

# Variety of naphthalene coordination modes in the polynuclear (pentamethylcyclopentadienyl) lutetium naphthalene complex

$$\{[(C_5Me_5Lu)_3(C_{10}H_8)(C_{10}H_7)(H)][(Na(THF)_3)]_2C_{10}H_8$$

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## Abstract

The reaction of  $C_5Me_5LuCl_2$  with sodium naphthalenide in DME solution affords the mononuclear complex  $C_5Me_5LuC_{10}H_8(DME)$  (**1**) in 48% yield besides naphthalene and NaCl. The same reaction in THF solution gives a series of products:  $(C_5Me_5)_2Lu(C_{10}H_8)_2Na(THF)_x$  (**2**),  $\{[(C_5Me_5Lu)_3(C_{10}H_8)(C_{10}H_7)(H)][(Na(THF)_3)]_2C_{10}H_8$  (**3**) and  $[(C_5Me_5)_2LuH(THF)_3(C_{10}H_7)]$  (**4**). The polynuclear complex **3** with several modes of Lu–naphthalene interaction has been isolated in low yield in a monocrystalline form. An X-ray diffraction study has shown that complex **3** consists of three  $C_5Me_5Lu$  units joined by two non-planar bridging  $C_{10}H_8$  and  $C_{10}H_7$  ligands via different kinds of naphthalene coordination mode. The third planar  $C_{10}H_8$  group is not involved in coordination sphere of the Lu atoms, and is on an inversion centre in the crystal structure. The Na atom in **3** is bonded to three THF molecules and  $\eta^3$ -bonded to the bridging  $C_{10}H_7$  group. © 1997 Elsevier Science S.A.

**Keywords:** Lutetium; Lanthanoid; Cyclopentadienyl; Naphthalene; Crystal structure

## 1. Introduction

Recently, we have found that the mixed cyclopentadienyl/naphthalene complex of lutetium  $CpLuC_{10}H_8(DME)$  is formed under the treatment of  $CpLuCl_2$  with sodium naphthalenide [1]. In this complex, one of the naphthalene rings bonded to a metal atom lost its aromaticity, forming two short and two long Lu–C bonds, and the coordination mode of the naphthalene can be described as  $2\sigma, \pi$ . Similar compounds have also been obtained for Y, Gd, Er and Tm [2]. In the case of divalent lanthanoids (Sm, Yb), the binuclear complexes of composition  $[CpLn(THF)_2]_2C_{10}H_8$  are formed [2]. Their structure was not determined by X-ray diffraction, but their IR spectra (in the part of the naphthalene bands) are identical to those of binuclear La(III) and Eu(II) complexes  $[I_2La(THF)_3]_2C_{10}H_8$  and  $[IEu(DME)_2]_2C_{10}H_8$ , which have been characterised structurally [3]. An X-ray anal-

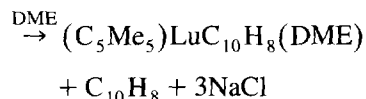
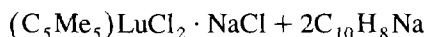
ysis showed that, in these complexes, the naphthalene dianion is  $\eta^4$ -coordinated to metal atoms. Evidently, the above-mentioned cyclopentadienyl/naphthalene complexes of Sm and Yb have the same arrangement of  $LnC_{10}H_8Ln$  fragments. An attempt to obtain a naphthalene derivative of dicyclopentadienyllutetium afforded the hydride  $[(Cp_2LuH)_3H][Na(THF)_6]$  and  $\sigma$ -naphthyl  $Cp_2Lu(2-C_{10}H_7)(THF)$  complexes [4]. Apparently, steric crowding of the  $Cp_2Lu$  unit prevents the formation of a stable naphthalene complex. It seemed interesting to investigate the synthesis and bonding mode of naphthalene–lanthanoid complexes containing pentamethylcyclopentadienyl ligands. Here we report on the reactions of  $(C_5Me_5)_2LuCl_2 \cdot NaCl$  with sodium naphthalenide and the structure of one of the complexes formed.

## 2. Results and discussion

Addition of sodium naphthalenide to a solution of  $(C_5Me_5)_2LuCl_2 \cdot NaCl$  in DME gives

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$(C_5Me_5)LuC_{10}H_8(DME)$  (**1**) as observed in the case of the unsubstituted Cp derivative [1].



The complex **1** crystallizes from a red–violet DME solution as dark crystals, which melt at 153–154 °C with decomposition. The IR spectrum of **1** is superimposable with that of  $CpLuC_{10}H_8(DME)$ , indicating a similarity of coordination mode of naphthalene in both complexes.

The other kinds of product are formed when the reaction is carried out in THF solution. In this case addition of  $C_{10}H_8Na$  to  $(C_5Me_5)LuCl_2$  (obtained in situ from  $LuCl_3$  and  $C_5Me_5Na$  in THF) leads to the formation of a dark-red solution. During several hours at room temperature, the colour of the mixture turns to yellow–brown. The dark-red crystals could be isolated from a freshly prepared dark-red solution by cooling to –10 °C. Their composition is close to the formula  $(C_5Me_5)Lu(C_{10}H_8)_2Na(THF)_x$  (**2**). However, this product quickly decomposes even at low temperatures, therefore it was not investigated more closely. Removal of THF from the yellow–brown solution leaves a dark-brown waxy solid, extraction of which with hexane and cooling of the extract at –10 °C gives dark-brown diamagnetic crystals of complex **3** in very low yield. Repeated extraction of the residue with hexane and subsequent slow evaporation of the solvent affords the product of composition  $[(C_5Me_5)LuH(THF)]_3(C_{10}H_7)$  (**4**) as small orange–red crystals with m.p. 240–245 °C (decomp.). Elemental analysis, IR spectroscopy and the set of hydrolysis products [ $Lu(OH)_3$ ,  $H_2$ ,  $C_5Me_5H$ ,  $C_{10}H_8$ ,  $C_{10}H_{10}$ ,  $C_{10}H_{12}$  (73:10:17), THF] reveal the presence in **4** of the fragments  $(C_5Me_5)Lu$ ,  $Lu-H$ ,  $C_{10}H_7$  and coordinated THF. Unfortunately, we failed to prepare good crystals of **4** suitable for X-ray analysis, therefore its structure remains unclear.

In contrast, compound **3** has been investigated by X-ray diffraction. It has been shown that the composition of **3** corresponds to the formula  $[(C_5Me_5Lu)_3(C_{10}H_8)(C_{10}H_7)(H)Na(THF)_3]_2C_{10}H_8$ , and the molecules of this complex consist of three  $C_5Me_5Lu$  units joined by two bridging  $C_{10}H_8$  and  $C_{10}H_7$  ligands (Fig. 1). The third  $C_{10}H_8$  group in the crystal structure is isolated, and not involved in the coordination of the Lu atoms. Both  $C_{10}H_8$  and  $C_{10}H_7$  bridging groups are non-planar: the bent angles along the  $C(2) \cdots C(5)$  and  $C(12) \cdots C(15)$  lines are 17.4 and 37.5° respectively. The isolated naphthalene is situated on an inversion centre, and planar within  $\pm 0.03$  Å.

The  $Lu(3)-C(12)$  and  $Lu(3)-C(15)$  distances (2.44(1) and 2.47(2) Å respectively) are comparable with the

$Lu-C$   $\sigma$ -bond lengths in  $Cp_2Lu^tBu(THF)$  (2.47 Å) [5], and somewhat longer than those in  $Cp_2LuCH_2SiMe_3(THF)$  (2.376 Å) and  $Cp_2LuC_6H_4Me_4(THF)$  (2.345 Å) [6] and shorter than the  $Lu(3)-C(13)$  and  $Lu(3)-C(14)$  distances (2.54(2) and 2.59(1) Å). The  $Lu(3)-C(11)$  and  $Lu(3)-C(16)$  distances are significantly longer (3.12 and 3.11 Å respectively). Thus, a coordination mode of the bridging  $C(11)-C(16)$  ring at the  $Lu(3)$  atom in **3** is  $2\eta^1:\eta^2$  and similar to that in molecules  $CpLnC_{10}H_8(DME)$  ( $Ln = Y$  [2],  $Lu$  [1]), although the differences between  $Lu-C$   $\eta^1$ - and  $\eta^2$ -distances in **3** are slightly less than in  $CpLnC_{10}H_8(DME)$  (2.397, 2.406 Å compared with 2.579, 2.562 Å for  $Ln = Lu$  and 2.452, 2.438 Å compared with 2.598, 2.599 Å for  $Ln = Y$ ).

Besides the mentioned interaction with the  $Lu(3)$  atom, there are two short distances between the  $C(11)-C(20)$  bridging naphthalene and the  $Lu(1)$  and  $Lu(2)$  atoms:  $C(14)-Lu(2)$  2.36(2) Å and  $C(13)-Lu(1)$  2.81(1) Å (Fig. 2(a)). The first value is close to the  $Lu-C$   $\sigma$ -bond lengths. The  $Lu(2)$  atom is somewhat out from the  $C(12)-C(15)$  plane: the deviation of the  $Lu(2)$  atom from the average plane of this fragment is 0.32 Å. These geometrical features indicate the existence of a direct  $Lu(2)-C(14)$  bond. Unfortunately, the H atoms were not located in **3**. If the H atoms at the  $C(13)$  and  $C(14)$  carbon atoms would be placed in the positions calculated from general geometrical conditions ( $C-C-H$  120°,  $C-H$  0.96 Å), the shortest  $Lu-H$  distances for these atoms,  $H(13) \cdots Lu(1)$  and  $H(14) \cdots Lu(2)$ , should be equal to 2.41 and 1.42 Å respectively. The last distance is very short for a real  $Lu-H$  bond and also indicates

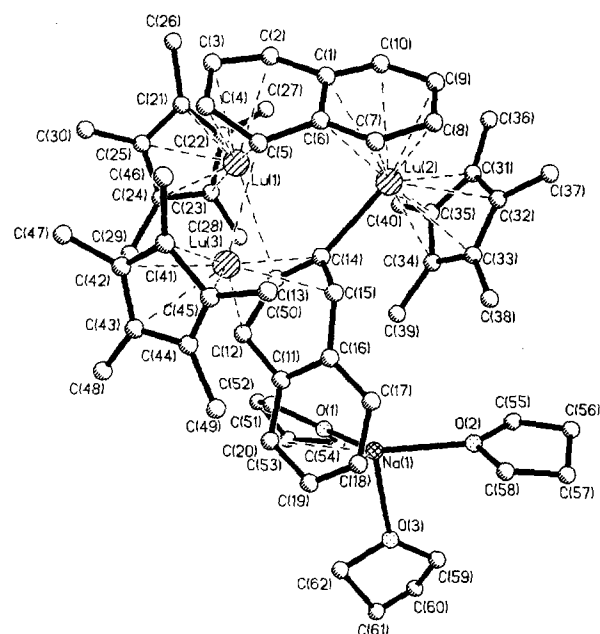
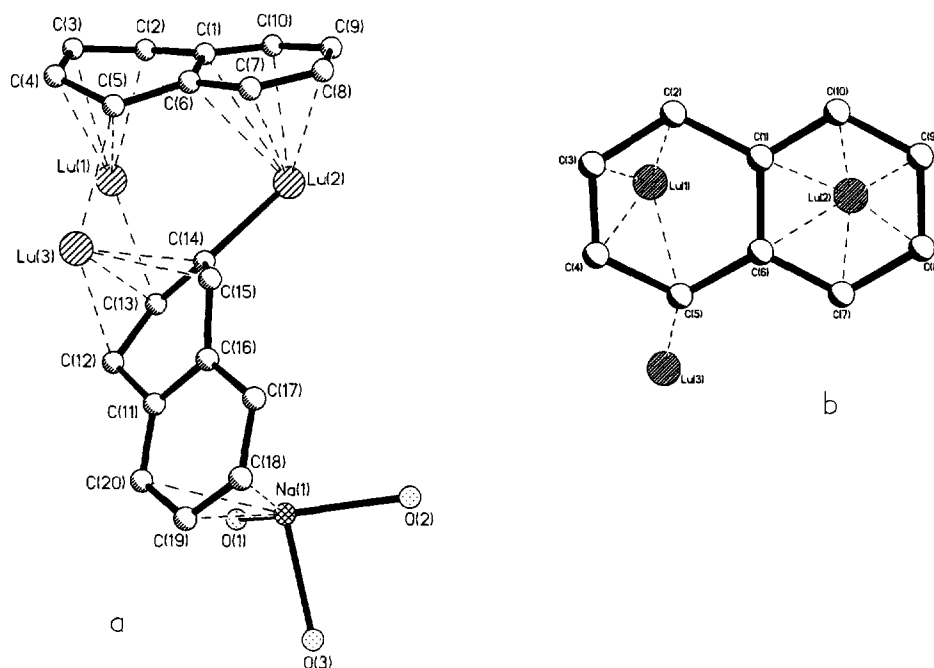


Fig. 1. The X-ray structure of  $[(C_5Me_5Lu)_3(C_{10}H_8)(C_{10}H_7)(H)Na(THF)_3]_2C_{10}H_8$  and atom labelling in **3**.

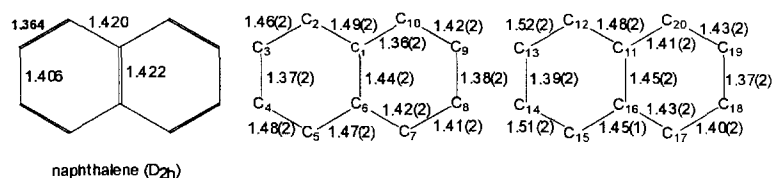
Fig. 2. Fragments of the X-ray structure of **3**.

that the C(14)–H(14) bond has been cleft. The H atom from the carbon C(14) atom seems to become as a terminal H atom at the Lu(2) atom or as a  $\mu$ -bridge between the Lu(2) and Lu(1) atoms.

The C(1)–C(10) naphthalene is also a bridge connecting all three Lu atoms in **3** (Fig. 2(a) and (b)). The C(1),C(6)–C(10) ring of naphthalene is planar within  $\pm 0.03$  Å. The C(2) and C(5) atoms are out from the average plane of this fragment by  $-0.03$  and  $0.16$  Å respectively. The C(2)–C(5) fragment is also planar (within  $\pm 0.004$  Å). The dihedral angle between the average plane of the C(2)–C(5) and C(1),C(2),C(5)–C(10) fragments is  $17.4^\circ$ . Both Lu(1) and Lu(2) atoms are on the same side of the C(1)–C(10) bridging naphthalene, but their arrangement relative to it differs. The Lu(1) atom is  $\eta^4$ -bonded to the C(2)–C(5) fragments, whereas the Lu(2) atom is  $\eta^6$ -bonded to the C(1),C(6)–C(10) fragment. A coordination mode in the Lu(1)–C(2),C(3),C(4),C(5) fragment is close to that of the Lu(3)–C(12),C(13),C(14),C(15) fragment. The Lu(1)–C(2) ( $2.58(2)$  Å), Lu(1)–C(3) ( $2.60(1)$  Å), Lu(1)–C(4) ( $2.67(2)$  Å) and Lu(1)–C(5) ( $2.77(2)$  Å) distances are comparable with  $\eta^2$ -bond lengths for the Lu(3)–C(13) and Lu(3)–C(14) bonds. The C(1) and C(6) atoms seem not to be involved in coordination of the Lu(1) atom, because the Lu(1)–C(1) ( $3.08$  Å) and Lu(1)  $\cdots$  C(6) ( $3.15$  Å) distances are significantly longer than the four

mentioned Lu(1)–C distances. The Lu(3)–C(5) distance ( $2.72(2)$  Å) is close to the Lu(1)–C(5) distance ( $2.77(2)$  Å), i.e. the C(5) atom is also a  $\mu$ -bridge connecting the Lu(1) and Lu(3) atoms (Fig. 2(a)). Thus, interaction of the Lu(1) atom with the C(2)–C(5) fragment can be described as a  $2\eta^1:\eta^2$ -bonding with geometrical parameters significantly distorted in comparison with those for the Lu(3)–C(12),C(13),C(14),C(15) fragment due to the existence of the additional Lu(3)–C(5) linkage.

The Lu–C distances between the Lu(2) atom and the planar C(1),C(6)–C(10) ring range from  $2.61(2)$  to  $2.88(1)$  Å (Table 1), the four distances Lu(2)–C(8) ( $2.62(2)$  Å), Lu(2)–C(9) ( $2.61(2)$  Å), Lu(2)–C(7) ( $2.71(2)$  Å) and Lu(2)–C(10) ( $2.65(2)$  Å) being shorter than the other two (Lu(2)–C(1)  $2.88(1)$  Å, Lu(2)–C(6)  $2.83(1)$  Å). The interaction of the Lu(2) atom with the C(1),C(6)–C(10) ring can be described as  $\eta^6$ -fashion bonding. A similar coordination mode was found in some organolanthanoid compounds, for example  $(C_6H_6)Ln(AlCl_4)_3$  (Ln = Nd, Sm, Yb) [7,8] and  $Yb(OC_6H_3Ph_2-2,6)_3$  [9]. It should be noted that the average Ln–C distances in molecules of this type ( $2.86$  Å in  $(C_6H_6)Yb(AlCl_4)_3$  [8] and  $2.978$  Å in  $Yb(OC_6H_3Ph_2-2,6)_3$  [9]) are longer than the Lu–C distances between the Lu(2) atom and the C(1),C(6)–C(10) ring in **3**.



There is an appreciable redistribution of the C–C bond distances in six-membered rings coordinated at the Ln atoms, in comparison with free naphthalene. In the six-membered C(1)–C(6) and C(11)–C(16) rings  $\eta^4$ -bonded to the Lu atoms, the C(1)–C(2), C(2)–C(3), C(4)–C(5), C(5)–C(6) and C(11)–C(12), C(12)–C(13), C(14)–C(15), C(15)–C(16) distances are longer, while the C(3)–C(4) and C(13)–C(14) distances are shorter than the lengths of the corresponding bonds in free naphthalene [10]. Thus, in **3** the  $\eta^4$ -bonded fragments have a ‘long–short–long’ distribution of C–C bond lengths. The geometry found indicates that in **3** the coordinated naphthalene is close to dianion form



The Na atom in **3** is bonded to three O(THF) atoms and a bridging C<sub>10</sub>H<sub>7</sub> fragment in  $\eta^3$ -fashion (Fig. 2(a)). The three Na–C distances between the Na atom and the C(11),C(16)–C(20) ring (Na(1)–C(19) 2.69(2) Å, Na(1)–C(18) 2.92(2) Å and Na(1)–C(20) 2.85(2) Å) are significantly shorter than others (Na(1)–C(11) 3.20(2) Å, Na(1)–C(17) 3.29(2) Å). The angle between the Na(1)–C(19) line and the average plane of the C(11),C(16)–C(20) ring is 77.3°. A similar  $\eta^2$ - and  $\eta^3$ -coordination of alkali metal cation to organolanthanoid fragment rather than to additional O-donor ligands was previously observed in anionic lanthanoid complexes such as [(<sup>t</sup>BuC<sub>5</sub>H<sub>4</sub>)<sub>3</sub>SmNa(THF)<sub>4</sub>] [11] and [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Y( $\mu$ -OCH<sub>3</sub>)<sub>3</sub>( $\mu_3$ -H)<sub>2</sub>][Li(THF)<sub>3</sub>]<sub>2</sub> [12] for example.

The Na(1)–O(1), Na(1)–O(2) and Na(1)–O(3) distances are 2.30(2), 2.32(1) and 2.35(2) Å. The O(1)–Na(1)–O(2) angle, 122.0(5)°, is significantly larger than the O(1)–Na(1)–O(3) (87.2(6)°) and O(2)–Na(1)–O(3) (85.3(6)°) angles. The main reason for such a difference seems to be repulsion of the THF molecules and Me group (C(39) atom) of the C<sub>5</sub>Me<sub>5</sub> fragment (Fig. 1): the Na(1)  $\cdots$  C(39) distance is 3.40 Å.

The average values of Lu–C(C<sub>5</sub>Me<sub>5</sub>)  $\eta^5$ -distances in **3** (2.61, 2.60 and 2.61 Å for the Lu(1), Lu(2) and Lu(3) atoms respectively) are comparable with those found in cyclopentadienyl compounds of Cp<sub>2</sub>Ln(III)R type: 2.63 Å in Cp<sub>2</sub>Lu<sup>t</sup>Bu(THF) [5], 2.61 Å in Cp<sub>2</sub>LuCH<sub>2</sub>SiMe<sub>3</sub>(THF) [6], 2.59 Å in Cp<sub>2</sub>LuC<sub>6</sub>H<sub>6</sub>Me-p(THF) [6]. Dihedral angles between the average plane of the  $\eta^5$ -bonded C<sub>5</sub>-ring and  $\eta^4$ - or  $\eta^6$ -bonded fragment at Lu atoms are 131.5° for the C(21)–C(25) and C(2)–C(5) fragments at the Lu(1) atom, 131.7° for the C(31)–C(35) and C(1),C(6)–C(10) fragments at the Lu(2) atom, and 125.5° for the C(41)–C(45) and C(12)–C(15) fragments at the Lu(3) atom. These values are in the range of average values of Cp(centre)–Ln–

Cp(centre) angles found in compounds of Cp<sub>2</sub>LnR type with a bent-sandwich structure [13]. The values of the C(14)–Lu(2)–X1A (107.0°), C(14)–Lu(2)–X1B

Table 1  
Interatomic distances (Å) in **3**

Lu(1) $\cdots$ Lu(2)	3.563(2)	Lu(1) $\cdots$ Lu(3)	3.355(2)
Lu(2) $\cdots$ Lu(3)	4.574(2)	Lu(1)–C(2)	2.579(15)
Lu(1)–C(3)	2.595(14)	Lu(1)–C(4)	2.669(16)
Lu(1)–C(5)	2.767(17)	Lu(1)–C(13)	2.807(14)
Lu(1)–C(21)	2.621(16)	Lu(1)–C(22)	2.622(21)
Lu(1)–C(23)	2.607(18)	Lu(1)–C(24)	2.573(17)
Lu(1)–C(25)	2.623(17)	Lu(2)–C(1)	2.880(14)
Lu(2)–C(6)	2.830(13)	Lu(2)–C(7)	2.713(16)
Lu(2)–C(8)	2.623(17)	Lu(2)–C(9)	2.608(17)
Lu(2)–C(10)	2.652(15)	Lu(2)–C(14)	2.355(16)
Lu(2)–C(31)	2.623(16)	Lu(2)–C(32)	2.618(15)
Lu(2)–C(33)	2.589(16)	Lu(2)–C(34)	2.579(14)
Lu(2)–C(35)	2.574(17)	Lu(3)–C(5)	2.721(15)
Lu(3)–C(12)	2.444(14)	Lu(3)–C(13)	2.538(16)
Lu(3)–C(14)	2.589(14)	Lu(3)–C(15)	2.471(15)
Lu(3)–C(41)	2.639(16)	Lu(3)–C(42)	2.615(22)
Lu(3)–C(43)	2.611(27)	Lu(3)–C(44)	2.587(22)
Lu(3)–C(45)	2.581(22)	Na(1)–O(1)	2.298(16)
Na(1)–O(2)	2.320(14)	Na(1)–O(3)	2.354(18)
Na(1)–C(18)	2.919(20)	Na(1)–C(19)	2.686(18)
Na(1)–C(20)	2.852(17)	O(1)–C(51)	1.433(27)
O(1)–C(54)	1.425(27)	O(2)–C(55)	1.395(28)
O(2)–C(58)	1.425(26)	O(3)–C(59)	1.364(42)
O(3)–C(62)	1.430(54)	C(1)–C(2)	1.486(23)
C(1)–C(6)	1.442(23)	C(1)–C(10)	1.362(22)
C(2)–C(3)	1.461(22)	C(3)–C(4)	1.374(24)
C(4)–C(5)	1.477(22)	C(5)–C(6)	1.472(22)
C(6)–C(7)	1.425(23)	C(7)–C(8)	1.412(23)
C(8)–C(9)	1.384(24)	C(9)–C(10)	1.420(24)
C(11)–C(12)	1.475(20)	C(11)–C(16)	1.452(22)
C(11)–C(20)	1.415(20)	C(12)–C(13)	1.523(21)
C(13)–C(14)	1.389(24)	C(14)–C(15)	1.505(23)
C(15)–C(16)	1.454(20)	C(16)–C(17)	1.431(22)
C(17)–C(18)	1.400(22)	C(18)–C(19)	1.372(27)
C(19)–C(20)	1.431(24)	C(21)–C(22)	1.414(23)
C(21)–C(25)	1.402(22)	C(21)–C(26)	1.477(24)
C(22)–C(23)	1.382(24)	C(22)–C(27)	1.517(28)
C(23)–C(24)	1.446(23)	C(23)–C(28)	1.503(23)
C(24)–C(25)	1.386(21)	C(24)–C(29)	1.511(25)
C(25)–C(30)	1.537(25)	C(31)–C(32)	1.408(25)
C(31)–C(35)	1.440(27)	C(31)–C(36)	1.499(25)
C(32)–C(33)	1.414(24)	C(32)–C(37)	1.459(28)
C(33)–C(34)	1.411(26)	C(33)–C(38)	1.511(27)
C(34)–C(35)	1.424(25)	C(34)–C(39)	1.509(25)
C(35)–C(40)	1.515(29)	C(41)–C(42)	1.401(31)
C(41)–C(45)	1.466(24)	C(41)–C(46)	1.537(27)
C(42)–C(43)	1.387(33)	C(42)–C(47)	1.518(36)
C(43)–C(44)	1.416(38)	C(43)–C(48)	1.437(47)
C(44)–C(45)	1.288(31)	C(44)–C(49)	1.469(30)
C(45)–C(50)	1.513(31)	C(51)–C(52)	1.492(44)
C(52)–C(53)	1.360(43)	C(53)–C(54)	1.446(61)
C(55)–C(56)	1.452(40)	C(56)–C(57)	1.441(39)
C(57)–C(58)	1.491(31)	C(59)–C(60)	1.468(82)
C(60)–C(61)	1.140(80)	C(61)–C(62)	1.734(53)
C(63)–C(64)	1.370(31)	C(63)–C(63A)	1.330(41)
C(63)–C(67A)	1.435(32)	C(64)–C(65)	1.349(33)
C(65)–C(66)	1.287(31)	C(66)–C(67)	1.385(31)
C(67)–C(63A)	1.435(32)		

(110.9°), C(5)–Lu(3)–X1C (109.6°), and C(5)–Lu(3)–X1D (98.8°) angles (X1A, X1B, X1C and X1D the geometrical centres of the C(1),C(6)–C(10), C(31)–

Table 2  
Selected bond angles (°) in **3**

Lu(2)···Lu(1)··· Lu(3)	82.7(1)	O(1)–Na(1)–O(2)	122.0(5)
O(1)–Na(1)–O(3)	87.2(6)	O(2)–Na(1)–O(3)	85.3(6)
Na(1)–O(1)–O(3)	124.5(13)	Na(1)–O(1)–O(54)	128.2(16)
C(51)–O(1)–C(54)	106.9(21)	Na(1)–O(2)–O(55)	135.3(14)
Na(1)–O(2)–C(58)	116.9(11)	C(55)–O(2)–C(58)	107.6(16)
Na(1)–O(3)–C(59)	130.0(24)	Na(1)–O(3)–C(62)	114.3(17)
C(59)–O(3)–C(62)	113.6(28)	C(2)–C(1)–C(6)	116.2(14)
C(2)–C(1)–C(10)	123.6(16)	C(6)–C(1)–C(10)	119.3(15)
C(1)–C(2)–C(3)	120.5(15)	C(2)–C(3)–C(4)	119.2(15)
C(3)–C(4)–C(5)	120.0(14)	Lu(1)–C(5)–Lu(3)	75.4(4)
C(4)–C(5)–C(6)	118.5(13)	C(1)–C(6)–C(5)	119.5(14)
C(1)–C(6)–C(7)	117.6(14)	C(5)–C(6)–C(7)	122.9(14)
C(6)–C(7)–C(8)	121.5(15)	C(7)–C(8)–C(9)	119.0(15)
C(8)–C(9)–C(10)	119.9(15)	C(1)–C(10)–C(9)	121.6(16)
C(12)–(11)–C(16)	114.8(12)	C(12)–C(11)–C(20)	122.9(14)
C(16)–C(11)–C(20)	122.0(14)	C(11)–C(12)–C(13)	113.3(13)
Lu(1)–C(13)–Lu(3)	77.6(4)	C(12)–C(13)–C(14)	119.9(15)
C(13)–C(14)–C(15)	113.9(14)	C(14)–C(15)–C(16)	115.1(14)
C(11)–C(16)–C(15)	118.2(13)	C(11)–C(16)–C(17)	117.5(13)
C(15)–C(16)–C(17)	124.3(15)	C(16)–C(17)–C(18)	119.4(16)
C(17)–C(18)–C(19)	122.4(16)	C(18)–C(19)–C(20)	121.3(15)
C(11)–C(20)–C(19)	117.2(16)	C(22)–C(21)–C(25)	107.9(13)
C(22)–C(21)–C(26)	125.6(16)	C(25)–C(21)–C(26)	125.4(14)
C(21)–C(22)–C(23)	109.2(15)	C(21)–C(22)–C(27)	123.4(15)
C(23)–C(22)–C(27)	126.9(16)	C(22)–C(23)–C(24)	106.3(14)
C(22)–C(23)–C(28)	126.4(17)	C(24)–C(23)–C(28)	126.7(16)
C(23)–C(24)–C(25)	108.6(14)	C(23)–C(24)–C(29)	123.3(14)
C(25)–C(24)–C(29)	127.5(15)	C(21)–C(25)–C(24)	108.0(13)
C(21)–C(25)–C(30)	127.1(14)	C(24)–C(25)–C(30)	124.9(16)
C(32)–C(31)–C(35)	107.9(15)	C(32)–C(31)–C(36)	128.0(17)
C(35)–C(31)–C(36)	123.8(17)	C(31)–C(32)–C(33)	108.1(15)
C(31)–C(32)–C(37)	123.5(16)	C(33)–C(32)–C(37)	127.7(16)
C(32)–C(33)–C(34)	108.9(16)	C(32)–C(33)–C(38)	124.2(16)
C(34)–C(33)–C(38)	127.0(16)	C(33)–C(34)–C(35)	107.8(15)
C(33)–(34)–C(39)	128.0(16)	C(35)–C(34)–C(39)	124.2(17)
C(31)–(35)–C(34)	107.3(17)	C(31)–C(35)–C(40)	126.2(17)
C(34)–C(35)–C(40)	126.0(17)	C(42)–C(41)–C(45)	104.8(15)
C(42)–C(41)–C(46)	128.3(20)	C(45)–C(41)–C(46)	126.3(21)
C(41)–C(42)–C(43)	110.0(20)	C(41)–C(42)–C(47)	128.4(21)
C(43)–C(42)–C(47)	121.3(24)	C(42)–C(43)–C(44)	104.7(22)
C(42)–C(43)–C(48)	130.8(26)	C(44)–C(43)–C(48)	124.4(24)
C(43)–C(44)–C(45)	112.7(19)	C(43)–C(44)–C(49)	124.1(26)
C(45)–C(44)–C(49)	123.0(27)	C(41)–C(45)–C(44)	107.7(18)
C(41)–C(45)–C(50)	121.2(19)	C(44)–C(45)–C(50)	130.9(21)
O(1)–C(51)–C(52)	105.0(20)	C(51)–C(52)–C(53)	106.0(30)
C(52)–C(53)–C(54)	105.7(31)	O(1)–C(54)–C(53)	106.2(22)
O(2)–C(55)–C(56)	110.5(22)	C(55)–C(56)–C(57)	104.0(23)
C(56)–C(57)–C(58)	105.5(22)	C(2)–C(58)–C(57)	106.1(18)
O(3)–C(59)–C(60)	104.3(39)	C(59)–C(60)–C(61)	105.9(51)
C(60)–C(61)–C(62)	108.2(41)	O(3)–C(62)–C(61)	91.9(32)
C(64)–C(63)– C(63A)	121.0(27)	C(64)–C(63)– C(67A)	121.8(20)
C(63A)–C(63)– C(67A)	116.8(26)	C(63)–C(64)–C(65)	116.0(20)
C(64)–C(65)–C(66)	130.9(22)	C(65)–C(66)–C(67)	111.4(22)
C(66)–C(67)– C(63A)	123.3(20)		

C(35), C(41)–C(45) and C(12)–C(15) fragments respectively) are also typical for such kinds of structure [13].

The third C(63)–C(67a) naphthalene lies on an inversion centre (0,0,0) in the crystal structure of **3**. Calculation of formal valent electrons for this complex indicates that this molecule exists in the form of a dianion  $C_{10}H_8^{2-}$ . Its geometrical parameters are given in Tables 1 and 2. The lengths of the shortest distances between this naphthalene dianion and the cationic polynuclear fragment are typical for van der Waals contacts, revealing an absence of direct coordination to Lu atoms.

Thus, in complex **3** five different kinds of interaction between Lu atom and naphthalene ligand have been found: pure ionic,  $\sigma$ -,  $\eta^1$ -,  $\eta^4$ - and  $\eta^6$ -interactions.

### 3. Experimental

All manipulations were carried out in vacuum using standard Schlenk techniques. The solvents were dried and freed of oxygen by refluxing and maintaining over sodium ketyl.  $C_5Me_5LuCl_2 \cdot NaCl \cdot THF$  was prepared similarly to its ether analogue  $C_5Me_5LuCl_2 \cdot NaCl \cdot (Et_2O)_2$  [14], but in THF medium. IR spectra were obtained using a Perkin–Elmer 577 infrared spectrometer with the samples as Nujol mulls between CsI discs.

#### 3.1. Synthesis of $C_5Me_5LuCl_2 \cdot NaCl \cdot THF$

To a suspension of 5.2 g (18.5 mmol)  $LuCl_3$  in THF, a solution of  $C_5Me_5Na$  (2.6 g, 16.5 mmol) in THF was added with shaking. The solution was centrifuged and decanted from the precipitate of non-reacted  $LuCl_3$  and formed NaCl. Then the solvent was evaporated in vacuum up to a minimum volume of mixture, while small white crystals were precipitated. The crystals were filtered off, washed with cold THF and dried under vacuum. The yield of  $C_5Me_5LuCl_2 \cdot NaCl \cdot THF$  was 1.37 g (15%).

Anal. Found: Lu, 35.1.  $C_{14}H_{23}OCl_3LuNa$  Calc.: Lu, 34.2%.

Owing to the low yield of  $C_5Me_5LuCl_2 \cdot NaCl \cdot THF$  in most cases, this complex was used in future reactions without isolation.

#### 3.2. Reaction of $C_5Me_5LuCl_2 \cdot NaCl \cdot THF$ with $C_{10}H_8Na$ in DME

A solution of sodium naphthalenide obtained from 0.06 g (2.61 mmol) Na and 0.40 g (3.12 mmol)  $C_{10}H_8$  in 15 ml DME was added to 0.668 g (1.34 mmol)  $C_5Me_5LuCl_2 \cdot NaCl \cdot THF$ . After 30 min of vigorous shaking the reaction mixture was centrifuged, a dark-red solution was decanted from the NaCl precipitated and concentrated in vacuum to half its volume. Cooling of the solution to  $-10^\circ C$  gave 0.338 g (48%) of **1** as black crystals with m.p.  $153\text{--}154^\circ C$ .

Table 3

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^4$ ) in **3**

Atom	x	y	z	$U_{eq}^*$
Lu(1)	2117(1)	4296(1)	1728(1)	212(2)
Lu(2)	2366(1)	5611(1)	3492(1)	213(2)
Lu(3)	4405(1)	3391(1)	2153(1)	234(2)
Na(1)	7196(6)	7873(5)	3209(4)	447(26)
O(1)	6613(10)	8540(9)	2261(7)	488(49)
O(2)	6948(10)	8685(9)	4339(7)	455(47)
O(3)	8766(14)	9201(16)	3251(11)	1097(94)
C(1)	798(13)	3706(12)	2990(9)	294(57)
C(2)	358(12)	3440(12)	2262(8)	271(53)
C(3)	710(12)	2555(12)	1779(10)	339(60)
C(4)	1681(14)	2213(12)	1913(9)	339(59)
C(5)	2341(12)	2722(12)	2546(9)	276(54)
C(6)	1806(12)	3321(11)	3123(9)	240(52)
C(7)	2255(13)	3573(12)	3815(9)	292(57)
C(8)	1766(12)	4221(13)	4345(9)	292(56)
C(9)	833(13)	4626(13)	4185(9)	326(60)
C(10)	406(13)	4419(12)	3491(8)	270(54)
C(11)	6185(12)	5457(10)	2485(7)	197(48)
C(12)	5315(12)	5171(11)	1938(8)	209(49)
C(13)	4199(12)	5381(12)	2201(9)	294(57)
C(14)	3884(12)	5158(11)	2853(9)	260(53)
C(15)	4730(12)	4719(11)	3239(9)	263(54)
C(16)	5852(12)	5220(11)	3166(8)	246(51)
C(17)	6661(12)	5477(12)	3719(9)	321(57)
C(18)	7746(14)	5846(14)	3572(10)	371(64)
C(19)	8059(14)	6022(12)	2919(10)	329(60)
C(20)	7286(11)	5833(12)	2348(10)	327(61)
C(21)	719(12)	4373(12)	728(8)	241(51)
C(22)	1073(14)	5470(16)	1030(9)	417(70)
C(23)	2167(13)	5750(12)	904(9)	297(58)
C(24)	2506(13)	4789(14)	510(9)	324(60)
C(25)	1609(13)	3971(12)	395(9)	286(56)
C(26)	-426(16)	3825(17)	649(11)	594(88)
C(27)	306(16)	6228(14)	1354(10)	536(77)
C(28)	2826(19)	6873(14)	1055(12)	627(92)
C(29)	3619(14)	4784(17)	197(10)	538(79)
C(30)	1620(19)	2824(17)	-15(11)	646(94)
C(31)	1760(13)	7400(12)	4151(9)	291(58)
C(32)	2446(13)	7056(12)	4624(9)	253(55)
C(33)	3511(14)	7145(14)	4360(9)	308(62)
C(34)	3497(12)	7540(12)	3720(9)	279(56)
C(35)	2405(15)	7683(14)	3575(10)	353(67)
C(36)	593(15)	7568(15)	4238(11)	411(72)
C(37)	2111(16)	6834(16)	5312(11)	528(80)
C(38)	4486(14)	6862(14)	4723(10)	376(68)
C(39)	4447(14)	7812(13)	3264(11)	418(71)
C(40)	2029(17)	8187(14)	2975(10)	438(73)
C(41)	4529(13)	1293(13)	2055(10)	287(61)
C(42)	4812(20)	1585(18)	1407(12)	605(90)
C(43)	5794(22)	2294(19)	1468(14)	572(107)
C(44)	6106(17)	2430(15)	2181(14)	563(92)
C(45)	5399(17)	1909(16)	2538(9)	335(75)
C(46)	3621(18)	398(16)	2219(19)	1187(174)
C(47)	4248(29)	1150(28)	703(14)	1775(227)
C(48)	6439(29)	2770(26)	950(20)	1388(268)
C(49)	7163(18)	3020(19)	2476(22)	1454(219)
C(50)	5403(29)	1798(25)	3301(12)	1271(173)
C(51)	6185(23)	7877(21)	1623(14)	766(120)
C(52)	-5976(32)	8666(25)	1157(15)	1067(163)
C(53)	6622(25)	9624(27)	1412(24)	1510(240)
C(54)	-6701(24)	9648(17)	2157(20)	1042(174)

Table 3 (continued)

Atom	x	y	z	$U_{eq}^*$
C(55)	6390(22)	9514(18)	4646(14)	764(111)
C(56)	6562(22)	9701(19)	5396(16)	870(126)
C(57)	7516(21)	9210(19)	5502(14)	699(112)
C(58)	-7549(19)	8364(16)	4877(11)	586(84)
C(59)	9052(42)	10155(33)	3698(23)	2454(321)
C(60)	9566(39)	10924(42)	3256(41)	3484(744)
C(61)	10083(35)	10444(33)	2879(34)	1881(308)
C(62)	-9364(25)	9144(33)	2624(29)	1713(386)
C(63)	295(17)	-148(16)	-272(11)	794(52)
C(64)	1171(17)	-675(15)	-204(12)	1090(52)
C(65)	1362(17)	-903(16)	437(12)	1037(52)
C(66)	854(16)	-711(15)	1007(12)	893(52)
C(67)	-51(17)	-221(15)	909(11)	1049(52)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Anal. Found: Lu, 33.1.  $C_{24}H_{33}O_2Lu$  Calc.: Lu, 33.1%. IR: 1320, 1250, 1236, 1137, 1105, 1088, 1050, 1022, 997, 862, 777, 752, 731, 716, 710, 474  $cm^{-1}$ .

### 3.3. Reaction of $C_5Me_5LuCl_2 \cdot NaCl \cdot THF$ with $C_{10}H_8Na$ in THF

(a) A solution of sodium naphthalenide, obtained from 0.047 g (2.04 mmol) of Na and 0.287 g (2.24 mmol) of  $C_{10}H_8$  in 15 ml of THF was added to 0.512 g (1.02 mmol) of  $C_5Me_5LuCl_2NaCl \cdot THF$ . The reaction mixture immediately turned dark-red. After 15 min of vigorous shaking the reaction mixture was centrifuged and concentrated in vacuum. Cooling of the solution to  $-10^\circ C$  gave 0.235 g (28%) of product **2** as dark-red crystals, which melt at  $93-95^\circ C$  with decomposition.

Anal. Found: Lu, 21.2; Na 2.8;  $C_{10}H_8$  29.2%. IR: 1330, 1255, 1215, 1180, 1045, 1020, 890, 780, 743, 695, 515, 473  $cm^{-1}$ .

(b) A solution of  $C_5Me_5LuCl_2 \cdot NaCl \cdot THF$ , obtained from 0.921 g (3.27 mmol) of  $LuCl_3$  and 0.523 g (3.31 mmol) of  $C_5Me_5Na$  in 25 ml of THF, was mixed with a solution of  $C_{10}H_8Na$ , obtained from 0.165 g (7.20 mmol) of Na and 1.024 g (8.0 mmol) of naphthalene in 20 ml of THF. The resulting dark-red mixture was allowed to stay at room temperature for one day, until its colour changed to brown. The solution was centrifuged and decanted from the NaCl precipitate. THF was removed in vacuum and the residue was extracted with hexane (ca. 50 ml). Concentration of hexane solution to half volume under vacuum and cooling to  $-10^\circ C$  overnight produced several brown crystals of **3**, which have been used for X-ray analysis. Prolonging of the crystallization led to the disappearance of the crystals, evidently due to decomposition of **3** in solution.

The dark-brown residue remaining after THF removal and extraction with hexane was repeatedly extracted with hexane ( $2 \times 50$  ml). The obtained hexane

solution was slowly evaporated in vacuum at room temperature until a dark-brown resin began to precipitate. Simultaneously, orange–red crystals formed on the wall of the vessel. The crystals were separated from the resin precipitate, washed with cool hexane and dried in vacuum, yielding 0.39 g (21%) of complex **4** with m.p. 240–245 °C (dec.).

### 3.4. X-ray diffraction studies

X-ray data for **3** were collected on a Siemens P3/PC diffractometer at 153 K (Mo K $\alpha$  radiation, graphite monochromator,  $\theta$ – $2\theta$  scan mode  $2^\circ \leq \theta \leq 25^\circ$ , 12415 independent reflections measured, 6730 reflections observed with  $F > 4\sigma(F)$ ). Crystal data for **3** at 153 K: C<sub>67</sub>H<sub>89</sub>O<sub>3</sub>Na<sub>1</sub>Lu<sub>3</sub>, fw 1490.28, space group  $P\bar{1}$ ,  $a = 12.394(2)$ ,  $b = 12.556(3)$ ,  $c = 19.471(4)$  Å,  $\alpha = 98.95(2)^\circ$ ,  $\beta = 90.36(2)^\circ$ ,  $\gamma = 98.73(2)^\circ$ ,  $V = 2957(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 1.674$  g cm<sup>-3</sup>,  $\mu = 5.029$  mm<sup>-1</sup>. The structure was solved using a combination of direct and difference Fourier map methods. The Lu atoms were located by the direct method, the other non-hydrogen atoms by subsequent electron density synthesis. All non-H atoms were refined anisotropically except the C atoms of the discrete C<sub>10</sub>H<sub>8</sub> fragment, refined isotropically. The positions of the H atoms for the C<sub>5</sub>Me<sub>5</sub> groups, THF molecules and discrete C<sub>10</sub>H<sub>8</sub> fragments were calculated using a geometrical condition with  $d(\text{C}–\text{H}) = 0.96$  Å and refined in a riding group model with fixed isotropic thermal parameters ( $B_{\text{iso}} = 0.08$  Å<sup>2</sup>). The H atoms of bridging naphthalenes were not included in the refinement in calculated positions, taking into account a complicated coordination mode in **3**. Absorption was taken into account using the DIFABS program [15]. The final refinements converged at  $R = 0.072$ ,  $R_w = 0.062$ ,  $S = 1.82$  for observed reflections. The weighting scheme was  $w = 1/[\sigma^2(F) + 0.001F^2]$ . All calculations were performed using the SHELXTL PLUS program [16]. Interatomic distances, selected angles and atomic coordinates for **3** are given in Tables 1–3 respectively.

The X-ray structure of **3** has a few problems which must be noted. The discrete naphthalene was refined with isotropic thermal parameters because the accuracy of its location is less than that for the main part of **3**. There is some unaccounted for residual electron density near the C(3) and C(4) atoms. The two largest difference peaks are 4.77 and 4.68 e Å<sup>-3</sup> at distances of 1.68 Å from C(4) and 1.54 Å from C(3), larger than for

a peak suitable for a H atom. The nearest contact from one of these peaks to a H atom of the adjacent C<sub>5</sub>Me<sub>5</sub> group (1.49 Å) is very short. This residual density makes no crystallographic or chemical sense, and may be attributed to a small satellite crystal. There were a few spurious intensities, but it was decided to proceed with this crystal since it was the best one available. It is believed that the mentioned problems do not compromise the results of this structure determination severely.

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