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Synthesis and characterization of the lutetium naphthalene complex, $CpLuC_{10}H_8(DME)$

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Abstract

The title compound (**1**) was obtained as black diamagnetic crystals by reaction of $CpLuCl_2$ with sodium naphthalide in DME. The naphthalene moiety in **1** is bent about the C(1) ··· C(4) plane (dihedral angle 148.5°). The Lu–C($C_{10}H_8$) bond lengths and redistribution of C–C bond distances in the coordinated naphthalene ring suggest $2\eta^1:\eta^2$-interaction of the Lu atom with the naphthalene moiety.

1. Introduction

We recently found that naphthalene complexes of divalent lanthanoids $C_{10}H_8Ln(THF)_x$ (Ln = Sm, Eu, Yb; $x = 2$–4), formed by reaction of lanthanoid diiodides with lithium naphthalide, were highly reactive towards organic and organometallic reagents [1–5]. These complexes were however insoluble and could not be obtained in a monocrystalline form suitable for X-ray investigation. In order to obtain a soluble naphthalene derivative of a lanthanoid we tried the reaction of $CpLuCl_2$ with sodium naphthalide. The lutetium cyclopentadienyl derivative was chosen because the $CpLu^{2+}$ particle is an isoelectronic analogue of Yb^{2+}, and the ytterbium naphthalene complex can easily be obtained by such a reaction.

2. Results and discussion

Addition of sodium naphthalide to a suspension of $CpLuCl_2(THF)_3$ in DME results in a deep purple solution with pale precipitate. After centrifugation, cooling of the solution to −10°C gives $CpLu\text{-}C_{10}H_8\text{-}(DME)$ (**1**) as black needle diamagnetic crystals in 80% yield.

$$CpLuCl_2 + 2C_{10}H_8Na \xrightarrow{DME} \underset{\mathbf{1}}{CpLuC_{10}H_8(DME)} + C_{10}H_8 + 2NaCl$$

The analogous complex with two THF molecules replacing DME, $CpLuC_{10}H_8(THF)_2$ (**2**), was obtained when the reaction was carried out in THF but it was less stable than **1**, exhibiting partial desolvation in vacuum.

Complex **1** is very sensitive to moisture and air but stable in vacuum or under argon. It melts with decomposition at 120°C.

Some reactions of complex **1** are similar to those of naphthalene complexes of Sm, Eu and Yb [1].

$$\mathbf{1} + H_2O \xrightarrow{C_6H_6} Lu(OH)_3 + C_{10}H_{10} + CpH$$

$$\mathbf{1} + O_2 \xrightarrow{C_6H_6} Lu_2O_3 + C_{10}H_8$$

$$\mathbf{1} + CpH \xrightarrow{DME} Cp_3Lu + C_{10}H_{10} + C_{10}H_8 + H_2$$

The reactivity of the lutetium naphthalene complex **1** towards organometallic reagents is lower than that of the ytterbium complex. Thus the latter reacts with Ph_4Sn giving triphenylstannyl derivatives of ytterbium

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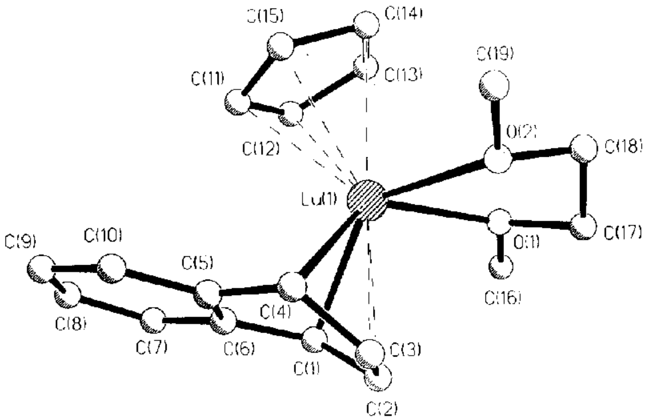
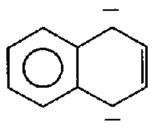


Fig. 1. Molecular structure of **1** with atom labelling.

[4,5] while complex **1** does not split the Ph–Sn bond under the same conditions.

The lutetium naphthalene complex reacts readily with compounds containing the C≡C triple bond. The results of this investigation will be published elsewhere.

The structure of **1** was determined by the single-crystal X-ray diffraction method. Figure 1 shows the first structural characterization of the lanthanoid naphthalene complex, **1**. The lutetium atom is bonded to the η^5-cyclopentadienyl ligand, to naphthalene and to the chelate DME molecule. The six-membered ring of naphthalene bonded to the Lu atom is not planar: the dihedral angle between the average planes of C(1)C(2)C(3)C(4) and C(4)C(1)C(5)–C(10) fragments is 148.5°. There is an appreciable redistribution of the C–C bond distances in this ring compared with free naphthalene. The C(1)–C(2), C(1)–C(6), C(3)–C(4) and C(4)–C(5) distances (at 1.46(1), 1.49(1), 1.46(1) and 1.46(1) Å respectively) are longer while C(2)–C(3) (at 1.36(1) Å) is shorter than the lengths of corresponding bonds in free naphthalene (1.422, 1.364 and 1.406 Å) [6]. The C–C distances in the non-bonded ring of naphthalene range from 1.39 to 1.43 Å (average 1.40 Å). Thus the geometry found indicates that the coordinated naphthalene molecule in **1** is close to the dianion form:



The Lu–C(1) and Lu–C(4) distances in the molecule of **1**, 2.406(8) and 2.397(8) Å, are comparable with the lengths of the Lu–C σ-bond in $Cp_2Lu^tBu(THF)$ 2.47 Å [7], $Cp_2LuCH_2SiMe_3(THF)$ 2.376 Å and $Cp_2LuC_6H_4Me$-4(THF) 2.345 å [8]. The Lu–C(2) and Lu–C(3) distances, 2.579(8) and 2.562(8) Å, are close to the average Lu–C(Cp) distance, 2.60 Å, and suggest an η^2-interaction of the C(2)–C(3) double bond with the Lu atom. The Lu–C(5) and Lu–C(6) distances, 2.819(8) and 2.830(8) Å, seem to be too long for appreciable contribution to naphthalene–Lu bonding.

The above-mentioned structural features show that the bonding of the naphthalene moiety with the Lu atom in **1** may be described as $2\eta^1:\eta^2$ (2σ, π)-interaction of Lu atom with the C(1)–C(2)=C(3)–C(4) fragment.

The Lu–C(Cp) η^5-distances are in the range 2.57–2.64 Å (average 2.60 Å). The Lu–O(1) and Lu–O(2) distances, 2.534(5) and 2.374(6) Å, differ only slightly.

It is interesting to note that the geometry of the coordinated ring of naphthalene molecule found in **1** is close to that in the lithium derivative of the naphthalene dianion $[Li(TMEDA)]_2C_{10}H_8$ [9], in which both rings of naphthalene molecule are bent (15.4°) on the C(1) ··· C(4) plane. However, the positions of the metal atoms relative to the naphthalene ligand in this structure and in the molecule of **1** differ significantly: the Li–C(2) and Li–C(3) distances, 2.27(1) and 2.26(1) Å, are shorter than the Li–C(1), Li–C(4) and Li–C(5), Li–C(6) distances (2.32, 2.33 and 2.66, 2.67 Å respectively).

Evidently for both the compounds the σ and π components of the bonding between metal atom and aromatic ring are important.

TABLE 1. Atomic coordinates (×10^4) and temperature factors U ($Å^2 \times 10^3$) for **1**

Atom	x	y	z	U [a]
Lu(1)	844(1)	7102(1)	282(1)	21(1)
O(1)	962(4)	8510(3)	−346(3)	24(2)
O(2)	−470(4)	7457(4)	−586(3)	24(2)
C(1)	1377(6)	7647(5)	1670(5)	25(3)
C(2)	447(7)	8035(6)	1638(4)	30(3)
C(3)	−293(6)	7494(6)	1510(5)	25(3)
C(4)	−164(6)	6549(5)	1401(5)	27(3)
C(5)	632(6)	6187(5)	1870(5)	25(3)
C(6)	1423(6)	6734(6)	2011(5)	26(3)
C(7)	2217(6)	6382(6)	2403(5)	28(3)
C(8)	2262(7)	5503(6)	2647(5)	39(3)
C(9)	1494(7)	4960(6)	2529(6)	37(3)
C(10)	681(7)	5305(6)	2150(5)	33(3)
C(11)	1896(7)	5750(6)	140(5)	32(3)
C(12)	2442(7)	6456(5)	−147(5)	35(3)
C(13)	2063(7)	6745(6)	−956(5)	36(3)
C(14)	1273(7)	6242(6)	−1147(5)	31(3)
C(15)	1176(7)	5606(5)	−455(5)	27(3)
C(16)	1648(7)	9142(6)	−71(6)	35(3)
C(17)	128(7)	8906(5)	−677(6)	32(3)
C(18)	−379(7)	8195(6)	−1166(5)	29(3)
C(19)	−1038(6)	6794(6)	−962(6)	32(3)

[a] Equivalent isolropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

3. Experimental details

The instrumentation and general procedures employed for this study were identical to those given in a previous paper [1].

3.1. Synthesis of $CpLuC_{10}H_8(DME)$ (1)

To a suspension of 1.00 g (1.90 mmol) of $CpLuCl_2(THF)_3$ [10] in 10 ml of DME at 0°C a solution of $C_{10}H_8Na$ obtained from 0.087 g (3.8 mmol) of Na and 0.512 g (4.0 mmol) of naphthalene in 10 ml of DME was added with shaking. After 15 min of vigorous stirring at room temperature the reaction was complete, as indicated by dissolution of $CpLuCl_2(THF)_3$. The solution was centrifuged and decanted from the NaCl precipitate. Cooling to -10°C yielded 0.523 g (60%) of **1** as diamagnetic black crystals, m.p. 120°C (dec.). An additional 0.170 g of **1** (overall yield 80%) was obtained by concentration in vacuum and cooling of the mother solution.

TABLE 2. Bond lengths (Å) in 1

Lu(1)-O(1)	2.354(5)
Lu(1)-O(2)	2.374(6)
Lu(1)-C(1)	2.406(8)
Lu(1)-C(2)	2.579(8)
Lu(1)-C(3)	2.562(8)
Lu(1)-C(4)	2.397(8)
Lu(1)-C(5)	2.819(8)
Lu(1)-C(6)	2.830(8)
Lu(1)-C(11)	2.565(9)
Lu(1)-C(12)	2.59(1)
Lu(1)-C(13)	2.64(1)
Lu(1)-C(14)	2.622(8)
Lu(1)-C(15)	2.587(8)
O(1)-C(16)	1.44(1)
O(1)-C(17)	1.44(1)
O(2)-C(18)	1.44(1)
O(2)-C(19)	1.42(1)
C(1)-C(2)	1.46(1)
C(1)-C(6)	1.49(1)
C(2)-C(3)	1.36(1)
C(3)-C(4)	1.46(1)
C(4)-C(5)	1.46(1)
C(5)-C(6)	1.43(1)
C(5)-C(10)	1.41(1)
C(6)-C(7)	1.40(1)
C(7)-C(8)	1.39(1)
C(8)-C(9)	1.39(1)
C(9)-C(10)	1.41(1)
C(11)-C(12)	1.40(1)
C(11)-C(15)	1.40(1)
C(12)-C(13)	1.42(1)
C(13)-C(14)	1.40(1)
C(14)-C(15)	1.44(1)
C(17)-C(18)	1.50(1)

TABLE 3. Bond angles (°) in 1

O(1)-Lu(1)-O(2)	67.8(2)
O(1)-Lu(1)-C(1)	91.3(2)
O(2)-Lu(1)-C(1)	132.0(2)
O(1)-Lu(1)-C(2)	81.0(2)
O(2)-Lu(1)-C(2)	98.5(2)
O(1)-Lu(1)-C(3)	97.7(2)
O(2)-Lu(1)-C(3)	81.3(2)
O(1)-Lu(1)-C(4)	130.9(2)
O(2)-Lu(1)-C(4)	89.9(2)
Lu(1)-O(1)-C(16)	122.6(5)
Lu(1)-O(1)-C(17)	117.8(4)
C(16)-O(1)-C(17)	113.3(6)
Lu(1)-O(2)-C(18)	116.8(5)
Lu(1)-O(2)-C(19)	121.6(5)
C(18)-O(2)-C(19)	111.0(6)
O(1)-C(17)-C(18)	106.2(6)
O(2)-C(18)-C(17)	107.5(6)
C(1)-Lu(1)-C(4)	71.5(3)
Lu(1)-C(1)-C(2)	79.5(4)
Lu(1)-C(1)-C(6)	90.1(5)
C(2)-C(1)-C(6)	115.4(7)
C(1)-C(2)-C(3)	118.5(8)
C(2)-C(3)-C(4)	120.9(8)
Lu(1)-C(4)-C(3)	79.2(5)
Lu(1)-C(4)-C(5)	90.6(5)
C(3)-C(4)-C(5)	114.6(7)
C(4)-C(5)-C(6)	118.6(7)
C(4)-C(5)-C(10)	123.3(8)
C(6)-C(5)-C(10)	118.0(8)
C(1)-C(6)-C(5)	117.3(7)
C(1)-C(6)-C(7)	123.0(8)
C(5)-C(6)-C(7)	119.5(8)
C(6)-C(7)-C(8)	121.5(8)
C(7)-C(8)-C(9)	119.9(8)
C(8)-C(9)-C(10)	119.5(8)
C(5)-C(10)-C(9)	121.4(8)
C(12)-C(11)-C(15)	109.5(7)
C(11)-C(12)-C(13)	107.1(8)
C(12)-C(13)-C(14)	108.9(8)
C(13)-C(14)-C(15)	107.0(7)
C(11)-C(15)-C(14)	107.5(8)

Anal. Found: Lu, 37.8. Calc. for $C_{19}H_{23}O_2Lu$: Lu, 38.2%. IR data (Nujol, cm^{-1}): 1247s, 1235sh, 1173m, 1088m, 1050s, 1005m, 862s, 790sh, 779s, 770s, 756m, 745s, 740sh, 719s.

3.2. Reactions of 1

To a suspension of 0.194 g (0.42 mmol) of **1** in benzene (2 ml) were added a few drops of degassed water. After the reaction mixture lost its colour, layers were separated and the benzene layer was analyzed by GLC: 0.0498 g (0.39 mmol, 93%) of dihydronaphthalene was detected as a mixture of 1,4- and 1,2-isomers.

A suspension of 0.245 g (0.53 mmol) of **1** in benzene (2 ml) was treated with dry air. GLC analysis of a yellow benzene solution gave 0.056 g (0.44 mmol, 82%) of naphthalene.

TABLE 4. Anisotropic temperature factors U_{ij} ($Å^2 \times 10^3$) in the form $-2\pi(H^2a^{*2}U_{11} + K^2b^{*2}U_{22} + \cdots + 2HKa^*b^*U_{12})$ in **1**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Lu(1)	22(1)	21(1)	21(1)	−3(1)	0(1)	2(1)
O(1)	20(3)	19(3)	34(3)	−0(2)	−5(3)	−3(2)
O(2)	28(4)	22(3)	23(3)	−2(2)	−3(2)	0(3)
C(1)	24(5)	23(5)	27(4)	−4(4)	−0(4)	−4(4)
C(2)	41(6)	34(5)	13(4)	3(4)	−0(4)	6(5)
C(3)	21(5)	36(4)	19(4)	−6(4)	1(4)	−2(5)
C(4)	24(5)	29(5)	28(4)	−6(4)	0(4)	−0(4)
C(5)	25(6)	29(5)	21(4)	−4(4)	3(4)	−6(4)
C(6)	37(6)	28(4)	13(4)	−3(3)	−0(4)	2(4)
C(7)	17(5)	42(5)	24(4)	−7(4)	−4(3)	4(4)
C(8)	42(8)	43(6)	32(4)	−4(4)	−6(4)	17(5)
C(9)	52(7)	29(5)	31(4)	−7(4)	−8(5)	15(5)
C(10)	36(6)	34(5)	30(4)	−4(4)	4(4)	−2(4)
C(11)	42(6)	25(4)	30(4)	−0(4)	11(5)	15(4)
C(12)	24(5)	36(5)	45(5)	−18(4)	−4(5)	8(5)
C(13)	38(6)	30(5)	39(5)	2(4)	17(5)	7(5)
C(14)	29(5)	39(5)	25(4)	−9(4)	6(4)	−7(5)
C(15)	35(6)	18(4)	27(4)	−4(4)	4(4)	−4(4)
C(16)	31(6)	32(5)	43(5)	−2(4)	−13(4)	−5(4)
C(17)	39(6)	24(5)	33(5)	9(4)	−9(4)	−1(4)
C(18)	25(6)	32(5)	29(4)	11(4)	1(4)	−6(4)
C(19)	20(6)	34(5)	41(5)	−1(4)	−4(4)	−1(4)

To a solution of 0.622 g (1.36 mmol) of **1** in DME (15 ml) was added a large excess of cyclopentadiene. The reaction mixture lost its colour and a white crystalline solid precipitated. Removal of volatile organic products at 90°C and sublimation of the residue at 200–220°C/10^{-2} Torr gave 0.462 g (1.25 mmol, 92%) of Cp_3Lu. GLC analysis of the organic products indicated the presence of naphthalene and dihydronaphthalene in a ratio of 1:1.2.

3.3. X-Ray analysis

The X-ray study of **1** was carried out using a Siemens R3/PC diffractometer at 193 K (λ(Mo Kα), $\theta/2\theta$ scan in the range $2° < 2\theta < 50°$, 1629 reflections with $F > 3\sigma(F)$). The crystal of **1** is orthorhombic, a = 14.393(2), b = 15.225(3), c = 15.302(4) Å, $\rho_c = 1.816$ g cm^{-3}, Z = 8, space group *Pbca*. The structure was obtained using a combination of direct and difference map methods. The Lu atom was located by a direct method, the other non-hydrogen atoms by subsequent electron density synthesis. The absorption of X-rays in the crystal (μ(Mo Kα) = 5.90 mm^{-1}) was taken into account by the DIFABS program [10]. The positions of the H atoms were calculated using geometrical conditions. These positions and their isotropic thermal parameters (B_{iso} = 0.08 $Å^2$) were not refined but were recalculated after each cycle of structure refinement. The final discrepancy factors were $R = 0.036$, $R_w = 0.032$ ($w^{-1} = \sigma^2(F) + 0.0003F^2$), $Q = 1.22$. All calculations were performed with the SHELXTL PLUS package. Coordinates of atoms, bond lengths and angles are given in Tables 1–3. Anisotropic thermal factors for non-hydrogen atoms are in Table 4.

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