

Short review

X-ray study of organic and organoelement compounds of the lanthanides¹

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Abstract

The crystal structures of the mono- and binuclear phenyl derivatives of the lanthanides and the organoelement compounds of the lanthanides with a direct Ln–E bond (E = Si, Ge, Sn) are reviewed. © 1997 Elsevier Science S.A.

Keywords: Lanthanides; Silicon; Germanium; Tin; Crystal structure

1. Introduction

The organometallic chemistry of the lanthanides is one of the most rapidly developing areas of organometallic chemistry (see, for example, Refs. [1–3]). Part of our investigation in recent years was related to the study of crystal and molecular structures of organic and organoelement compounds of the lanthanides by the X-ray single crystal diffraction method. There are three main groups among the compounds for which X-ray structures have been determined in these investigations: mono- and binuclear phenyl derivatives of the lanthanides; organoelement compounds of the lanthanides with a direct Ln–E bond (E = Si, Ge, Sn); organolanthanides containing an organic ligand with double C=C, C=N or triple C≡C bonds (naphthalene, diphenylbutadiene, –C≡CPh group and other) coordinated to the Ln atom. Herein the results found for compounds of two first groups are given.

2. Results and discussion

The X-ray structural data for neutral di-, triaryl or alkyl derivatives of lanthanides R₂Ln, R₃Ln are very poor [1,2]. Only a few crystal structures of such type are known: Yb[C(SiMe₃)₃]₂ with a non-linear C–Yb–C fragment [4]; Ln[CH(SiMe₃)₂]₃ (Ln = La, Sm) with a flat pyramidal coordination of the Ln atom [5]; Lu(Me₂NCH₂C₆H₄)₃ in which the Lu atom is bonded to three chelate ligands Me₂NCH₂C₆H₄ by the C and N atoms of ligands [6]. Thus any structural information for such compounds is very useful. In the course of our study the crystal structures of monomeric triphenyl derivatives Ph₃Ln(THF)₃ (Ln = Er (**I**), Tm (**II**) [7], Yb (**III**) [8]) and dimeric compounds Ph₂(THF)Yb(μ-Ph)₃Yb(THF)₃ (**IV**) [9] and Ph₃Sn(THF)₂Yb(μ-Ph)₃Yb(THF)₃ (**V**) [10] with μ-bridging Ph groups have been determined.

Crystals of **I**, **II** and **III** are isostructural and consist of monomeric molecules. The Ln atoms in these complexes have a distorted *fac*-octahedral environment (Fig. 1). The CLnC angles (99.2(2)–103.5(2)° for Ln = Er; 99.8(2)–102.9(2)° for Ln = Tm and 99.5(4)–103.2(4)° for Ln = Yb) are significantly more than 90°, whereas the OLnO angles (80.6(1)–77.7(1)° for Ln = Er; 81.0(2)–78.0(2)° for Ln = Tm and 80.9(2)–77.6(2)° for Ln = Yb) are accordingly less than 90°. The similar

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¹ I am happy that for many years I was able to work with such an outstanding man as Yuri T. Struchkov and his colleagues from the laboratory he founded – Lev Zakharov.

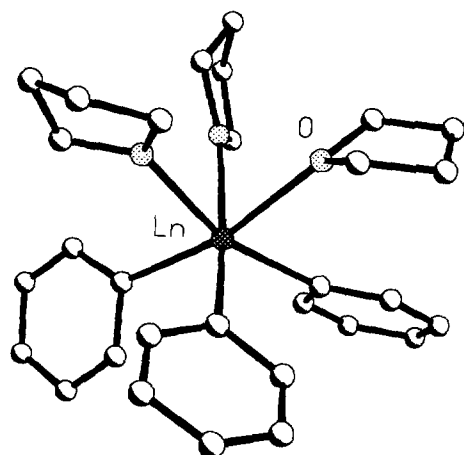


Fig. 1. A general view of I–III.

intervals of the $O(R)LnO(R)$ and $O(THF)LnO(THF)$ angles were found in the *fac*-octahedral complexes $Y(OSiPh_3)_3(THF)_3$ (100.8 – 102.3° and 79.6 – 82.2°) [11] and $Ce(OSiPh_3)_3(THF)_3$ (100.4 – 103.3° and 76.5 – 83.1°) [12].

The Ln–C σ -bond distances in I–III are 2.412(5), 2.442(5) and 2.440(6) Å for Ln = Er; 2.421(6), 2.425(6) and 2.416(7) Å for Ln = Tm; and 2.39(1), 2.40(1) and 2.43(1) Å for Ln = Yb. The differences between the average Er–C, Tm–C and Yb–C distances in I–III (2.431, 2.421 and 2.41 Å respectively) are comparable with the differences in radii for six-coordinate Er^{3+} , Tm^{3+} and Yb^{3+} reported by Shannon (0.890, 0.880 and 0.868 Å respectively) [13]. The Ln–C distances in I–III may be compared with the Ln–C(Aryl) distances found in other organolanthanide complexes: the average Lu–C distance (2.435 Å) in $(o-Me_2NCH_2C_6H_4)_3Lu$ [6]; the average Yb–C distance (2.42 Å) for terminal Ph groups in IV; the Gd–C distance (2.412 Å) in $PhGdCl_2(THF)_4$ [14]; the Sm–C distance (2.511 Å) in $(Me_5C_5)_2SmPh(THF)$ [15]; the Lu–C distance (2.345 Å) in $Cp_2LuC_6H_4Me-p(THF)$ [16]; the average Y–C distance (2.41 Å) in $Cp_2YC_6H_4CH_2NMe_2-o$ [17].

Both molecules IV and V are binuclear ytterbium complexes in which two Yb atoms are connected by three μ -bridging Ph groups (Figs. 2 and 3). The Yb(2) atoms in both molecules are also bonded to three THF molecules, and the Yb(1) atoms are bonded to two terminal Ph groups and THF molecules in IV and two THF molecules and an $SnPh_3$ group in V. The central $Yb(\mu-Ph)_3Yb$ fragments in both molecules are similar, and have a distorted trigonal-bipyramidal structure. The coordination of all Yb atoms is a distorted octahedron. All three bridging Ph groups in IV and two in V are bent to the Yb(2) atom. This seems to be related to the existence of additional interactions between these bridging Ph groups and the Yb(2) atom.

The Yb–C bridges in V are symmetrical: Yb(1)–C(1) 2.62(1) Å opposite Yb(2)–C(1) 2.596(9) Å; Yb(1)–C(7)

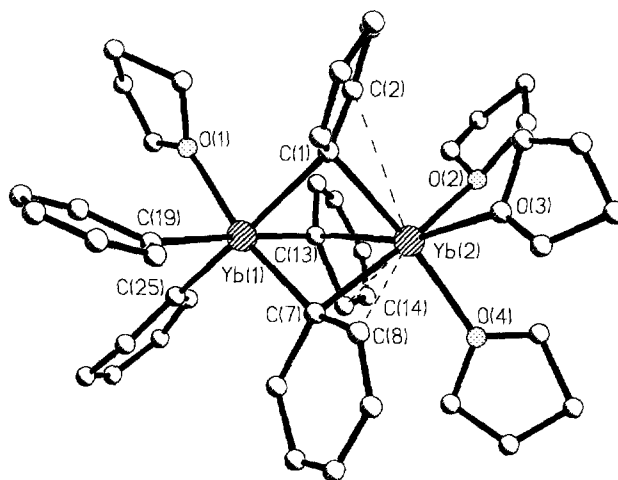


Fig. 2. The X-ray structure of IV.

2.61(1) Å opposite Yb(2)–C(7) 2.60(1) Å; Yb(1)–C(13) 2.66(1) Å opposite Yb(2)–C(13) 2.62(1) Å. The interval of Ln–C distances in V (2.60–2.66 Å) is narrower than that in IV (2.48–2.75 Å). In both cases the μ -bridging Yb–C distances are longer than the lengths of the terminal Ln–C(Ph) bonds in I–III and in IV (2.39–2.46 Å for two symmetrically independent molecules).

In contrast to IV, the positions of H atoms of bridging Ph groups in V were located from difference Fourier maps. The geometry of these C–H bonds has shown the absence of any interactions of these H atoms with the Yb(1) and Yb(2) atoms.

The average Ln–O distances (2.416, 2.407 and 2.395 Å for Ln = Er, Tm and Yb respectively) in I–III are somewhat shorter than the average Ln–O(THF) distances for the Ln(THF)₃ *cis*-fragment in complexes IV (2.44 Å) and V (2.468 Å). The Ln–O(THF) distances in I–III are longer than those in cyclopentadienyl-lanthanide complexes [18] if the differences in metal size and coordination number are considered. Steric crowding seems to be the predominant factor in such Ln–O(THF) bond lengthening. However, the *trans* influ-

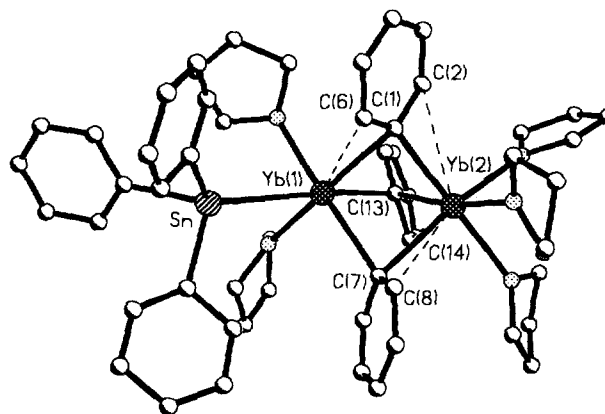


Fig. 3. The X-ray structure of V.

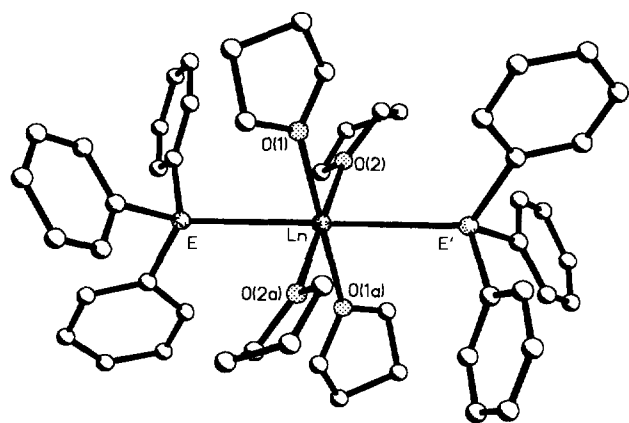
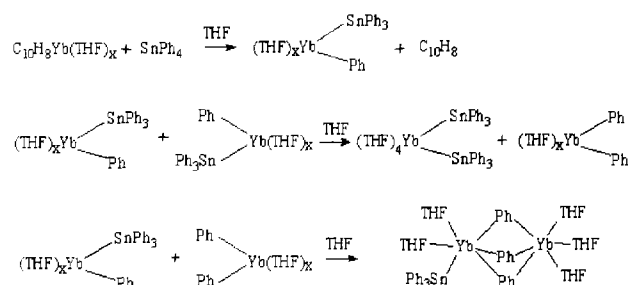


Fig. 4. A general view of VI–IX.

ence of the *fac*-phenyl groups can also be a reason. Unfortunately, the available X-ray data are not sufficient to evaluate such influences in I–III.

The molecules IV and V can be represented as an association of two units: $\text{Ph}_2(\text{THF})_3\text{Yb(II)}$ and $\text{Ph}_3(\text{THF})\text{Yb(III)}$ with Yb(II) and Yb(III) in IV; $\text{Ph}_3\text{Sn}(\text{THF})_2\text{Yb(II)Ph}$ and $\text{Ph}_2(\text{THF})_3\text{Yb(II)}$ with Yb(II) in V. On the basis of the structures of complexes $\text{Ph}_3\text{Sn}(\text{THF})_2\text{Yb}(\mu\text{-Ph})_3\text{Yb}(\text{THF})_3$ (V) and $(\text{Ph}_3\text{Sn})_2\text{Yb}(\text{THF})_4$ (VI), a scheme of the reaction of

$\text{C}_{10}\text{H}_8\text{Yb}(\text{THF})_2$ with Ph_4Sn leading to these two products [10] seems to be described as follows:



In the first stage of this reaction, the $(\text{THF})_x\text{Yb(II)PhSnPh}_3$ are formed. Association of two $(\text{THF})_x\text{Yb(II)PhSnPh}_3$ units with an exchange of ligands leads to the formation of $(\text{THF})_x\text{Yb(II)Ph}_2$ and the first product of this reaction, compounds $(\text{Ph}_3\text{Sn})_2\text{Yb(II)(THF)}_4$. The first products are associated with $(\text{THF})_x\text{Yb(II)PhSnPh}_3$, giving the second product of this reaction, compound V.

Thus the X-ray results determined not only provide direct and indirect evidence for the existence of stable

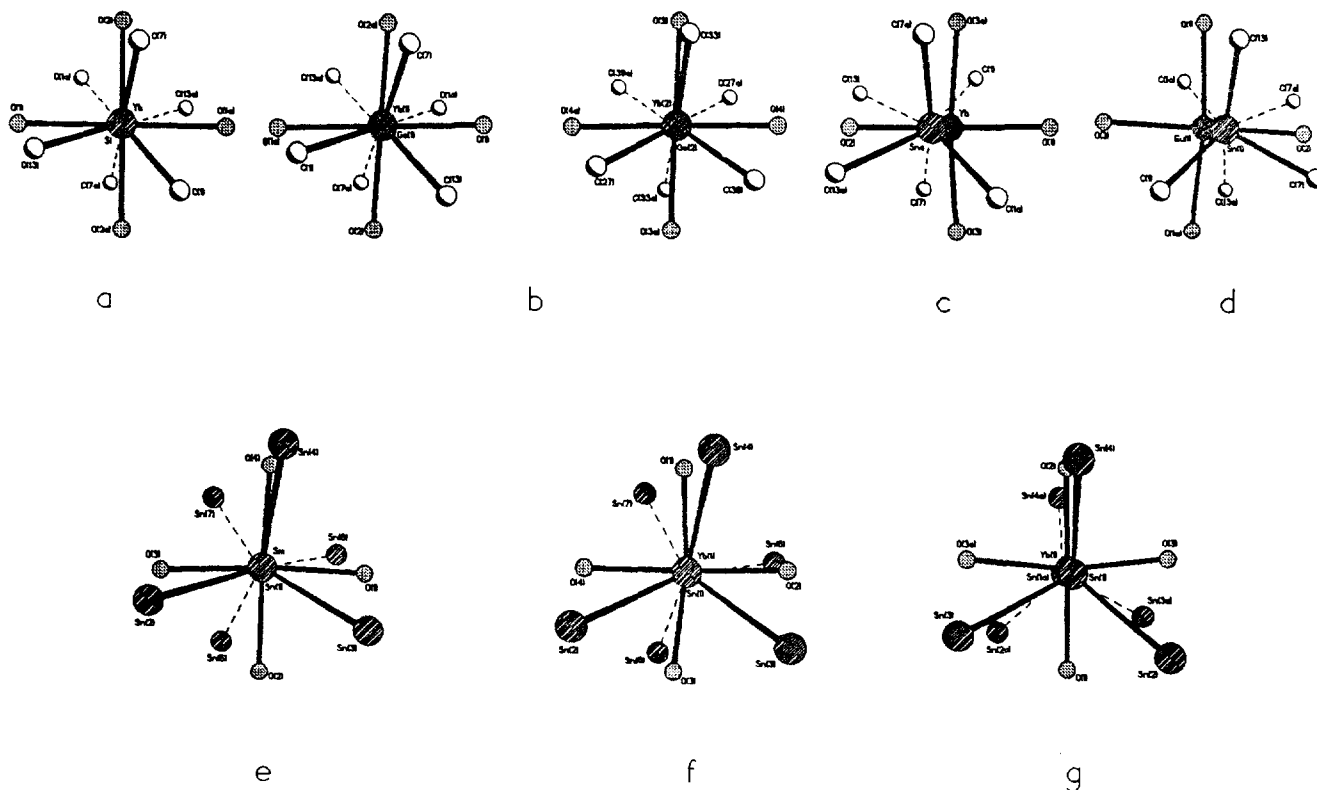
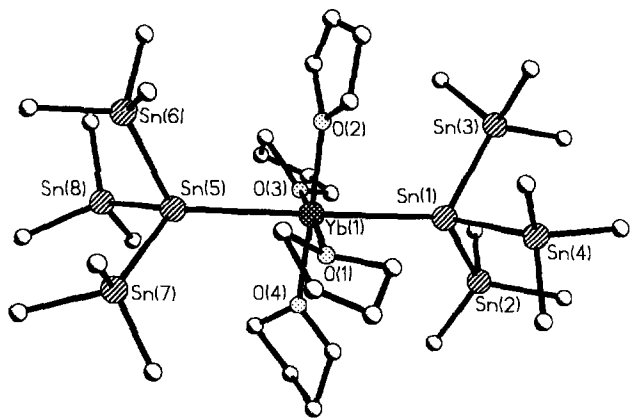


Fig. 5. Central $(\text{C}_3\text{E})_2\text{LnO}_4$ cores of VI–XII viewed along the $\text{E} \cdots \text{E}$ lines: (a) VIII; (b) VII (for two independent molecules); (c) VI; (d) IX; (e) X; (f) XI; (g) XII.

Fig. 6. The X-ray structure of **XII**.

$\text{Ph}_3\text{Ln(III)}$ and $\text{Ph}_2\text{Ln(II)}$ lanthanide derivatives, but allow us to evaluate their behavior in solution.

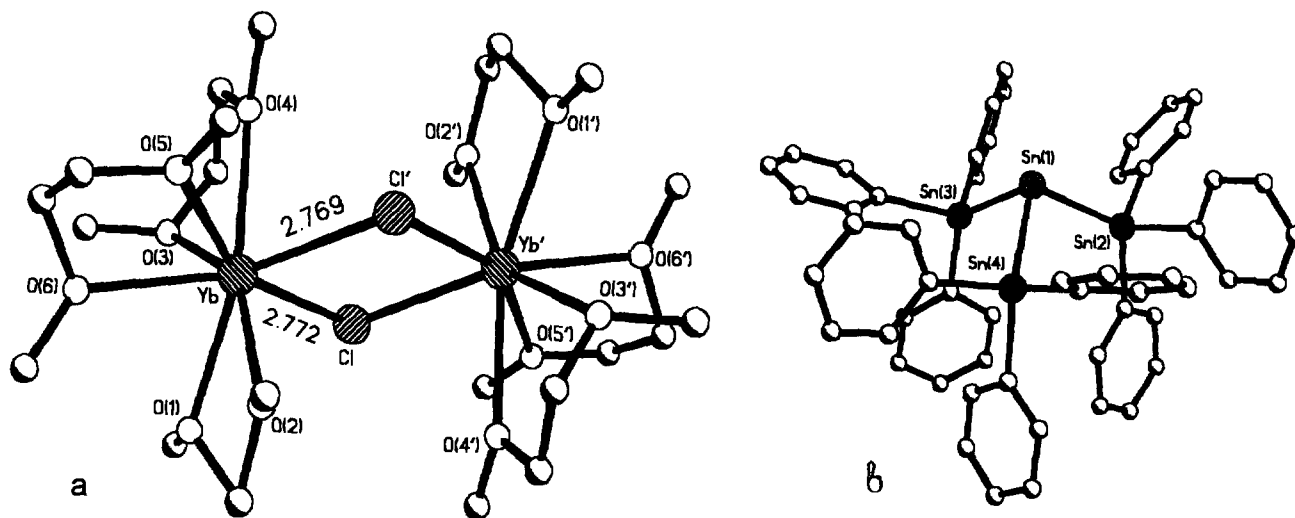
Another part of our investigation was related to an X-ray single crystal diffraction study of compounds containing a direct Ln–E bond (E = Si, Ge, Sn). Before starting this investigation there were no X-ray structural data for neutral lanthanide compounds of such type. For the last five years the structures of several compounds with Ln–E bonds have been determined. The complex $(\text{Ph}_3\text{Sn})_2\text{Yb}(\text{THF})_4$ (**VI**) was the first structurally characterized compound with a direct Yb–Sn bond [19,20]. Almost simultaneously the crystal structure of $(\text{t-Bu}_3\text{CH}_2)_3\text{Sn}]_2\text{Yb}(\text{THF})_2$, also containing a Yb–Sn bond, was determined [21]. Later the crystal structures of the first neutral lanthanide compounds $(\text{C}_5\text{Me}_5)_2\text{SmSiH}(\text{SiMe}_3)_2$ [22] and $(\text{Ph}_3\text{Ge})_2\text{Yb}(\text{THF})_4$ (**VII**) [23] with direct Ln–Si and Ln–Ge bonds and some compounds with Yb–Si, Sm–Sn, Eu–Sn, Yb–Sn bonds were determined: $(\text{Ph}_3\text{E})_2\text{Ln}(\text{THF})_4$ (Ln = Yb,

E = Si (**VIII**) [23]; Ln = Eu, E = Sn (**IX**) [8]; $(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Ln}(\text{THF})_4$ (Ln = Sm (**X**), Yb (**XI**)) and the second phase of $(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Yb}(\text{THF})_4$ (**XII**) [24].

All molecules **VI–IX** have a similar octahedral structure. The central Ln atom has a distorted octahedral environment, with the four O(THF) atoms in equatorial and the two E (Sn, Ge, Si) atoms of the Ph_3E groups in axial positions (Fig. 4). In all cases the arrangement of two Ph_3E groups has a staggered conformation (Fig. 5(a)–(d)).

In the case of Me groups, products of the reactions of Ln with $\text{Me}_4\text{SnCl}_{4-n}$ ($n = 1–3$) in THF are different from those for Ph groups [24]. Interaction of Me_3SnCl with Sm or Yb in THF gives the compounds $(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Sm}(\text{THF})_4$ **X** and $(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Yb}(\text{THF})_4$ **XI**, whereas the product of the reaction of MeSnCl_3 with Yb in THF is the complex **XII** having composition $(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Yb}(\text{THF})_4$, similar to **XI**. An X-ray study has shown that crystals of **XII** are tetragonal, while crystals of **X** and **XI** are orthorhombic [24]. The molecules of **X–XII** also have a distorted octahedral structure with four O(THF) atoms in the equatorial plane and two Sn atoms of the $(\text{Me}_3\text{Sn})_3\text{Sn}$ groups in axial positions (Fig. 6). The $(\text{Me}_3\text{Sn})_3\text{Sn}$ groups in these molecules are bonded to an Ln (Sm, Yb) atom by direct Ln–Sn bonds, in contrast to the structure of $(\text{DME})_3\text{Yb}(\mu\text{-Cl})_2^{2+}[(\text{Ph}_3\text{Sn})_3\text{Sn}]_2$ **XIII** [25] containing discrete dimeric cations $(\text{DME})_3\text{Yb}(\mu\text{-Cl})_2^{2+}$ and pyramidal anions $(\text{Ph}_3\text{Sn})_3\text{Sn}]^-$ (Fig. 7). The molecules of **X** and **XI** have an approximately staggered conformation of these groups, whereas the molecule of **XII** has C_2 symmetry and an approximately eclipsed conformation of $(\text{Me}_3\text{Sn})_3\text{Sn}$ groups (Fig. 5(e)–(g)).

The LnSnSn angles in **X–XII** ($117.4(1)–123.7(1)^\circ$ in **X**; $117.9(2)–124.2(2)^\circ$ in **XI**; $113.8(1)–128.9(1)^\circ$ in **XII**) are increased in comparison with the ideal tetrahedral

Fig. 7. The structure of (a) the cation $(\text{DME})_3\text{Yb}(\mu\text{-Cl})_2^{2+}$ and (b) the anion $(\text{Ph}_3\text{Sn})_3\text{Sn}]^-$ in **XIII**.

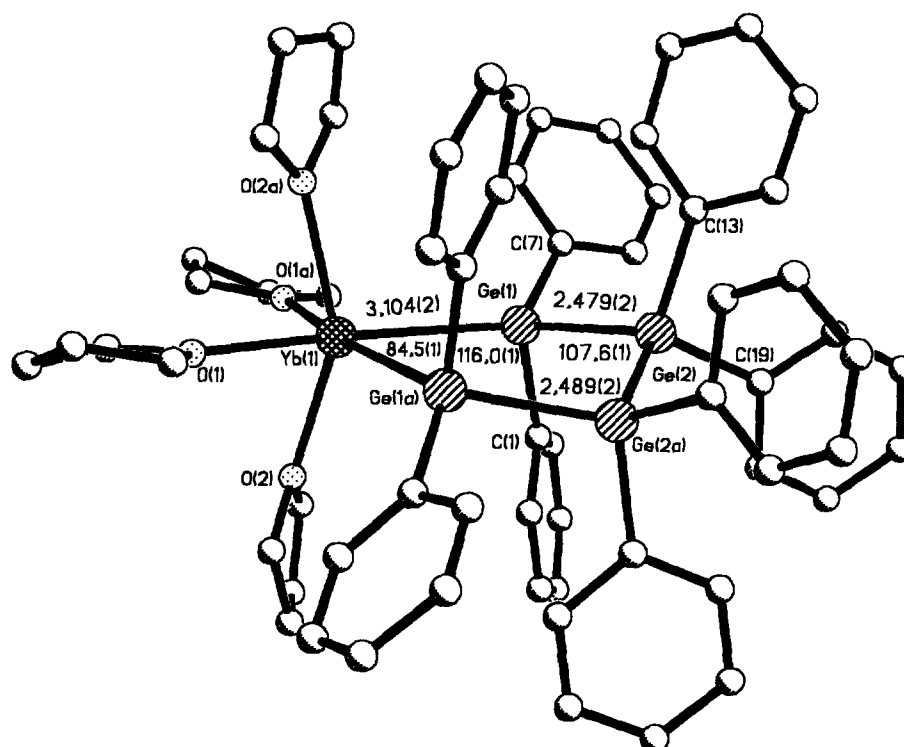


Fig. 8. The X-ray structure of XIV.

angle, i.e. Me_3Sn groups in these molecules are bent from the central part. The ranges of the Sn–Sn distances are 2.754(6)–2.800(6) Å (**X**), 2.775(6)–2.818(6) Å (**XI**) and 2.798(4)–2.803(4) Å (**XII**).

The molecular structure of compound $(\text{Ph}_2\text{Ge})_4\text{Yb}(\text{THF})_4$ (**XIV**) containing the five-membered Ge_4Yb metalocycle has also been determined (Fig. 8) [26]. The symmetry of **XIV** is C_2 : the Yb(1)

atom and the midpoint of the Ge(2)–Ge(2a) bond are on the two-fold axis. 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 $\text{Ph}_2\text{Ge}-\text{GePh}_2-\text{GePh}_2-\text{GePh}_2$ fragment. The five-membered Ge_4Yb metalocycle has a

Table 1

The main geometrical parameters for the octahedral compounds $\text{R}_3\text{E}-\text{Ln}(\text{THF})_4-\text{ER}_3$ containing a Ln–E bond

Compound	Bond lengths	Bond lengths ^a	The E–Ln–E' angle (°)	Ionic radius ^b of Ln (Å)	Covalent radius ^c of E (Å)
	Ln–E (Å)	Ln–O (Å)			
$(\text{Ph}_3\text{Si})_2\text{Yb}(\text{THE})_4$	3.158(2); 3.158(2)	2.460	180	1.02	1.17
$(\text{Ph}_3\text{Ge})_2\text{Yb}(\text{THE})_4$ ^d	3.170(2); 3.170(2) 3.141(2); 3.141(2)	2.42	180	1.02	1.22
$(\text{Ph}_3\text{Sn})_2\text{Yb}(\text{THE})_4$	3.305(1); 3.305(1)	2.40	164.5(1)	1.02	1.40
$(\text{Ph}_3\text{Sn})_2\text{Eu}(\text{THF})_4$	3.424(1); 3.424(1)	2.51	163.0(1)	1.17	1.40
$[(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Sm}(\text{THF})_4$	3.402(4); 3.386(4)	2.51	178.8(1)	1.11	1.40
$[(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Yb}(\text{THF})_4$ ^e	3.289(5); 3.299(4)	2.36	178.5(1)	1.02	1.40
$[(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Yb}(\text{THF})_4$ ^f	3.300(4); 3.300(4)	2.41	176.2(1)	1.02	1.40

^a Average values of the bond lengths are given.

^b Values for CN = 6 [13].

^c Ref. [27].

^d Values for two symmetrically independent molecules are given.

^e Orthorhombic phase.

^f Tetragonal phase.

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 \AA respectively. The Yb(1)–Ge(1) distance in **XIV** (3.104(2) Å) is somewhat shorter than that in the octahedral complex **VII** (3.170 and 3.141 Å in two independent molecules), with *trans*-arrangement of Ph₃Ge groups at the Yb atom. The main reason for this difference seems to be different steric crowding at the Yb atom in *cis*- and *trans*-octahedral complexes.

The X-ray data determined make it possible to compare the Ln–E (E = Si, Ge, Sn) distances for complexes with similar octahedral environment at the Ln atom, i.e. with a similar steric crowding around the Ln atom, in the two rows: in the lanthanide row Ln = Sm, Eu, Yb with fixed E = Sn and in the row E = Si, Ge, Sn with fixed Ln = Yb (Table 1). Such a comparison shows that the average Ln–Sn distances in these molecules decrease in the row Ln = Eu, Sm, Yb: Eu–Sn 3.424 Å, Sm–Sn 3.394 Å and Yb–Sn 3.305 Å. The differences between the Ln–Sn bond distances in the lanthanide row are comparable with the differences in ionic radii for six-coordinate Eu(2+), Sm(2+) and Yb(2+) cations (1.17, 1.11 and 1.02 Å respectively) [13]. The differences between the average Yb–E distances in the row E = Sn, Ge, Si (Yb–Sn 3.305 Å, Yb–Ge 3.156 Å and Yb–Si 3.158 Å) are closer to the differences in tetrahedral covalent radii of the Sn, Ge and Si atoms (1.40, 1.22 and 1.17 Å respectively) [27], although they cannot be so described exactly. Unfortunately, the available data are not sufficient to draw final conclusions about the nature of the Ln–E bond in the investigated complexes.

Note that the Yb–Sn distance in [(^tBu₃CH₂)₃Sn]₂Yb(THF)₂ (3.216 Å) [21], with a pseudo-tetrahedral coordination of the Yb atom, and the Sm–Si distance in (C₅Me₅)₂SmSiH(SiMe₃)₂ (3.052 Å) [22], with a bent-sandwich structure, are slightly shorter than in the octahedral complexes **VI** (3.305 Å) and **VIII** (3.158 Å).

It is interesting to note that the octahedral compounds R₃E–Ln(THF)₄–ER₃ with four THF groups in equatorial and two ER₃ groups in axial positions are stable complexes. The several compounds having such a structure type with different Ln–E bonds (Ln = Eu, Sm, Yb; E = Si, Ge, Sn) have been investigated by the X-ray diffraction method. Recently, the crystal structures of another divalent lanthanide species, namely [(mesityl)₂P]₂Yb(THF)₄ [28], [Ph₂P]₂Yb(*N*-methylimidazole)₄ [29], and also the compound (SCN)₂Ca(THF)₄ [30] having a similar octahedral structure, have been reported. Thus, the different stable compounds with a *trans*-octahedral structure containing various kinds of ligand (R₂E, R₃E, R₄E) can be stable. We think that this fact could be used to prepare new compounds R_{n1}M₁Ln(THF)₄M₂R_{n2} (M₁, M₂ =

transition metal, main group element; n₁, n₂ = 2≡4), with direct lanthanide–transition metal and lanthanide–main group element bonds.

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