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Unusual Coordination of Naphthalene in the Polynuclear Heteroligand Ytterbium–Erbium Complex

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Abstract—The reaction of Cp_3Er with $Yb(C_{10}H_8)(THF)_2$ in tetrahydrofuran affords hetero- and homoleptic complexes $CpYb(C_{10}H_8)(THF)_2$ (**I**), $[Er(Cp)H(THF)]_2$ (**II**), and $Cp_2Yb(THF)_2$ (**III**). Their structures are determined by X-ray diffraction (CIF files CCDC nos. 2165047 (**I**), 2165048 (**II**), and 2165049 (**III**)). This reaction in dimethoxyethane gives the naphthyl complex $[YbCp(DME)]_2(C_{10}H_6)ErCp_2$ (**IV**). Complex **IV** synthesized for the first time is structurally characterized (CIF file CCDC no. 2165050) and demonstrates an unusual coordination of the naphthalene ligand and contains two different lanthanoide ions in different oxidation states (Yb^{2+}, Yb^{3+}, and Er^{3+}).

Keywords: ytterbium, erbium, naphthalene complexes, cyclopentadienyl complexes, molecular structure, X-ray diffraction analysis

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INTRODUCTION

Arene complexes of rare-earth metals represent one of the most interesting and complicated classes of organometallic compounds. The ability to accept one or two electrons with the transformation into radical anions and dianions and a variety of possibilities for π coordination from η^2 to η^6 make these ligands rather promising for studying the chemistry of organolanthanoide compounds. The naphthalene derivatives of lanthanoides attracted considerable researchers' attention due to their high reactivity and became a well-studied class of lanthanoide arene complexes [1, 2]. A high electrical positive charge of lanthanoides [3] provides the ionic character of the metal–ligand bond in the naphthalene complexes. The majority of the presently synthesized compounds is presented by the Ln(III) derivatives: mixed naphthalene–iodine complexes $[LnI_2(THF)_3]_2(\mu\text{-}C_{10}H_8)$ [4, 5]; complexes containing no iodine, for example, three-deck thulium complex $[C_{10}H_8Tm(DME)]_2(\mu\text{-}C_{10}H_8)$ [6]; and various heteroligand naphthalene cyclopentadienyl complexes [7–9]. At the same time, the range of divalent lanthanoide compounds is much narrower. The Eu and Yb complexes $[ILn(DME)_2]_2(\mu\text{-}C_{10}H_8)$ [4] and three-deck complex $[Cp^{Bn5}Yb(DME)]_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-}C_{10}H_8)$ were synthesized [10]. The reactivity of the ytterbium naphthalenide $(C_{10}H_8)Yb(THF)_3$ synthesized first [11] and combining two strong reducing centers (Yb^{2+} ion and $(C_{10}H_8)^{2-}$ dianion) in one molecule is surprisingly high for organolanthanoides. All synthesized compounds contain either one ion, or several the same rare-earth metal ions. No heterobimetallic naphthalene complexes bearing different lanthanoides were synthesized. At the same time, the heterobimetallic Yb–Er complexes are known to exhibit the upconversion properties [12]. The ytterbium ion has a high effective absorption cross section in the IR range and, hence, is promising for using as a sensitizing ion [13–15]. The erbium ion with a prolonged lifetime of the excited metastable states to which an energy is transferred is often used as an emitting center [16–18]. Despite advantages of the upconversion materials with organic ligands, the number of these systems is very restricted [12, 19] because of synthetic difficulties. To produce materials of this kind, we attempted to synthesize the Yb–Er complexes with the bridging naphthalene dianion ($C_{10}H_8^{2-}$).

EXPERIMENTAL

The synthesis was carried out under the conditions excluding contact with air oxygen and moisture using the standard Schlenk technique. Tetrahydrofuran (THF) and dimethoxyethane (DME) were dried with sodium benzophenone ketyl using a standard procedure and sampled in vacuo prior to use. Compounds $Yb(C_{10}H_8)(THF)_2$ and Cp_3Er were synthesized using known procedures [11, 20]. IR spectra were recorded on an FSM-1201 FT-IR spectrometer in a range of 4000–400 cm^{-1}. Samples were prepared as a suspension in Nujol. Elemental analyses to C and H were carried out on an Elementar Vario ELcube Analyzer instrument.

Synthesis of complexes $CpYb(C_{10}H_8)(THF)_2$ (I), $[Er(Cp)H(THF)]_2$ (**II**), and $Cp_2Yb(THF)_2$ (**III**). Tetrahydrofuran (7 mL) was condensed onto a mixture of powdered $ErCp_3$ (214 mg, 0.59 mmol) and $Yb(C_{10}H_8)(THF)_2$ (262 mg, 0.59 mmol). The reaction mixture was stirred at −10°C for 4 h until ytterbium naphthalenide dissolved. Crystals of complex **I** gradually precipitated from a vinous-violet solution, and they were decanted, washed with cold THF, and dried in vacuo. The yield of complex **I** was 31 mg (62%).

For $C_{23}H_{29}O_2Yb$			
Anal. calcd., %	C, 54.11	H, 5.73	Yb, 33.90
Found, %	C, 54.40	H, 5.84	Yb, 34.04

IR for **I** (KBr; ν, cm^{-1}): 1595 w, 1254 m, 1191 m, 1108 m, 1059 m, 1010 m, 981 sh, 854 s, 827 w, 778 s, 756 s, 747 s, 720 s, 661 w, 476 m (coincides with the earlier described spectra [8, 21]).

Pink crystals of complex **II** and emerald-green crystals of complex **III** precipitated on concentrating and subsequent cooling of the mother liquor, and they were washed with cold THF and dried in vacuo.

The yield of complex **II** was 38 mg (26%).

For $C_{28}H_{38}O_2Er_2$			
Anal. calcd., %	C, 45.38	H, 5.17	Er, 45.14
Found, %	C, 45.45	H, 5.23	Er, 45.26

The IR spectrum of complex **II** coincides with that described previously [22].

The yield of complex **III** was 7 mg (16%).

For $C_{18}H_{26}O_2Yb$			
Anal. calcd., %	C, 48.32	H, 5.86	Yb, 38.67
Found, %	C, 48.17	H, 5.77	Yb, 38.59

The IR spectra of complexes **II** and **III** coincide with the previously described spectra [8, 23].

As found by HPLC, the volatile reaction products contain $C_{10}H_8$ and trace quantities of CpH. No individual compounds were isolated from the amorphous powder remained after the volatile products were removed.

Synthesis of complex $[YbCp(DME)]_2(C_{10}H_6)ErCp_2$ (IV). Dimethoxyethane (10 mL) was condensed onto a mixture of powdered $ErCp_3$ (104 mg, 0.29 mmol) and $Yb(C_{10}H_8)(THF)_2$ (128 mg, 0.29 mmol). The reaction mixture was stirred at −10°C for 6 h until the complete dissolution of the starting compounds. The formed violet solution was concentrated and cooled to −17°C. The precipitated crystals of complex **IV** were decanted, washed with cold DME, and dried in vacuo. The yield of complex **IV** was 21 mg (20%); $\mu_{eff} = 5.7\ \mu_B$.

For $C_{38}H_{46}ErO_4Yb_2$			
Anal. calcd., %	C, 42.26	H, 4.29	Er Yb, 47.53
Found, %	C, 42.31	H, 4.49	Er Yb, 47.39

IR (KBr; ν, cm^{-1}): 1259 m, 1069 m, 1010 s, 959 w, 915 w, 871 m, 781 s, 761 s, 664 w, 617 w, 498 w, 473 w.

We failed to separate other products and isolate them in the individual state.

X-ray diffraction (XRD) analyses of complexes **I**–**IV** were carried out on a Bruker D8 Quest automated diffractometer (graphite monochromator, MoK_α radiation, φ and ω scan modes, $\lambda = 0.71073$ Å). Experimental sets of intensities were integrated using the SAINT program [24]. Absorption corrections were applied using the SADABS [25] (**I**, **III**, and **IV**) and TWINABS (**II**) programs [26]. The structures were solved by the dual-space method in the SHELXT program [27]. Non-hydrogen atoms were refined by full-matrix least squares for F^2_{hkl} in the anisotropic approximation using the SHELXTL software [28]. Hydrogen atoms, except for H(1) in complex **II**, were placed in the geometrically calculated positions and refined by the riding model ($U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 groups, $U_{iso}(H) = 1.2U_{eq}(C)$ for other groups). In turn, the H(1) atom in complex **II** was objectively localized from the difference Fourier synthesis and refined in the isotropic approximation. The crystals of complexes **I** and **II** are two-component twins. The ratio of the domains is ~0.969 : 0.031 and ~0.937 : 0.063 in complexes **I** and **II**, respectively. One uncoordinated THF molecule falls onto one molecule of complex **I** in the crystal. The main crystallographic characteristics and experimental XRD parameters for compounds **I**–**IV** are given in Table 1.

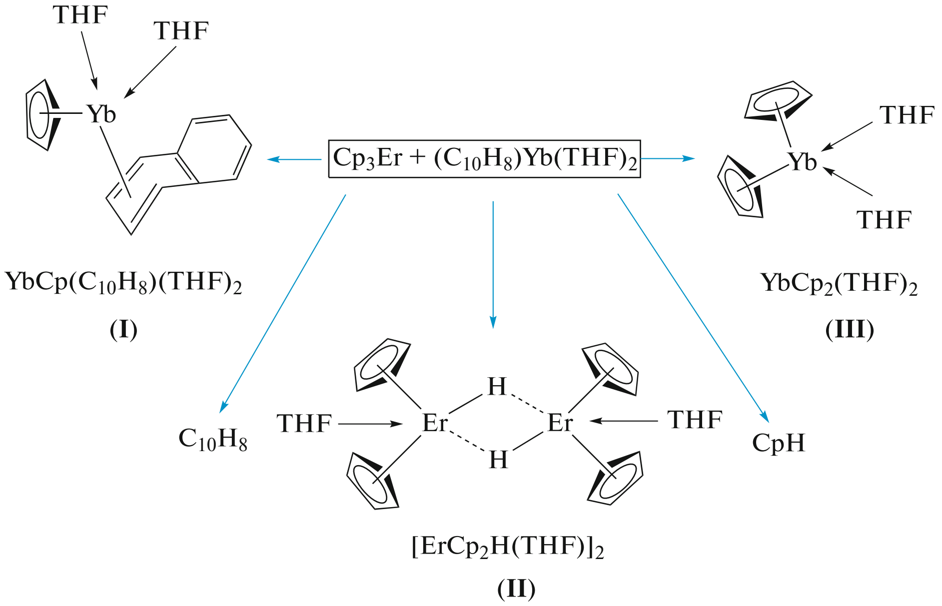
The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2165047 (**I**), 2165048 (**II**), 2165049 (**III**), and 2165050 (**IV**); http://ccdc.cam.ac.uk/structures/).

RESULTS AND DISCUSSION

The upconversion phenomenon has previously been observed for the ytterbium–erbium hexafluoroisopropoxide complex $Er_{0.67}Yb_{1.33}[(CF_3)_2CHO]_9$ [12]. We attempted to synthesize the heteroligand bimetallic Yb–Er complexes with the bridging naphthalene dianion in order to prepare new upconversion materials. The reaction of Cp_3Er with $Yb(C_{10}H_8)(THF)_2$ in a molar ratio of 1 : 1 in THF, which occurs readily at lowered temperatures (−10°C), was chosen as the synthetic approach. The products of the reaction of Cp_3Er with ytterbium naphthalenide are shown in Scheme 1.

Table 1. Crystallographic data and experimental and structure refinement parameters for complexes **I**–**IV**

Complex	Value			
	I	**II**	**III**	**IV**
Empirical formula	$C_{27}H_{37}O_3Yb$	$C_{28}H_{38}O_2Er_2$	$C_{18}H_{26}O_2Yb$	$C_{38}H_{46}O_4Yb_2Er$
FW	582.60	741.10	447.43	1080.09
Temperature, K	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$C2/c$
a, Å	12.1911(7)	7.9355(7)	13.2741(4)	15.1929(6)
b, Å	11.9207(7)	7.9913(7)	9.9058(3)	18.0544(7)
c, Å	16.7649(9)	10.8018(9)	13.6177(4)	13.7795(5)
α, deg	90	90.973(2)	90	90
β, deg	100.9173(17)	108.514(2)	110.1525(10)	111.0302(12)
γ, deg	90	103.344(2)	90	90
V, Å^3	2392.3(2)	628.98(9)	1680.98(9)	3527.9(2)
Z	4	1	4	4
ρ_{calc}, mg/cm^3	1.618	1.957	1.768	2.034
μ, mm^{-1}	3.934	6.647	5.565	7.653
Crystal size, mm	0.27 × 0.09 × 0.03	0.30 × 0.22 × 0.17	0.19 × 0.12 × 0.06	0.09 × 0.06 × 0.03
F(000)	1172	358	880	2056
2θ range, deg	2.285–26.022	2.632–38.421	2.601–29.129	2.256–26.367
Number of collected/ independent reflections	30698/4764	10865/10865	23343/4519	26097/3611
R_{int}	0.0691	0.0277	0.0387	0.0856
R_1, wR_2 ($I > 2\sigma(I)$)	0.0485, 0.1404	0.0284, 0.0654	0.0266, 0.0465	0.0323, 0.0558
R_1, wR_2 (for all data)	0.0732, 0.1602	0.0367, 0.0676	0.0496, 0.0512	0.0648, 0.0635
S	1.043	1.039	1.069	1.015
Residual electron density (max/min), e/Å^3	1.167/–1.410	1.811/–3.295	1.075/–0.884	1.310/–1.071



Scheme 1.

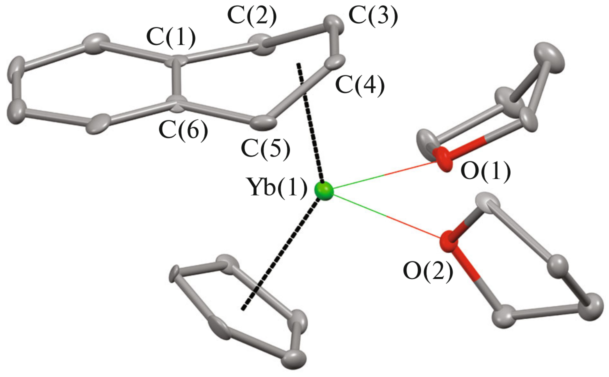
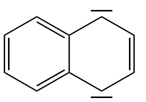


Fig. 1. Molecular structure of complex **I**. Selected bond lengths and angles: Yb(1)–O(1) 2.358(6), Yb(1)–O(2) 2.385(6), Yb(1)–C(2) 2.459(11), Yb(1)–C(3) 2.555(10), Yb(1)–C(4) 2.576(9), Yb(1)–C(5) 2.453(10), Yb(1)–C_{Cp} 2.604(9)–2.694(9), C(1)–C(2) 1.465(15), C(2)–C(3) 1.458(14), C(3)–C(4) 1.363(14), C(4)–C(5) 1.464(14), C(5)–C(6) 1.473(14), and C(1)–C(6) 1.424(13) Å and O(1)Yb(1)O(2) 76.4(2)°, C(1)C(2)C(3) 115.1(8)°, C(2)C(3)C(4) 119.9(9)°, C(3)C(4)C(5) 118.1(9)°, and C(4)C(5)C(6) 115.7(9)°. Thermal ellipsoids are given with 30% probability. Hydrogen atoms are omitted.

Complex **I** was isolated as dark violet needle-like crystals, which are very sensitive to air oxygen and moisture, in a yield of 60%. According to the XRD data, the molecular structure of complex **I** is similar to those of $CpYC_{10}H_8(DME)$ [8] and $CpLuC_{10}H_8(DME)$ [21]. The Yb atom is linked with the η^5-Cp ligand, η^4-naphthalene, and two THF molecules (Fig. 1). The six-membered naphthalene ring coordinated to the Yb atom is nonplanar. The inflection along the C(2)–C(5) line in the naphthalene molecule is 30.3° (26.1° in the Y complex [8] and 31.5° in the Lu complex [21]). Like the Y and Lu analogs, a molecule of complex **I** exhibits the redistribution of the C–C bond lengths in the coordinated naphthalene ring compared to that in free naphthalene. The C(1)–C(2), C(2)–C(3) and C(4)–C(5), C(5)–C(6) distances equal to 1.465(15), 1.458(14) and 1.464(14), 1.473(14) Å, respectively, exceed the C(3)–C(4) bond length (1.363(14) Å). The average distances in one aromatic ring of free naphthalene C(1)–C(6) are 1.415, 1.363, 1.378, 1.363, and 1.415 Å (Mogul 2020.2.0) [29, 30]. The C–C distances in the naphthalene ring unbound to the Yb atom range from 1.362(15) to 1.424(13) Å. Thus, naphthalene in compound **I** can be presented as the dianion.



This representation excellently agrees with the Yb–$C(C_{10}H_8)$ bond length distribution. The Yb–C(2) and Yb–C(5) interatomic distances in complex **I** (2.459(11) and 2.453(10) Å, respectively) are substantially shorter than Yb–C(3) and Yb–C(4) (2.555(10) and 2.576(9) Å). The Yb(1)–C(1) and Yb(1)–C(6) distances (2.983 and 2.958 Å) considerably exceed the sum of the ion radius of the ytterbium cation (0.985 Å) [31] and van der Waals radius of carbon (1.7 Å) [32]. An analogous bond length distribution was observed in similar Y and Lu complexes [8, 21]. Therefore, the bond of naphthalene with the Yb atom in complex **I** can be presented more correctly as the $2\eta^1:\eta^2$ $(2\sigma,\pi)$ interaction.

The Yb–C_{Cp} distances in complex **I** somewhat exceed the Yb–$C(C_{10}H_8)$ distances and vary in a range of 2.604(9)–2.694(9) Å. The distance between the ytterbium atom and the center of the cyclopentadienyl ligand in complex **I** (2.363 Å) is in good agreement with the previously published related Yb^{3+} complexes [33–35].

The formation of the trinuclear hydride lutetium complex was observed earlier in the reaction of Cp_2LuCl with $C_{10}H_8Na$ [7]. The reaction proceeds via the formation of an intermediate with the naphthalene dianion followed by the C–H bond cleavage and formation of the hydride and naphthyl fragments. The new type of C–H bond activation on the rare-earth metal complexes in the presence of a reducing agent was considered in detail [36]. These conditions make it possible to cleave the inactivated C–H aromatic bonds, resulting in the formation of hydride of the corresponding metal and its phenyl (or naphthyl) complex. The proposed mechanism includes the formation of an arene bimetallic intermediate product. The formation of hydride complex **II** and naphthyl complex **IV** proceeds, most likely, via the same mechanism: via C–H activation followed by the β-elimination of the hydrogen atom.

According to the XRD data, compound **II** is a centrosymmetric dimer in which each erbium atom is linked with two η^5-Cp ligands, one terminal THF molecule, and two μ_2-bridging hydrogen atoms (Fig. 2). Complex **II** is isostructural to the earlier published lutetium dimer [37]. The four-membered metallocycle ErHErH is planar, which is characteristic of the related dimeric hydride Lu [37] and Sm [38] complexes synthesized via the reactions of the alkyl or aryl derivatives of lanthanoides with hydrogen. The oxygen atoms of the THF molecules insignificantly deviate from the metallocycle plane (0.167 Å). The Ln–Ln distance in complex **II** (3.5721(4) Å) is longer than that in the $[Lu(Cp)H(THF)]_2$ complex (3.5216(6) Å) [25], which is in excellent correspondence with the difference in ion radii of erbium (1.062 Å) and lutetium (1.032 Å) [31].

The Er–C_{Cp} distances in complex **II** vary in a narrow range of 2.634(3)–2.665(3) Å. The distances between the ytterbium atom and centers of the cyclopentadienyl ligands in complex **II** (2.359 and 2.365 Å) are in good agreement with the earlier published related Er^{3+} complexes [39, 40]. The Er–O distances

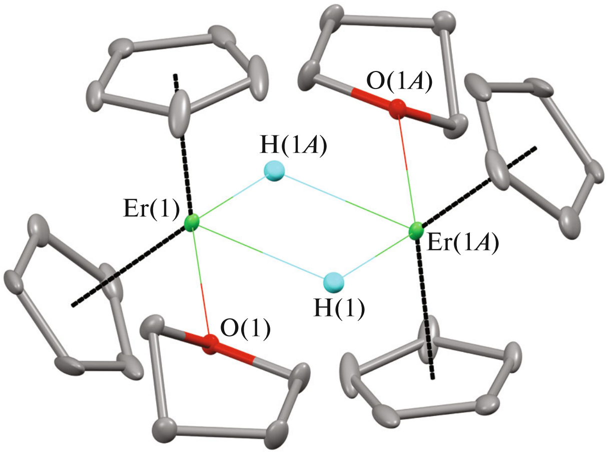


Fig. 2. Molecular structure of complex **II**. Selected bond lengths and angles: Er(1)–O(1) 2.417(4), Er(1)–C_{Cp} 2.634(3)–2.665(3), Er(1)–H(1) 2.15(3), Er(1)–H(1*A**) 2.10(4), and Er(1)...Er(1*A*) 3.5721(4) Å and O(1)Er(1)H(1) 70.5(9)°, H(1*A*)Er(1)O(1) 135.9(10)°, and H(1)Er(1)H(1*A*) 65.6(16)°. Thermal ellipsoids are given with 30% probability. Hydrogen atoms are omitted. * Symmetry procedure used for the generation of equivalent atoms in complex **II** (*A*): $-x, -y, -z$.

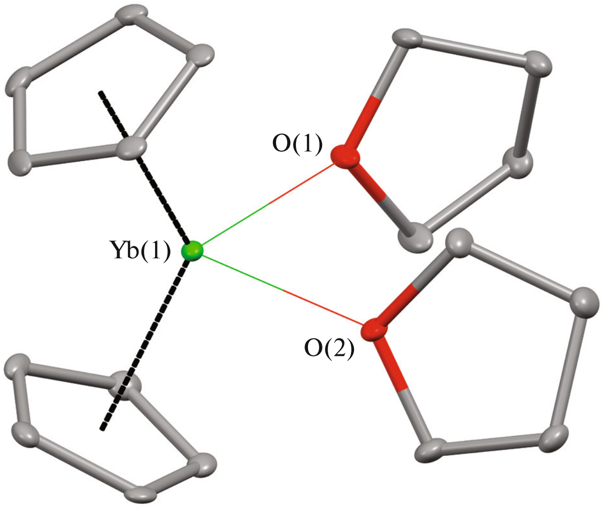
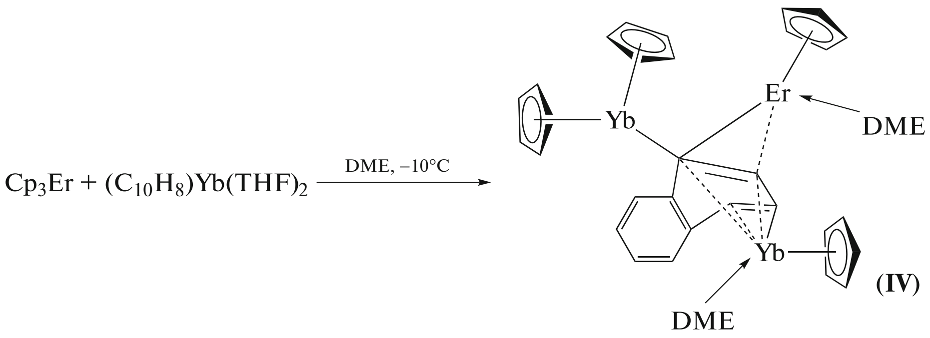


Fig. 3. Molecular structure of complex **III**. Selected bond lengths and angles: Yb(1)–O(1) 2.422(2), Yb(1)–O(2) 2.427(2), and Yb(1)–C_{Cp} 2.691(3)–2.741(3) Å and O(1)Yb(1)O(2) 81.90(8)°. Thermal ellipsoids are given with 30% probability. Hydrogen atoms are omitted.

in complex **II** systematically exceed the Yb–O distances in complex **I**, which agrees well with the difference in ion radii of these elements [31].

Emerald-green crystals of $Cp_2Yb(THF)_2$ are also formed as a side reaction product. The ytterbium atom in complex **III** is bound to two η^5-Cp ligands and two THF molecules (Fig. 3). The geometry of the nearest environment of the Yb(1) atom in complex **III** resembles those of the related cyclopentadienyl complexes with DME [41, 42] and TPPO (triphenylphosphine oxide) [43, 44]. The Yb(1)–C_{Cp} distances in complex **III** (2.691(3)–2.741(3) Å) are systematically longer than those in complex **I** (2.604(9)–2.694(9) Å), which is well consistent with the difference in ion radii for Yb^{2+} (1.140 Å) and Yb^{3+} (0.985 Å) [31]. An analogous tendency is observed for the Yb–O bonds.

We failed to isolate heterometallic complex **IV** as crystals suitable for XRD because of its high lability and low stability. The mixed Cp–naphthalene complexes of lanthanoides with THF ligands are less stable than those with DME [21]. The reaction of Cp_3Er with ytterbium naphthalenide in DME under the same conditions afforded compound **IV** (Scheme 2), which is an intermediate product, whose decomposition and further transformations already gave the above described complexes **I–III**.



Scheme 2.

All rare-earth naphthyl complexes synthesized to the present time [7, 24] are mononuclear compounds. According to the XRD data, compound **IV** is a trinuclear heterobimetallic complex.

The independent part of the crystal cell of complex **IV** contains only half a molecule. The Yb(1) and Er(1) atoms along with the coordinated to them cyclopentadienyl ligands and DME molecules, as well as the

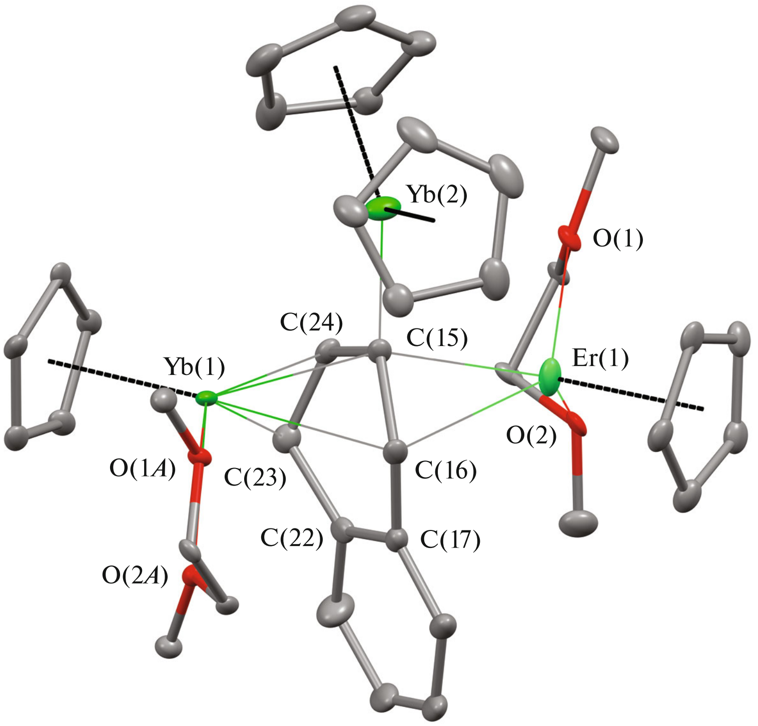


Fig. 4. Molecular structure of complex **IV**. Selected bond lengths and angles: Yb(2)–C(15) 2.481(10), Yb(2)–C_{Cp} 2.631(6)–2.657(6), Er(1)–O(1) 2.48(3), Er(1)–O(2) 2.354(16), Er(1)–C(15) 2.409(15), Er(1)–C(16) 2.577(13), Er(1)–C_{Cp} 2.635(13)–2.658(13), Yb(1)–O(1*A*) 2.43(3), Yb(1)–O(2*A*) 2.428(16), Yb(1)–C(15) 2.522(15), Yb(1)–C(16) 2.683(14), Yb(1)–C(23) 2.719(12), Yb(1)–C(24) 2.605(13), Yb(1)–C_{Cp} 2.679(13)–2.701(13), C(15)–C(24) 1.416(15), C(15)–C(16) 1.508(15), C(16)–C(17) 1.509(18), C(22)–C(23) 1.471(17), C(23)–C(24) 1.426(16), Yb(1)–Yb(2) 3.633, Yb(1)–Er(1) 4.830, and Yb(2)–Er(1) 3.832 Å and O(2)Er(1)O(1) 65.3(8)°, O(2*A*)Yb(1)O(1*A*) 65.4(8)°, C(24)C(15)C(16) 115.2(11)°, C(17)C(16)C(15) 118.6(11)°, C(24)C(23)C(22) 118.1(11)°, and C(15)C(24)C(23) 119.6(11)°. Thermal ellipsoids are given with 30% probability. Hydrogen atoms are omitted.

naphthalene molecule, are disordered over two positions with a population of 50 : 50. As a result, the complex is asymmetric (Fig. 4).

The C–C distances in the uncoordinated naphthalene ring vary from 1.35(2) to 1.434(19) Å. The averaged C–C bond length in this six-membered ring is 1.396 Å and well consistent with the aromatic structure [45]. As in complex **I**, the C(16)–C(17) (1.509(18) Å) and C(22)–C(23) (1.471(17) Å) distances correspond to an ordinary C–C bond. Unlike complex **I**, two hydrogen atoms on the C(15) and C(16) atoms are lacking from the naphthalene molecule in complex **IV**. A similar situation was observed earlier in the tetranuclear rhenium complex [46]. Thus, the naphthalene molecule is common, which corresponds to the presence of three different ions (Yb^{3+}, Yb^{2+}, and Er^{3+}) in the molecule. The C(16)–C(15)=C(24)–C(23) fragment in complex **IV** is more distorted compared to complex **I** and the published rhenium complex [46], which is probably related to steric factors. The C(15)–C(16) distance (1.508(15) Å) well corresponds to an ordinary C–C bond. In turn, the C(15)–C(24) distance (1.416(15) Å) somewhat exceeds a C=C double bond, and the C(23)–C(24) distance (1.426(16) Å), on the contrary, is somewhat shorter than an ordinary C–C bond [29, 30]. However, an assumption that the Er(1), Yb(1), and Yb(2) atoms in complex **IV** represent the trivalent erbium and di- and trivalent ytterbium atoms is well consistent with the Ln–O and Ln–C_{Cp} distances in complexes **I**–**III**.

The Yb(2)–C(15) distance (2.481(10) Å) can be treated as the σ-Yb–C bond. This value is well consistent with the Yb(III)–arene bond lengths [47, 48]. The erbium atom is linked with the naphthalene molecule via the Er(1)–C(15) and Er(1)–C(16) interactions (2.409(15) and 2.577(13) Å). As in complex **I**, the Yb(1) atom in complex **IV** is simultaneously bound to four carbon atoms of the naphthalene molecule. However, in the case of complex **IV**, the Yb–C distances vary in a broader range (2.522(15)–2.719(12) Å). As in the case of the bond length redistribution in the naphthalene ring, this asymmetric coordination is determined, most likely, by steric factors. In addition, note that the Yb–C($C_{10}H_8$) distances in complex **IV** are systematically longer compared to complex **I**, which is well consistent with the difference in ion radii of Yb(II) and Yb(III) atoms [31].

The XRD data are confirmed by the results of magnetic measurements. The magnetic moment of complex **IV** is 5.7 μ_B, which corresponds to the presence of Yb^{2+}, Yb^{3+}, and Er^{3+} in the molecule. The effective magnetic moments for the organic compounds of the corresponding lanthanoide ions are 0, 3.8–4.3, and 9.0–9.6 μ_B [49]. The calculated magnetic moment of the compound in which all the three ions are in a ratio of 1 : 1 : 1 ranges from 5.6 to 6.0 μ_B.

Contrary to the expected results, complex **IV** turned out to be luminescence-inactive, which did not allow us to observe the upconversion phenomenon in this system.

To conclude, the reaction of $ErCp_3$ with ytterbium naphthalenide is a complicated, multistage, and many-vector process resulting in the formation of the complexes $CpYb(C_{10}H_8)(THF)_2$ (**I**), $[Er(Cp)H(THF)]_2$ (**II**), $Cp_2Yb(THF)_2$ (**III**), and $[YbCp(DME)ErCp(DME)](C_{10}H_6)YbCp_2$ (**IV**), which were isolated and structurally characterized. The heteroligand heterometallic naphthyl Yb–Er complex was synthesized first. The method proposed for its synthesis includes the formation of an unstable complex containing the $[(Cp_2Er^+)_2(C_{10}H_8^{2-})]$ fragment and its decomposition with the formation of the hydride and σ-naphthyl product. The naphthyl complex, which can be considered to be intermediate, contains Er^{3+}, Yb^{2+}, and Yb^{3+} as indicated by the XRD data and results of magnetic measurements. The compound turned out to be luminescence-inactive. However, all synthesized complexes are reactive thus providing rich possibilities for the synthesis of various Er and Yb compounds, which are unavailable by other synthetic methods.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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