.5(1)	C(7)–C(8)–C(9)	119.2(23)
Sn–Yb–O(3a)	89.5(3)	C(8)–C(9)–C(10)	117.5(22)
O(3)–Yb–O(3a)	172.9(7)	C(9)–C(10)–C(11)	117.6(26)
Yb–Sn–C(1)	120.7(5)	C(10)–C(11)–C(12)	124.1(22)
Yb–Sn–C(7)	129.8(7)	C(7)–C(12)–C(11)	122.9(20)
C(1)–Sn–C(7)	96.7(8)	Sn–C(13)–C(14)	121.9(14)
Yb–Sn–C(13)	108.8(5)	Sn–C(13)–C(18)	123.9(13)
C(1)–Sn–C(13)	98.2(7)	C(14)–C(13)–C(18)	114.2(17)
C(7)–Sn–C(13)	96.2(7)	C(13)–C(14)–C(15)	122.9(19)
Yb–O(1)–C(19)	130.0(25)	C(14)–C(15)–C(16)	118.6(20)
C(19)–O(1)–C(19a)	100.0(50)	C(15)–C(16)–C(17)	120.6(19)
Yb–O(2)–C(21)	125.3(16)	C(16)–C(17)–C(18)	119.9(19)
C(21)–O(2)–C(21a)	109.5(32)	C(13)–C(18)–C(17)	123.7(17)
Yb–O(3)–C(23)	128.2(16)	O(1)–C(19)–C(20)	112.7(55)
Yb–O(3)–C(26)	128.6(15)	C(19)–C(20)–C(20a)	101.2(39)
C(23)–O(3)–C(26)	103.0(21)	O(2)–C(21)–C(22)	109.3(42)
Sn–C(1)–C(2)	123.1(16)	C(21)–C(22)–C(22a)	105.9(35)
Sn–C(1)–C(6)	117.6(13)	O(3)–C(23)–C(24)	109.9(30)
C(2)–C(1)–C(6)	119.3(19)	C(23)–C(24)–C(25)	105.2(30)
C(1)–C(2)–C(3)	122.2(23)	C(24)–C(25)–C(26)	106.1(30)
C(2)–C(3)–C(4)	122.3(24)	O(3)–C(26)–C(25)	114.1(28)
C(3)–C(4)–C(5)	114.9(24)		

longer than in the wedge-shaped sandwich complex $Cp_2YbMe(THF)$ (2.311 Å) [12]. Similar values for Yb–O(THF) distances were observed in octahedral complexes $CpYbX_2(THF)_3$ in which Yb–O distances are 2.336, 2.365 and 2.417 Å for X = Cl [13] and 2.335, 2.348 and 2.428 Å for X = Br [14]. The complete geometry of THF is given in Tables 2 and 3.

The phenyl rings in the molecule of I are slightly bent away from the equatorial plane. This is confirmed by the increase of the YbSnC(1,7) angles (120.7(5) and 129.8(7)°) and decrease of the C(1)SnC(7), C(1)SnC(13) and C(7)SnC(13) angles (96.7(8), 98.2(7) and 96.2(7)°) in comparison with the ideal tetrahedral angle. Similar deviations of the angles were observed in the molecule $(Ph_3GeH)_2Yb(THF)_4$. The Sn–C(1,7) bonds (2.24(2) and 2.25(3) Å) are longer than the Sn–C(13) bond (2.17(2) Å), and noticeably exceed the sum of covalent tetrahedral radii of these atoms (2.17 Å according to Pauling [11]). Average values of C–C distances and CCC valent angles in Ph-rings are equal, 1.38 Å and 120°. The full geometry of Ph_3Sn groups is given in Tables 2 and 3. Intermolecular H ··· H contacts between Ph rings and THF molecules approximate the sum of the van der Waals radii of these atoms (2.4 Å [11]).

Thus the structure of I is very similar the structure of $(Ph_3GeH)_2Yb(THF)_4$ [6], with the slight but important difference of an absence of bridging H-atoms between atoms of ytterbium and group 14 element in I, and the presence of these bridges in bis(germane)–ytterbium. Absence of H-bridges in I is confirmed by the absence of corresponding maxima in the (zero) electron density syntheses of the molecule.

Experimental

All experiments were carried out *in vacuo* by use of standard Schlenk techniques. Solvents were thoroughly dried and distilled from ketyl benzophenone solution. The IR spectra were recorded on a Perkin–Elmer 577 spectrometer. Samples of the solid compounds were prepared in the form of a suspension in petroleum jelly.

X-Ray analysis was carried out with a Siemens *R*3*m* diffractometer at 193 K (λ Mo-K_α; $\theta/2\theta$-scan in the range $2 < 2\theta < 56°$). 3462 reflections with $F > 3.0\ \sigma(F)$ were used in the structure determination and refinement. The Yb and Sn atoms were located by a direct method. The positions of the other non-hydrogen atoms were revealed by subsequent electron density syntheses. The structure was refined by a least-squares method with anisotropic thermal parameters for non-hydrogen atoms. Positions of H atoms were calculated by geometrical conditions. These positions and their isotopic thermal parameters (adopted B_{iso} 0.08 Å^2) were not refined but were recalculated after each cycle of refinement of positions of H atoms. Absorption was taken into account by the DIFABS program [15]. The final discrepancy factors were $R = 0.064$ and $R_w = 0.109$. Coordinates of atoms are given in Table 1. All calculations were performed with the SHELXTL PLUS package.

Synthesis of $(Ph_3Sn)_2Yb(THF)_4$ *(I)*

$C_{10}H_8Yb(THF)_2$ (2.65 g, 5.92 mmol) was added to a solution of Ph_4Sn (2.53 g, 5.92 mmol) in 20 ml of THF. The mixture was shaken at room temperature for 48 h, during which the precipitate of $C_{10}H_8Yb(THF)_x$ dissolved almost completely and the solution became dark-brown. After centrifuging, the solution was decanted from the small amount of precipitate and THF was evaporated *in vacuo* to 5 ml. The addition of 25 ml ether precipitates dark-ruby, almost black crystals (0.82 g, m.p. 110–115 °C (dec.)) The solvents were removed *in vacuo* from the mother solution. The remaining solid was extracted with ether (30 ml × 2). Cooling at −5 °C for 24 h yielded yellow crystals of I. The crystals were washed in cold ether (5 ml × 2) and dried *in vacuo*. The yield of I 0.81 g, 23.5%, m.p. 127–132 °C (dec.). IR: 3040, 1420 (doublet), 1060 (doublet), 1020, 990, 860, 725, 695, 450 (doublet) cm^{-1}. Naphthalene (0.61 g, 80% by GLC) was detected in the mother liquor.

The reaction of naphthaleneytterbium with hexaphenyldistannane was carried out similarly, giving I in 5% yield.

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