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Binuclear complexes of La(III) and Eu(II) with the bridging naphthalene dianion. Synthesis and X-ray crystallographic analysis of $[\mu_2\text{-}\eta^4:\eta^4\text{-}C_{10}H_8][LaI_2(THF)_3]_2$ and $[\mu_2\text{-}\eta^4:\eta^4\text{-}C_{10}H_8][EuI(DME)_2]_2$

Igor L. Fedushkin [a], Mikhail N. Bochkarev [a,*], Herbert Schumann [b,*], Lothar Esser [b], Gabriele Kociok-Köhn [b]

[a] *Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina 49, 603600 Nizhny Novgorod GSP-445, Russia*
[b] *Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Straße des 17.Juni 135, D-10623 Berlin, Deutschland*

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Abstract

The treatment of $LaI_3(THF)_3$ with equimolar amounts of Li and excess of $C_{10}H_8$ in THF results in the formation of $[C_{10}H_8][LaI_2(THF)_3]_2$ (**1**) and the reaction of $EuI_2(THF)_2$ with Li and $C_{10}H_8$ in DME leads to $[C_{10}H_8][EuI(DME)_2]_2$ (**2**), which have been characterized by IR and UV-VIS spectroscopy as well as by X-ray crystallography. **1** is monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$, with $a = 1314.2(6)$, $b = 1256.7(5)$, $c = 1697.2(4)$ pm, $\beta = 93.53(3)°$. The structure was refined to $R = 0.045$ for 2377 observed reflections ($F_o > 4\sigma(F_o)$). **2** is monoclinic, space group $P2_1/n$, $Z = 4$, with $a = 1015.1(3)$, $b = 1389.8(4)$, $c = 1269.8(3)$ pm, $\beta = 97.51(2)°$. The structure was refined to $R = 0.0408$ for 2687 observed reflections ($F_o > 4\sigma(F_o)$). Both molecules contain two LaI_2(THF) (**1**) or EuI(DME) moieties (**2**), bridged η^4 each by a non planar naphthalene with dihedral angles of 15° (**1**) and 6° (**2**) respectively.

Keywords: Lanthanum; Europium; Bridging naphthalene dianion; X-ray structure

1. Introduction

Organolanthanide compounds, known for exactly 40 years since the discovery of the tris(cyclopentadienyl) lanthanide complexes [1] are predominantly ionic due to low electronegativity of the lanthanide metals. On the other hand, the high Lewis acidity of their empty 5d-orbitals opens a chance to accept π-electrons of organic ligands to form π-arene complexes similar to the d-transition metals, which could be proved during the last decade when the first arene complexes of the lanthanides have been discovered [2–9]. We found that europium and ytterbium react with naphthalene in liquid ammonia yielding separated ion pairs [10] and that lanthanide halides are reduced by alkali metal naphthalenides in THF or DME to form $C_{10}H_8Ln(B)_n$ (Ln = Sm, Eu, Yb, B = THF, DME; n = 2,3), which evidently exist as contact ion pairs, although originally they have been interpreted as π-complexes of the zerovalent metals [10]. In contrast, the mixed cyclopentadienyl(naphthalene)- [9], and cyclopentadienyl(anthracene) complexes of lutetium [8] have arene metal bonds with essentially σ-character like in anthracene magnesium complexes [11].

The black pyrophoric naphthalene Ytterbium complexes $C_{10}H_8Yb_x(THF)_y$(x = 1–2, y = 2–4) [10] are very reactive towards a variety of substrates and have been used successfully for the synthesis of some very interesting new organoytterbium derivatives [12–16]. The real nature and the structure of this starting material could not been determined by an X-ray structural analysis because of its amorphous character and its insolubility in common organic solvents. To understand the nature of bonding in such compounds, we prepared now two new complexes of La(III) and Eu(II) which may be precursors of the halogen free lanthanide naphthalene complexes and determined their structure by single crystal X-ray analysis.

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[*] Corresponding authors.

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2. Results and Discussion

Lanthanum triiodide reacts with an equimolar amount of lithium and an excess of naphthalene in THF at room temperature with formation of a blue microcrystalline solid, which was identified as bis(lanthanum diiodo) naphthalene (**1**):

$$2\ \mathrm{LaI_3(THF)_3} + 2\ \mathrm{Li} + \mathrm{C_{10}H_8} \xrightarrow{\mathrm{THF}} \underbrace{[\mu_2\text{-}\eta^4{:}\eta^4\text{-}\mathrm{C_{10}H_8}][\mathrm{LaI_2(THF)_3}]_2}_{\mathbf{1}} + 2\ \mathrm{LiI}$$

The reaction of $LaI_3(THF)_3$ with equimolar amounts of $C_{10}H_8Li$, prepared in situ, results also in the formation of **1**; but that can be isolated only in lower yields. The reaction of $LaI_3(THF)_3$ with two or three equivalents of $C_{10}H_8Li$ results in the formation of a black solution, from which no clearly identifiable products could be isolated until now [17]. **1** is only slightly soluble in THF and insoluble in dimethoxyethane (DME), where it changes its colour to purple when suspended in that solvent. The diamagnetic compound decomposes even in an inert atmosphere above 80°C. The IR spectrum of **1** is similar to that of dilithium-naphthalene; it shows the characteristic bands of the naphthalene dianion. The UV-VIS spectrum, recorded in THF solution shows an absorption maximum at 604 nm. Hydrolysis of **1** results in the formation of isomers of dihydronaphthalene in quantitative yields and it is a reducing agent as demonstrated by the reaction with samarium(III) iodide, which is reduced to Sm(II), accompanied by the formation of neutral naphthalene.

The reaction of europium(II) iodide with lithium and naphthalene in DME results in the formation of dark red crystals of **2** in 47% yield:

$$2\ \mathrm{EuI_2(THF)_2} + 2\ \mathrm{C_{10}H_8Li} \xrightarrow{\mathrm{DME}} \underbrace{[\mu_2\text{-}\eta^4{:}\eta^4\text{-}\mathrm{C_{10}H_8}][\mathrm{EuI(DME)_2}]_2}_{\mathbf{2}} + 2\ \mathrm{LiI} + \mathrm{C_{10}H_8}$$

The paramagnetic europium(II) complex is insoluble in DME but soluble in cold THF yielding a deep blue solution, which shows decomposition above 20°C. The IR spectrum of **2** indicates the presence of the naphthalene dianion. The plot of the magnetic susceptibility of **2** satisfies the Curie-Weiss Law $\chi^{-1} = (T - \theta)(C)^{-1}$. The part of the plot of χ^{-1} at the high temperature range (285–169 K) is linear with $\theta = -28$ and a magnetic moment at 285 K of 8.57 BM. Between 105 and 78 K χ^{-1} is also linear in temperature with $\theta = -55$ and $\mu_{\mathrm{eff}} = 9.86$ BM. In contrast to **1**, hydrolysis of **2** leads to the formation of naphthalene $C_{10}H_8$ in addition to isomers of dihydronaphthalene, which can be considered as an indirect proof of less ionic character of the metal–arene bond in **2**.

An excess of $EuI_2(THF)_2$ reacts with naphthalene and sodium in THF at 0°C with formation of [μ_2-η^4:η^4-$C_{10}H_8$][EuI(THF)$_2$]$_2$ (**3**), which was isolated after cooling the resulting blue solution down to −20°C as very thin, red-brown, rhombic crystals. Attempts to grow crystals, suitable for an X-ray analysis failed.

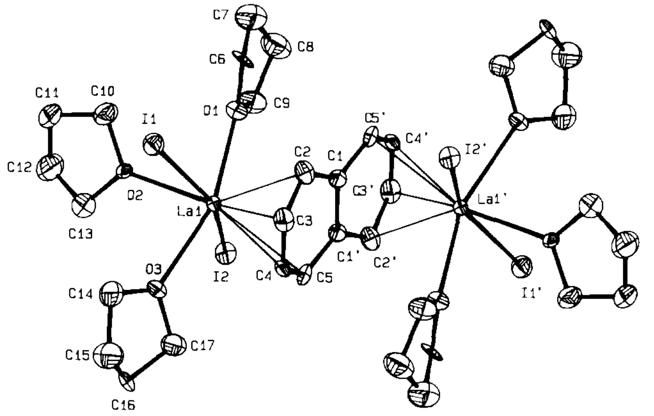

Fig. 1. ORTEP [18] projection of one molecule of [μ_2-η^4:η^4-$C_{10}H_8$][LaI$_2$(THF)$_3$]$_2$ (**1**) with the numbering scheme. Hydrogen atoms are excluded for clarity.

The UV-VIS absorption spectra of **1**, **3** and [Li(THF)$_x$]$_2$[$C_{10}H_8$] exhibit strong bands at 16556, 17391 and 18116 cm^{-1}, respectively. Evidently, these bands occur at similar electron transitions, which can be assigned to either the electron transitions from the HOMO's contributed by the metals and the ligands or to charge transfers from the ligands to the metals.

3. Molecular structure of [μ_2-η^4:η^4-$C_{10}H_8$][LaI$_2$(THF)$_3$]$_2$ (1) and [μ_2-η^4:η^4-$C_{10}H_8$][EuI(DME)$_2$]$_2$ (2)

In the solid state **1** (Fig. 1) crystallizes with 3.5 THF. The binuclear complex consists of two units of LaI$_2$(THF)$_3$ which are connected through the bridging naphthalene ligand. The nine coordinate La atom is the center of a distorted octahedron with the η^4-naphthalene ligand in one corner and the two iodines are trans to each other. The distance La(1)–O(2) (256.1(8) pm) to the THF, *trans* to the naphthalene is longer than the *cis* located La–O bonds (La(1)–O(1) = 251.1(8) and La(1)–O(3) = 253.6(8) pm). Each La atom is bonded to the naphthalene ligand in η^4 fashion with distances La(1)–C(η^4) between 278.2(12) and 280.8(12) pm. The same situation has been found in [Li{(TMED)}$_2$$C_{10}H_8$] [19], which is interpreted in a substantial participation of bonding between the HOMOs of the naphthalene dianion and lithium p-orbitals. Evidently, a similar bonding fashion is realized in **1** with donation of electron density to vacant orbitals of the lanthanum atoms. The bonded naphthalene dianion shows a different C–C bond pattern compared to those retrieved from low temperature data at 143 K of

Table 1
Selected bond distances (in pm) and bond angles (in °) in $[\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8][LaI_2(THF)_3]_2$ (**1**) (estimated standard deviations in the last significant figures are given in parentheses)

	Bond distance (pm)		Bond angle (°)
La(1)–I(1)	321.8(1)	I(1)–La(1)–I(2)	156.14(5)
La(1)–I(2)	322.2(1)	I(1)–La(1)–O(1)	89.6(2)
La(1)–O(1)	251.1(8)	I(1)–La(1)–O(2)	77.3(2)
La(1)–O(2)	256.1(8)	I(1)–La(1)–O(3)	88.5(2)
La(1)–O(3)	253.6(8)	I(2)–La(1)–O(1)	87.8(2)
La(1)–C(2)	278.2(12)	I(2)–La(1)–O(2)	79.0(2)
La(1)–C(3)	279.4(13)	I(2)–La(1)–O(3)	84.7(2)
La(1)–C(4)	278.5(12)	O(1)–La(1)–O(2)	75.9(3)
La(1)–C(5)	280.8(12)	O(1)–La(1)–O(3)	157.0(3)
La(1)...C(1)	311.3(12)	O(2)–La(1)–O(3)	81.3(3)
La(1)...C(1) [a]	311.9(12)		
C(1)–C(1) [a]	146(2)		
C(1)–C(2)	142.1(17)		
C(2)–C(3)	143.4(18)		
C(3)–C(4)	132.8(18)		
C(4)–C(5)	143.4(18)		

[a] Symmetry transformation: $-x$, $-y$, $-z$.

free naphthalene [20]. In the η^4 connection the C(2)–C(3) bond is much longer (143.4(18) pm) and the C(3)–C(4) bond much shorter (132.8(19) pm) than those bonds in free naphthalene (137.4(2) and 141.2(2) pm), respectively [20]. Due to the anionic character of the naphthalene, the ligand is not flat but bend with a dihedral angle of 15.2(16)° between the planes C(2)–C(3)–C(4)–C(5) and C(5)–C(1)–C(1)^a–C(2) (C(1)^a: symmetry transformation: $-x$, $-y$, $-z$). Other selected bond distances and angles are given in Table 1.

The crystal structure of **2** (Fig. 2) is similar to that of **1**. It shows a binuclear complex composed of two $[EuI(DME)_2]$ units which are bridged via a naphthalene molecule in the same manner like in **1**, but with the naphthalene ring system less distorted than in **1**. The coordination sphere around the Eu atom is nine showing a distorted octahedron with the η^4-bonded naphthalene in one corner and the iodine atom in cis position to the naphthalene centroid. Each Eu atom is bonded to the naphthalene ligand in η^4-fashion with distances Eu(1)–C(η^4) between 281.5(8) and 285.8(8) pm. The average bond distance Eu(1)–O of the DME ligands which are located in cis position is 258.7 pm. Noticably longer is the bond Eu(1)–O(1) (272.6(5) pm) trans to the naphthalene ligand. The angle O(1)–Eu(1)–CT$_{(naphthalene)}$ is 166.8(2)° and shows some deviation from an ideal octahedron. The europium atom is

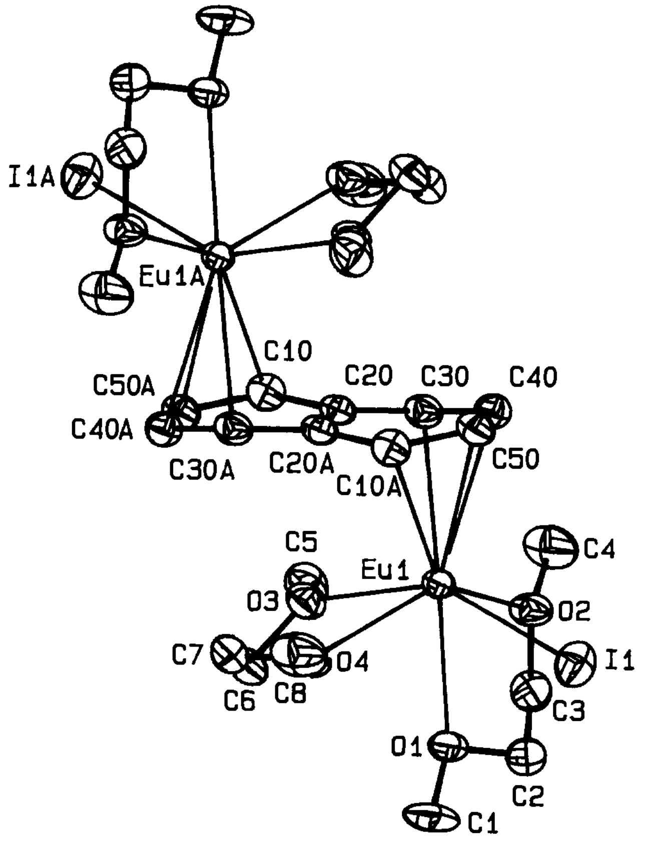

Fig. 2. ORTEP [18] projection of one molecule of $[\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8][EuI(DME)_2]_2$ (**2**) with the numbering scheme. Hydrogen atoms are excluded for clarity.

Table 2
Selected bond distances (in pm) and bond angles (in °) in $[\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8][EuI(DME)_2]_2$ (**2**) (estimated standard deviations in the last significant figures are given in parentheses)

	Bond distance (pm)		Bond angle (°)
Eu(1)–I(1)	323.7(1)	O(1)–Eu(1)–I(1)	79.6(1)
Eu(1)–O(1)	272.6(5)	O(2)–Eu(1)–I(1)	95.5(1)
Eu(1)–O(2)	259.2(5)	O(2)–Eu(1)–O(1)	62.8(2)
Eu(1)–O(3)	257.8(5)	O(3)–Eu(1)–I(1)	150.0(1)
Eu(1)–O(4)	259.2(5)	O(3)–Eu(1)–O(1)	75.3(2)
Eu(1)–C(10)	283.3(9)	O(3)–Eu(1)–O(2)	87.5(2)
Eu(1)–C(30)	285.8(8)	O(4)–Eu(1)–I(1)	93.8(1)
Eu(1)–C(40)	282.0(9)	O(4)–Eu(1)–O(1)	75.3(2)
Eu(1)–C(50)	281.5(8)	O(4)–Eu(1)–O(2)	134.4(2)
C(10)–C(20)	143(1)	O(4)–Eu(1)–O(3)	64.3(2)
C(20)–C(20A)	143(1)	C(30)–Eu(1)–I(1)	129.4(2)
C(30)–C(40)	146(1)	C(30)–Eu(1)–O(1)	140.6(2)
C(40)–C(50)	137(1)	C(30)–Eu(1)–O(2)	85.7(2)
C(10)–C(50A)	142(1)	C(30)–Eu(1)–O(3)	80.6(2)
Eu(1A)–C(20)	317.2(8)	C(30)–Eu(1)–O(4)	120.8(2)
Eu(1A)–C(20A)	315.2(7)	C(40)–Eu(1)–I(1)	99.7(2)
Eu(1)–CT [a]	258.3(3)	C(40)–Eu(1)–O(1)	151.7(2)
		C(40)–Eu(1)–O(2)	89.3(2)
		C(40)–Eu(1)–O(3)	110.2(2)
		C(40)–Eu(1)–O(4)	132.7(2)
		C(50)–Eu(1)–I(1)	83.9(2)
		C(50)–Eu(1)–O(1)	162.6(2)
		C(50)–Eu(1)–O(2)	113.9(2)
		C(50)–Eu(1)–O(3)	122.1(2)
		C(50)–Eu(1)–O(4)	111.4(2)
		O(1)–Eu(1)–CT [a]	166.8(2)
		I(1)–Eu(1)–CT [a]	113.6(2)

[a] CT defines the centroid of the ring formed by C(20), C(30), C(40), C(50), C(10A), C(20A).

not located exactly above the center of the one of the naphthalene rings but is 40.6 pm off center.

Due to electron transfer from the Eu atom to the naphthalene dianion the bond distances C(30)–C(40) with 146(1) and C(10)–C(50A) with 142(1) pm are elongated compared to those low temperature (143 K) bond lengths in free naphthalene with 137.4(2) and 137.6(2) pm, respectively [20]. On the other hand the bond C(40)–C(50) is with 137(1) pm much shorter than in free naphthalene (141.2(2) pm). As in **1** the localized double bonds in free naphthalene switched places after bonding to the lanthanide atoms. The naphthalene ligand is not flat and the dihedral angle between the planes C(30)–C(40)–C(50)–C(10A) and C(10A)–C(20A)–C(20)–C(30) is 5.8(16)°. These data suggest some back donation from the HOMO of the naphthalene dianion to empty orbitals of the Eu atom resulting in a somewhat higher covalent character of the arene–metal bond in **2** compared with that in **1**, which is in agreement with the results of hydrolysis of **2** mentioned above. Other selected bond distances and angles for **2** are given in Table 2.

4. Experimental details

The complexes described below are extremely sensitive to moisture and air. Therefore, both the synthesis and subsequent manipulations of these compounds were conducted in vacuum lines with rigorous exclusion of air and water using Schlenk techniques. THF and DME were distilled from sodium benzophenone ketyl. $LaI_3(THF)_3$ was prepared from La metal and CH_2I_2 in THF solution. Crystallization from THF yields $LaI_3(THF)_3$ as colourless crystals. Solutions of $EuI_2(THF)_2$ were prepared from excess Eu metal and CH_2I_2 in THF solution. Evaporation of the solvent and drying in vacuum leads to a lemon-yellow powder, formulated as $EuI_2(THF)_2$ on the basis of its europium and iodine content. IR spectra were recorded as Nujol

Table 3
Crystal data and details of the structure analysis for $C_{10}H_8(LaI_2(THF)_3)_2 \cdot 3.5$ THF **1** and $C_{10}H_8(EuI(DME)_2)_2$ **2**

	1	**2**
	a. Crystal data	
Empirical formula	$C_{34}H_{56}I_2La_2O_6$	$C_{26}H_{48}Eu_2IO_8$
Mol wt (g mol^{-1})	1346.2	1046.39
Crystallized from	THF	DME
Cryst system	Monoclinic	Monoclinic
Space group	$p2_1/c$ (no. 14)	$p2_1/n$ (no. 14)
a (pm)	1314.2(6)	1015.1(3)
b (pm)	1256.7(5)	1389.8(4)
c (pm)	1697.2(4)	1269.8(3)
β (°)	93.53(3)	97.51(2)
V (Å^3)	2797.7(18)	1776.0(8)
Z	4	4
D (calcd), g cm^{-3}	1.85	1.96
$F(000)$, electrons	1492	1000
μ (Mo Kα) (cm^{-1})	37.4	52.6
Cryst size (mm^3)	0.18 × 0.15 × 0.12	0.36 × 0.12 × 0.18
	b. Data collection	
Temp (K)	140(5)	136(5)
Radiation (Å)	0.71069	0.71069
Θ range ω-2Θ-scan	$2° \leq 2\Theta \leq 45°$	$2° \leq 2\Theta \leq 52°$
X-ray exposure time (h)	66.8	51.6
Decay (%)	−1.0	−6.5
Total data	4000	3833
Total unique	2607	2712
Obsd data ($F_o \geq 4\sigma(F_o)$)	2377 R(int) = 0.035	2687 R(int) = 0.046
	c. Refinement	
No. of refined parameters	263	188
ψ-scan, transm.% min., max.		67.42, 99.89
DIFABS min, max abs corr fac	0.82, 1.11	0.82, 1.22
Min, max dens, e Å^{-3}	−0.95, 1.0	−1.84, 1.89
$R = \Sigma \Vert F_o \vert - \vert F_c \Vert / \Sigma \vert F_o \vert$	0.045	0.041
$R_w = [\Sigma_w(\vert F_o \vert - \vert F_c \vert)^2 / \Sigma_w(F_o)^2]^{1/2}$	0.043	0.044
Weighting scheme:	$1/(\sigma^2(F_o) + 0.0003\ F_o^2)$	$1/(\sigma^2(F_o) + 0.0004\ F_o^2)$

mulls with a Perkin-Elmer 577 spectrometer, UV-VIS spectra were recorded on a Specord M40 spectrophotometer and magnetic susceptibility measurements were carried out by the Faraday method as previously published [21].

4.1. $[C_{10}H_8][LaI_2(THF)_3]_2$ (1)

A mixture of 4.2 g (5.70 mmol) of $LaI_3(THF)_3$, 0.04 g (5.71 mmol) of lithium and 1.3 g (10.5 mmol) of naphthalene were placed in a Schlenk tube and 30 ml of THF were added with vigorous stirring. The lithium gradually dissolved and a blue microcrystalline solid precipitated. After 2 h of stirring, the mixture was filtered through a fine frit and the resulting solid was rinsed twice with cold THF and dried in vacuum, yielding 3.42 g (89%) of a blue powder of **1**, which decomposed between 80 and 100°C. IR: 1495 (m), 1400 (s), 1335 (m), 1305 (w), 1285 (w), 1230 (m), 1195 (s), 1170 (w), 1130 (w), 1060 (m), 1005 (vs), 985 (s), 910 (s), 850 (vs), 830 (s), 800 (m), 755 (s), 740 (s), 730 (s), 660 (s), 470 (w), 460 (s) cm^{-1}. UV-VIS (THF, 20°C): 354 (sh), 604 nm (extinction coefficients could not be determined satisfyingly because of the extreme sensitivity of this material). Anal.: Found: C, 32.62; H, 5.01; La, 21.27. $C_{34}H_{56}I_4La_2O_6$ (**1**) Calc.: C, 30.33; H, 4.19; La, 20.63%.

Table 4
Atomic coordinates and equivalent isotropic displacement parameters [Å^2] for $C_{10}H_8(LaI_2(THF)_3)_2 \cdot 3.5THF$

Atom	x	y	z	B_{eq}
La1	0.19523(6)	−0.00406(6)	0.10468(4)	1.17
I1	0.36511(7)	−0.17816(8)	0.06701(5)	2.37
I2	0.10893(7)	0.21187(7)	0.17827(5)	2.15
O1	0.2463(7)	0.1044(7)	−0.0107(5)	2.31
O2	0.3613(6)	0.0864(7)	0.1551(5)	2.02
O3	0.2027(7)	−0.0712(7)	0.2458(5)	2.25
O4	0.7589(11)	0.0609(10)	0.2681(7)	5.58
O5 [a]	0.462(3)	−0.012(4)	0.420(2)	10.55
C1	0.0285(9)	−0.0157(10)	−0.0335(7)	1.54
C2	0.0936(10)	−0.1054(10)	−0.0229(8)	2.12
C3	0.0835(10)	−0.1768(11)	0.0420(8)	2.27
C4	0.0330(10)	−0.1468(11)	0.1037(7)	1.79
C5	−0.0150(9)	−0.0443(10)	0.1040(8)	1.68
C6	0.2918(11)	0.0652(11)	−0.0813(7)	2.33
C7	0.3151(14)	0.1624(14)	−0.1262(10)	4.96
C8	0.2397(14)	0.2429(14)	−0.1047(9)	4.23
C9	0.2215(12)	0.2177(11)	−0.0205(8)	2.99
C10	0.4478(11)	0.1071(13)	0.1074(8)	3.35
C11	0.5297(11)	0.1511(14)	0.1627(8)	3.62
C12	0.4725(12)	0.1992(15)	0.2282(9)	4.67
C13	0.3865(11)	0.1222(12)	0.2347(8)	2.89
C14	0.2750(11)	−0.1478(13)	0.2820(9)	3.95
C15	0.2206(12)	−0.1917(13)	0.3517(9)	4.16
C16	0.1575(11)	−0.1013(12)	0.3766(7)	2.74
C17	0.1187(11)	−0.0542(13)	0.2986(8)	3.28
C18	0.8560(17)	0.089(2)	0.3003(13)	8.28
C19	0.7755(13)	0.0149(14)	0.4018(10)	4.53
C20	0.8808(13)	0.0357(13)	0.3731(12)	4.75
C21	0.7075(14)	0.0124(17)	0.3298(10)	5.96
C22	0.497(2)	−0.079(2)	0.459(2)	9.15
C23	0.4444(18)	0.063(2)	0.4657(15)	7.24

$$B_{eq} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} \cdot \boldsymbol{a}_i \cdot \boldsymbol{a}_j \cdot a_i^* \cdot a_j.$$

[a] Side occupation factor $K = 0.5$.

Table 5
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $(C_{10}H_8)$ $(EuI(DME)_2)_2$

Atom	x	y	z	B_{eq}
EU1	0.08423(4)	0.14421(3)	0.33715(3)	2.02
I1	0.35434(5)	0.15819(4)	0.22787(5)	3.55
O1	0.0009(5)	0.2591(4)	0.1675(4)	2.79
O2	0.0672(6)	0.3271(4)	0.3730(5)	3.05
O3	−0.1715(5)	0.1384(4)	0.3200(5)	3.03
O4	−0.0307(6)	0.0280(4)	0.1940(5)	3.21
C1	0.0128(10)	0.2288(7)	0.0613(7)	4.38
C2	0.0529(9)	0.3527(6)	0.1885(7)	3.40
C3	0.0121(9)	0.3879(6)	0.2902(7)	3.28
C4	0.0499(12)	0.3680(6)	0.4721(8)	4.81
C5	−0.2491(9)	0.2058(7)	0.3678(8)	3.90
C6	−0.2353(8)	0.1013(7)	0.2212(7)	3.61
C7	−0.1678(9)	0.0088(6)	0.1989(7)	3.39
C8	0.0408(11)	−0.0545(7)	0.1683(8)	4.88
C10	−0.1603(8)	0.0282(5)	0.5522(7)	2.63
C20	−0.0266(8)	0.0382(5)	0.5286(6)	2.22
C30	0.0522(8)	0.1204(5)	0.5559(7)	2.51
C40	0.1945(8)	0.1175(5)	0.5507(7)	2.62
C50	0.2458(8)	0.0438(6)	0.4978(7)	2.91
H101	−0.18(9)	0.07(6)	0.60(7)	4.28
H301	0.02(7)	0.16(5)	0.61(6)	2.29
H401	0.27(6)	0.17(4)	0.59(5)	0.88
H501	0.35(7)	0.05(5)	0.49(6)	1.90

$$B_{eq} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} \cdot \boldsymbol{a}_i \cdot \boldsymbol{a}_j \cdot a_i^* \cdot a_j^* .$$

4.2. $[C_{10}H_8][EuI(DME)_2]_2$ (2)

0.4 g (0.72 mmol) of $EuI_2(THF)_2$, 0.5 g (3.9 mmol) of $C_{10}H_8$ and 10 ml of DME were added to a Schlenk flask containing 0.0051 g (0.72 mmol) of lithium chips on the bottom of the flask. The mixture was stirred a few minutes until a black colour appeared and then stored for 48 h. Then the clear solution was decanted from the crystalline solid. After washing the crystals four times with 10 ml DME each, and drying in vacuo, 0.18 g (47%) of dark red crystals of **2** were obtained without further purification, which were suitable for single crystal X-ray structural analysis. IR: 1490 (w), 1395 (s), 1275 (w), 1235 (w), 1190 (s), 1150 (w), 1110 (s), 1060 (vs), 1020 (m), 1005 (m), 970 (m), 855 (vs), 830 (w), 780 (m), 755 (m), 740 (m), 720 (w), 700 (m), 590 (w), 470 (w), 460 (w) cm^{-1}. Magnetic susceptibility: χ (285 K) = 29296×10^{-6} cgsu; $\mu_{eff} = 8.57$ BM; χ (169 K) = 46321×10^{-6} cgsu; $\mu_{eff} = 9.86$ BM. Anal. Found: C, 32.59; H, 5.07; Eu, 28.76. $C_{26}H_{48}Eu_2I_2O_8$ (**2**) Calc.: C, 29.84; H, 4.62; Eu, 29.04%.

4.3. $[C_{10}H_8][EuI(THF)_4]_2$ (3)

A mixture of 0.062 g (2.69 mmol) of Na, 2.5 g (4.54 mmol) of $EuI_2(THF)_2$ and 2 g (15.6 mmol) of $C_{10}H_8$ were placed in a Schlenk tube at 0°C and 20 ml of cold THF were added with vigorous stirring. The reaction mixture turned dark blue after 20 min. After filtration and cooling down to -20°C 0.2 g (6%) of thin rhombic crystals of **3** were precipitated. IR: 1500 (w), 1400 (m), 1340 (w), 1300 (w), 1285 (w), 1240 (w), 1225 (w), 1190 (s), 1130 (w), 1070 (m), 1060 (m), 1030 (vs), 975 (s), 910 (s), 875 (vs), 780 (m), 745 (s), 720 (m), 700 (s), 595 (w), 460 (m) cm^{-1}. UV-VIS (THF, 20°C): 575 nm. Magnetic susceptibility: χ (293 K) $= 28600 \times 10^{-6}$ cgsu; $\mu_{eff} =$ 8.2 BM. Anal.: Found: Eu, 24.11. $C_{42}H_{72}Eu_2I_2O_8$ (**3**) Calc.: Eu, 24.07%.

4.4. X-Ray crystal structure determination of 1 and 2

Crystal data and other details of the structure determination are collected in Table 3. The crystals were selected using a modified device, similar to that of Veith and Bärninghausen [22]. The crystals were mounted on a glass fiber and transferred to an Enraf-Nonius CAD 4 four circle diffractometer equipped with a low temperature device. Unit cell parameters from 25 reflections in the range of $16.0° \leq 2\theta \leq 25.4°$ for **1** and $16.6° \leq 2\theta \leq 20.78°$ were obtained. Data were collected with ω-2θ scans in the hkl ranges, $-14 \leq h \leq 14$, $0 \leq k \leq 13$ and $0 \leq l \leq 18$ for **1** and $0 \leq h \leq 12$, $0 \leq k \leq 17$ and $-15 \leq l \leq 15$ for **2**. Every 200 reflections intensity data were monitored through the measurement of three standard reflections. All data were corrected for Lorentz and polarization effects and absorption effects (DIFABS [23]). Due to some intensity loss during data collection a linear decay correction was undertaken for **2** (Lindecay min. 1.0, max. 1.034). Systematic absent reflections of the type $0k0$ ($k =$ odd) and $h0l$ ($l =$ odd) indicated the space group $P2_1/c$ (No. 14) for **1** and systematic extinctions of reflections $h00$ ($h =$ odd), $0k0$ ($k =$ odd), $00l$ ($l =$ odd) and $h0l$ ($h + l =$ odd) indicated the space group $P2_1/n$ (No. 14) for **2**. The positions of the heavy atoms were determined using Patterson (SHELX 86 [24]) and the rest of the molecule using difference-fourier methods (SHELX 76 [25]). The molecules were refined against F by full-matrix least-squares techniques.

For **1**: all atoms except C(13), O(5), C(22) and C(23) were refined anisotropically. C(13) was not positively defined in an isotropical state. However there is no disorder of the THF ligands. Hydrogen atoms were placed on calculated positions ($d_{CH} = 95$ pm, $U_{iso} = 0.07$ Å). The asymmetric unit contains one molecule of non-coordinated THF [O(4)–C(18)–C(19)–C(20)–C(21)] with regular bond distances and one half molecule of THF [O(5)–C(22)–C(23)] which is located on an inversion center. The latter molecule contains strong bond distortions since the symmetry operation -1 cannot easily be accommodated within a folded five membered ring. No attempts were undertaken to calculate the missing hydrogen atoms on the isotropically refined carbon atoms C(22) and C(23). The final values of the refined positional parameters are presented in Table 4.

For **2**: Hydrogen atoms for the DME ligands were placed on calculated positions with $d_{CH} = 108$ pm and $U_{iso} = 0.08$ Å^2 whereas the hydrogen atoms of the naphthalene system were refined isotropically. Due to inhomogeneous absorption of the crystal during data collection a relatively high residue of electron density (1.9 e Å^{-3}) is observed within 42 pm from iodine. The final fractional coordinates are displayed in Table 5. Further details of the structure investigation is available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH D-76344 Eggenstein-Leopoldshafen, Germany, upon quoting the depository number (CSD 58606), the authors names, and the full citation of the journal.

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References

[1] G. Wilkinson and J.M. Birmingham, *J. Am. Chem. Soc.*, *76* (1954) 6210.

[2] F.A. Cotton and W. Schwotzer, *J. Am. Chem. Soc.*, *108* (1986) 4657.

[3] F.A. Cotton and W. Schwotzer, *Organometallics*, *6* (1987) 1275.

[4] T. Arkawa, S. Shimada, G.Y. Adachi and J. Shiokawa, *Inorg. Chim. Acta*, *145* (1988) 327.

[5] D.M. Andersen, F.G.M. Cloke, P.A. Cox, N. Edelstein, J.C. Green, T. Pang, A.A. Sameh and G. Shalimoff, *J. Chem. Soc., Chem. Commun.*, (1989) 53.

[6] Baochen Fan, Qi Shen and Yonghua Lin, *J. Organomet. Chem.*, *376* (1989) 61.

[7] Baochen Fan, Qi Shen and Yonghua Lin, *J. Organomet. Chem.*, *377* (1989) 51.

[8] D.M. Roitershtein, A.M. Ellern, M. Yu. Antipin, L.F. Rybakova, Yu. T. Struchkov and E.S. Petrov, *Mendeleev Commun.*, (1992) 118.

[9] A.B. Protchenko, L.N. Zakharov, M.N. Bochkarev and Yu. T. Struchkov, *J. Organomet. Chem.*, *447* (1993) 209.

[10] M.N. Bochkarev, A.A. Trifonov, E.A. Fedorova, N.S. Emelyanova, T.A. Basalgina, G.S. Kalinina and G.A. Razuvaev, *J. Organomet. Chem.*, *372* (1989) 217.

[11] L.M. Engelhardt, S. Harvey, C.L. Raston and A.H. White, *J. Organomet. Chem.*, *341* (1988) 39.

[12] M.N. Bochkarev, I.M. Penyagina, L.N. Zakharov, Yu. F. Radkov, E.A. Fedorova, S. Ya. Khorshev and Yu. T. Struchkov, *J. Organomet. Chem.*, *378* (1989) 363.

[13] M.N. Bochkarev, V.V. Khramenkov, Yu. F. Radkov, L.N. Zakharov and Yu. T. Struchkov, *Metalloorgan. Khim.*, *3* (1990) 1438.

[14] M.N. Bochkarev, V.V. Khramenkov, Yu. F. Radkov, L.N. Zakharov and Yu. T. Struchkov, *J. Organomet. Chem.*, *408* (1991) 329.

[15] M.N. Bochkarev, V.V. Khramenkov, Yu. F. Radkov, L.N. Zakharov and Yu. T. Struchkov, *J. Organomet. Chem.*, *421* (1991) 29.

[16] M.N. Bochkarev, I.L. Fedushkin, V.K. Cherkasov, V.I. Nevodchikov, H. Schumann and F.H. Görlitz, *Inorg. Chim. Acta*, *201* (1992) 69.

[17] N.S. Emelyanova, A.V. Protchenko, E.A. Fedorova, O.A. Vasina and M.N. Bochkarev, *Metalloorgan. Khim.*, *4* (1991) 895.

[18] C.K. Johnson, ORTEP II Rep. ORNL-5138, 1976, Oak Ridge National Laboratory, Oak Ridge, TN.

[19] J.J. Brooks, W. Rhine and G.D. Stucky, *J. Am. Chem. Soc.*, *94* (1972) 7346.

[20] C.P. Brock and J.D. Dunitz, *Acta Crystallogr., Sect. B*, *38* (1982) 2218.

[21] A.V. Protchenko and M.N. Bochkarev, *Prybory i technika experimenta* [Instruments and methods of experiments], 1990, p. 194.

[22] M. Veith and H. Bärninghausen, *Acta Crystallogr. B*, *30* (1974) 1806.

[23] N. Walter, D. Stewart, *Acta Crystallogr. A*, *39* (1983) 159.

[24] G.M. Sheldrick, SHELX 86 *Program for Crystal Structure Solution*, Universität Göttingen, 1986.

[25] G.M. Sheldrick, SHELX 76 *Program for Crystal Structure Determination*, University of Cambridge, UK, 1976.