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Preliminary communication

Synthesis and crystal structure of the organogermanium complex of ytterbium $[(Ph_2Ge)_4Yb(THF)_4] \cdot 4THF$ with a five-membered Ge_4Yb cycle

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Abstract

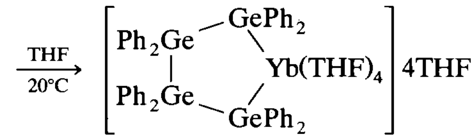
The organogermanium complex of ytterbium $[(Ph_2Ge)_4Yb(THF)_4] \cdot 4THF$ (**1**) was synthesized by the reaction of metallic ytterbium with Ph_2GeCl_2 in THF at room temperature. X-ray study has shown that the molecule of $(Ph_2Ge)_4Yb(THF)_4$ is an octahedral Yb complex with the C_2 symmetry. The four coordination positions at the Yb atom are occupied by the oxygen atoms of THF molecules and the two *cis*-positions are occupied by two terminal germanium atoms of the $Ph_2Ge–GePh_2–GePh_2–GePh_2$ fragment. Thus, the $(Ph_2Ge)_4Yb(THF)_4$ molecule involves the five-membered Ge_4Yb metallocycle with a twist conformation. The Yb–Ge and Yb–O distances are 3.104(2) and 2.475(8), 2.402(10) Å.

Keywords: Heterometallic cycle; Germanium; Ytterbium

In the course of our study of reactions of metallic lanthanoids with organosilicon, -germanium and -tin chlorides R_nECl_{4-n} (E = Si, Ge, Sn; R = Me, Ph; n = 1–3) we found that these reactions can be used as a synthetic route to organosilicon, -germanium and -tin derivatives of lanthanoids. This approach allowed to synthesize and structurally characterize complexes containing the direct Ln–E bonds: $(Ph_3E)_2Yb(THF)_4$ (E = Si, Ge, Sn) [1–3], $[(Me_3Sn)_3Sn]_2Ln(THF)_4$ (Ln = Sm, Yb) [4], and the ionic compound $[(Ph_3Sn)_3Sn]_2^-$-$[(DME)_3Yb(\mu\text{-}Cl)_2Yb(DME)_3]^{2+}$ [1]. Only a few compounds with the direct Ln–Ge bond are known: $(Ph_3Ge)_3Ln$ (Ln = Nd, Gd, Er) [5], $Cp_2ErGePh_3$ [5], $[Li(DME)_3][\{(C_5H_5)_3Sm\}_2Ge(CH_3)_3]$ [6], $(Ph_3Ge)_2Yb(THF)_4$ [3]. The complex $(Ph_3Ge)_2Yb(THF)_4$ is the only compound with the Ln–Ge bond whose structure was confirmed by the X-ray diffraction method [3]. Here we report the synthesis and crystal structure of the first organogermanium metallocyclic complex of lanthanoids **1**.

Complex **1** was formed in the reaction of metallic Yb with Ph_2GeCl_2 in THF at room temperature for ca. 170 h [7].

$4Ph_2GeCl_2 + 5Yb$



1

$+ 4YbCl_2(THF)_2$

The course of the reaction was monitored by measuring ytterbium content in the reaction solution. Complex **1** was isolated in 48.9% yield as unstable in air light-brown crystals, soluble in THF, DME, sparingly soluble in benzene, insoluble in hexane. It melts with decomposition at 168–170°C. The IR spectrum of **1** shows the absorption bands of Ph–Ge fragments (1020,

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750, 690, 450 cm^{-1}), coordinated (860 cm^{-1}) and solvated (1070 cm^{-1}) THF molecules.

It is interesting to note that the reaction of Yb with Ph_2SnCl_2 does not lead to derivatives with Sn–Yb bonds but gives ionic complex consisting of isolated $[(DME)_3Yb(\mu\text{-}Cl)_2Yb(DME)_3]^{2+}$ cation and pyramidal anions $[(Ph_3Sn)_3Sn]^-$ [1].

The molecule structure of $(Ph_2Ge)_4Yb(THF)_4$ determined by the X-ray diffraction study [8] is shown in Fig. 1. The symmetry of the $(Ph_2Ge)_4Yb(THF)_4$ molecule is C_2. The Yb(1) atom and the middle point of the Ge(2)–Ge(2a) bond are on the two-fold axis. (Besides the main molecule the crystal of **1** contains also two symmetrically independent solvating THF molecules). The Yb and Ge atoms have a distorted octahedral and tetrahedral environment, respectively. The four coordination positions at the Yb atom are occupied by the oxygen atoms of THF molecules and the two *cis*-positions are occupied by two terminal germanium atoms of the $Ph_2Ge–GePh_2–GePh_2–GePh_2$ fragment. Thus, the $(Ph_2Ge)_4Yb(THF)_4$ molecules involves the five-membered Ge_4Yb metallocycle having a twist conformation. The deviations of the Ge(2) and Ge(2a) atoms from the Yb(1)Ge(1)-Ge(1a) plane are equal to 0.18 and −0.18 Å, respectively. The torsion angles in this cycle are Yb(1)Ge(1)–Ge(2)Ge(2a) 25.4°, Ge(1)Ge(2)–Ge(2a)Ge(1a) −30.3°, Ge(2)Ge(2a)–Ge(1a)Yb(1) 25.4°, Ge(2a)Ge(1a)–Yb(1)-Ge(1) −9.5°, Ge(1a)Yb(1)–Ge(1)Ge(2) −9.5°. The similar five-membered Ge_4Se cycle in $(Ph_2Ge)_4Se$ is more planar [9] and the Ge_4S cycle in $(Ph_2Ge)_4S$ has an envelope conformation [10].

The Yb(1)–Ge(1) distance in **1**, 3.104(2) Å, is somewhat shorter then that in the octahedral complex $(Ph_3Ge)_2Yb(THF)_4$ (3.170 and 3.141 Å in two independent molecules) with *trans*-arrangement of Ph_3Ge groups at the Yb atom. The Ge(1)–Ge(2) and Ge(2)–Ge(2a) distances (2.479(2) and 2.489(2) Å) in **1** are longer by ca. 0.3 Å than those in molecules $(Ph_2Ge)_4Se$ [9] and $(Ph_2Ge)_4S$ [10]. The Ge–C distances in **1** (1.973(11)–2.017(9) Å) are also slightly longer than the average Ge–C distances in mentioned molecules; 1.961 and 1.959 Å, respectively.

The dihedral angles between the average plane of Ge_4Yb cycle and the Yb(1)O(1)O(1a) plane is 4.7°. The dihedral angles between two mentioned planes and the O(2)Yb(1)O(2a) plane (92.5 and 87.7°, respectively) are close to 90°. However, the O(2) atom is bent away from the nearest Ph_2Ge fragment owing to non-bonded repulsions between the THF molecules and Ph rings (Fig. 1). The O(1)Yb(1)O(1a) and O(2)Yb(1)O(2a) angles (103.7(4) and 150.3(5)°), respectively) are signifi-

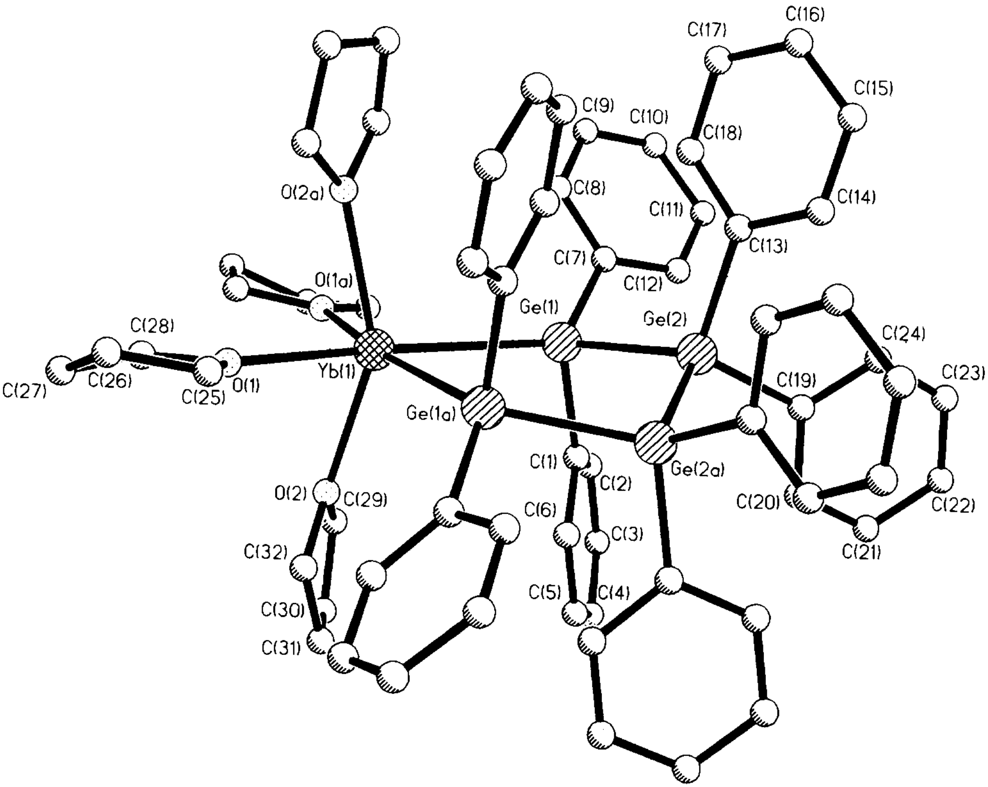

Fig. 1. The general view of $(Ph_2Ge)_4Yb(THF)_4$ molecule and atom labelling. The main distances (in Å) and angles (in deg.): Yb(1)–Ge(1) 3.104(2), Ge(1)–Ge(2) 2.479(2), Ge(2)–Ge(2a) 2.489(2), Yb–O(1) 2.475(8), Yb(1)–O(2) 2.402(10), Ge(1)–C(1) 2.012(11), Ge(1)–C(7) 2.017(9), Ge(2)–C(13) 1.973(11), Ge(2)–C(19) 1.980(11), C–C_{av} 1.38(2), Ge(1)Yb(1)Ge(1a) 84.5(1), O(1)Yb(1)O(1a) 103.7(4), O(2)Yb(1)O(2a) 150.3(5), Yb(1)Ge(1)Ge(2) 116.0(1), Ge(1)Ge(2)Ge(2a) 107.6(1), C(1)Ge(1)C(7) 102.8(4), C(13)Ge(2)C(19) 104.1(4).

cantly larger and respectively smaller than ideal octahedral angles. The similar distortions of the octahedral coordination of the Yb atom were found in the cation $[(THF)_4Yb(\mu\text{-}Cl)_2Yb(THF)_4]^{2+}$ [11].

The Yb–O(1) distance, 2.475(8) Å, for the oxygen atom in *trans*-position relatively to the Ge atom is slightly longer then the Yb–O(2) distance, 2.402(10) Å, for oxygen atom in *cis*-position. The difference between the similar Yb–O distances (2.39 and 2.37 Å) found in cation $[(THF)_4Yb(\mu\text{-}Cl)_2Yb(THF)_4]^{2+}$ [11] is smaller. The Yb–O(THF) distances in **1** can be also compared with the similar values in $(Ph_3Ge)_2Yb(THF)_4$, 2.42–2.43 Å [3], and cation $[Yb(THF)_6]^{2+}$, 2.390(7) Å [11].

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[7] The synthesis and isolation of **1** were performed under vacuum in sealed ampoules using thoroughly dried solvents. Preparation of **1**. The mixture of Ph_2GeCl_2 (1.28 g, 4.30 mmol) and Yb in the form of filings (2.57 g, 14.85 mmol) in 20 ml of THF was stirred using a magnetic stirrer for ca. 170 h at room temperature. Excess of Yb and formed fine grey deposit of ytterbium dichloride were separated from brown solution and washed repeatedly with THF. Ytterbium dichloride in the form of suspension in THF was separated from excess of Yb, dried in vacuum at room temperature to yield 1.28 g (76.7%) of $YbCl_2(THF)_2$ (identified by elemental analysis and IR spectrum). The reaction solution and washings were combined, total volume was reduced to 10 ml and kept at 0°C for 20 h to yield 0.50 g of crystalline **1**. The mother solution was reduced to 5 ml and kept at 0°C for 20 h to yield additional amount (0.35 g) of crystalline **1**. The total yield of crystalline complex **1** was 0.87 g (48.9%). M.p. 168–170°C (dec.). Anal. found: C, 57.04; H, 6.17; Yb, 11.35. Calcd. for $C_{80}H_{104}Ge_4O_8Yb_1$: C, 57.98; H, 6.33; Yb, 10.44%.

[8] The X-ray diffraction experiment for **1** was carried out with the crystal of dimensions ca. $0.4 \times 0.4 \times 0.5$ mm^3 using Siemens P3/PC diffractometer at 153 K (MoKα radiation, graphite monochromator, Θ-2Θ scan mode, $2 < 2\Theta < 50°$, 3500 independent measured reflections, 2497 observed reflections with $F > 4\sigma(F)$ were used in the refinement). Crystal data for **1** at 153 K: $C_{64}H_{72}Ge_4O_4Yb_1 \cdot 4(OC_4H_8)$, monoclinic space group $C2/c$, $a = 21.311(8)$, $b = 16.251(4)$, $c = 22.763(6)$ Å, $\beta = 105.30(2)°$, $V = 7604(4)$ Å^3, $Z = 4$ (for the mentioned formula), $D_{calc} = 1.447$ g cm^{-3}, $\mu = 2.807$ mm^{-1}. The structure was solved using Patterson function. Besides the main molecule the crystal structure of **1** contains two symmetrically independent solvating THF molecules. All non-hydrogen atoms were refined anisotropically. The positions of H atoms were calculated and refined in the riding model with fixed isotropic parameters $U = 0.08$ Å^2. Absorption was taken into account by the DIFABS program ($T_{min} = 0.844$, $T_{max} = 1.178$) (N. Walker and D. Stuart, *Acta Crystallogr., Sect. A., A39* (1983) 158). The final refinements converged at $R = 0.041$, $R_W = 0.050$, $GOF = 0.96$ for observed reflections. The weighting scheme $W^{-1} = \sigma^2(F) + 0.0017F^2$ was used for refinement of structure. All calculations were performed using the SHELXTL-PLUS package (PC version) (G.M. Sheldrick, Structure Determination Software Program Package, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1989).

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