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Lutetium complexes with an anthracene dianion ligand. Molecular structure of [(C$_5$H$_5$)$_2$Lu(C$_{14}$H$_{10}$$^{2-}$)][Na$^+$(diglyme)$_2$]

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Abstract

The interaction of (C$_5$H$_5$)LuCl$_2$ · 3THF (1) and (C$_5$H$_5$)LuCl (2) with dianionic [Na$_2$$^+$(C$_{14}H_{10}$$^{2-}$)] (3) or radical-ionic [Na$^+$(C$_{14}$H$_{10}$$^{-}$)] (4) sodium-anthracenide adducts results in the formation of organolutetium derivatives [(C$_5$H$_5$)Lu(C$_{14}$H$_{10}$$^{2-}$) · 2THF] (5) and [(C$_5H_5$)$_2$Lu(C$_{14}H_{10}$$^{2-}$)][Na$^+$(diglyme)$_2$] (7) (after recrystallization from diglyme), containing anthracene dianion as a ligand. The structures of the complexes formed were established by an X-ray diffraction study. The decrease in the electron density of the anthracenide ligand on coordination with Lu^{3+} is demonstrated by NMR- and UV-spectroscopy.

1. Introduction

According to [1–3], maximum stability of organolanthanoid compounds may be achieved when using bulky ligands with a negative charge. Therefore, the synthesis of organolanthanides, containing radical ions and dianions of aromatic hydrocarbons, for example anthracene [4–8], is of essential interest.

There are two synthetic routes to these complexes: a single electron transfer reaction with aromatic hydrocarbons as oxidants and a methathetic reaction between halogenide complexes of lanthanides and anthracene adducts with alkali metals.

The formation of Yb^{2+} complexes with an anthracene dianion and radical ion by a single-electron transfer reaction between zero-valent ytterbium and anthracene has been reported previously [4–6]. Unfor-

tunately, investigations on the lanthanoid-anthracene adducts formed were complicated due to the complex character of this reaction and the variety of reaction products. A similar reaction between Yb^0 and benzophenone [9] led to the ytterbium complex with benzophenone dianion [Yb{OCPh$_2$}{OP(NMe$_2$)$_3$}$_2$]$_2$. In the present paper, mono- and bis-cyclopentadienylanthracenide derivatives of lutetium, whose synthesis has been preliminary reported [7,8], are prepared by exchange reaction of (C$_5$H$_5$)LuCl$_2$ · 3THF and (C$_5$H$_5$)$_2$LuCl with sodium-anthracene adducts.
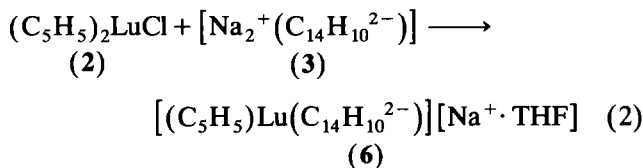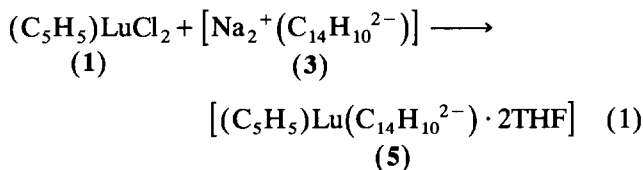
2. Results and discussion

We have studied the reactions of (C$_5$H$_5$)LuCl$_2$ · 3THF (1) and (C$_5$H$_5$)$_2$LuCl (2) with the dianion [Na$_2$$^+$(C$_{14}H_{10}$$^{2-}$)] (3) and the radical ion [Na$^+$(C$_{14}$H$_{10}$$^{-}$)] (4) sodium-anthracene adducts.

The interaction of 1 and 2 with an equimolar amount of 3 in THF results in the formation of organolutetium

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complexes containing the anthracene dianion as a ligand.

$$(C_5H_5)LuCl_2 + [Na_2^+(C_{14}H_{10}^{2-})] \longrightarrow$$
$$\mathbf{(1)} \qquad\qquad \mathbf{(3)}$$

$$[(C_5H_5)Lu(C_{14}H_{10}^{2-}) \cdot 2THF] \quad (1)$$
$$\mathbf{(5)}$$

$$(C_5H_5)_2LuCl + [Na_2^+(C_{14}H_{10}^{2-})] \longrightarrow$$
$$\mathbf{(2)} \qquad\qquad \mathbf{(3)}$$

$$[(C_5H_5)Lu(C_{14}H_{10}^{2-})][Na^+ \cdot THF] \quad (2)$$
$$\mathbf{(6)}$$

Complex 5 was isolated after recrystallization from THF as red-orange crystals. The synthesis and molecular structure of 5 have been described previously [8]. Isolation of 6 from THF led to a red-orange oil; all attempts to isolate 6 from THF in a crystalline form were unsuccessful. The dissolution of 6 in diglyme followed by slow crystallization with pentane addition led to large red-orange crystals of [(C_5H_5)_2Lu(C_{14}-H_{10}^{2-})][Na^+(diglyme)_2] (7). The molecular and crystal structure of 7 was established by an X-ray structural study (Fig. 1). The main geometrical parameters of 7 are listed in Table 1; relevant parameters of the structure 5 [7] are listed in the same table for comparison.

Crystals of the complex 7 are composed of isolated cations [Na(diglyme)_2]^+ and anions [(C_5H_5)_2Lu(C_{14}-H_{10}^{2-})]. The Lu–C(C_5H_5) and Lu–Cp distances (Cp is a centroid of the C_5H_5^- ring) are equal to 2.631(8)–2.678(6) Å and 2.35(1) Å, respectively; the Cp–Lu–Cp angle is equal to 122.5°.

An interesting feature of the structure studied is the conformation of the coordinated anthracene dianion, which is bent on the C(9)...C(10) line with an interplanar angle of 40.1°, while both its parts are planar (within 0.027 Å). Thus, the central cycle of the anthracene ligand has lost its aromatic character and acquired a boat conformation, the folding angles along the C(11)...C(13) and C(12)...C(14) lines being equal to 36.9 and 39.4°, respectively. The Lu(1)–C(9, 10) bond distances are equal to 2.473(6) and 2.482(6) Å, respectively, and are somewhat longer than in the structure 5. This elongation may be explained by the presence of two cyclopentadienyl ligands in complex 7 (there is only one C_5H_5^- ligand in 5). Coordination of the C(9, 10) atoms bound to Lu is close to distorted tetrahedral (C–C–H bond angles are in the range 112–118°). It should be noted that structural data for 7 are in good agreement with those obtained earlier for 5 (cf. Table 1). The differences in the geometrical parameters of the compounds 5 and 7 may be explained by the presence of two cyclopentadienyl ligands in the

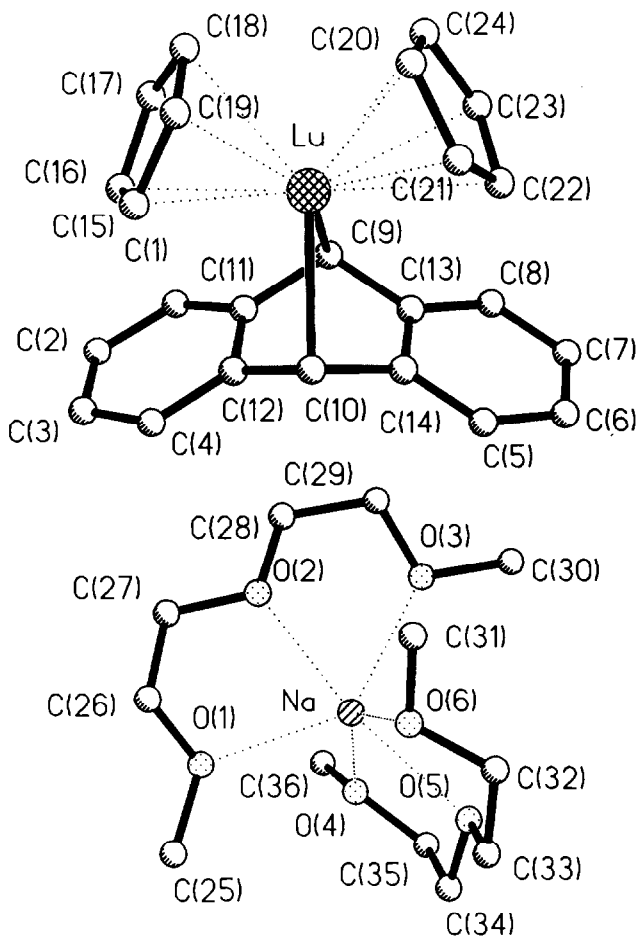Fig. 1. The molecular structure of [(C_5H_5)_2Lu(C_{14}H_{10}^{2-})][Na^+-(diglyme)_2].

latter, oriented to the side aromatic cycles of the anthracenide ligand by their vertices. This all results in shortened contact between the carbon atoms of these ligands (C(16)–C(11, 12) and C(22)–C(13, 14)); the interligand distances are equal to 3.14–3.19 Å (the doubled Van-der-Waals carbon atom radius is 3.42 Å [10]). In the structure 5, a similar orientation of the ligands was found only in one of two independent molecules. In the second molecule, the cyclopentadienyl ring is oriented to the anthracene dianion in "side-on" fashion resulting in differences in the geometry of two independent molecules.

Reactions (1) and (2) were monitored by electronic absorption spectroscopy. Absorption bands in the spectra of solutions 5 and 6 in THF are strongly shifted to the shorter wavelengths as compared with 3 (λ_{max} = 600 nm) [11] (5, λ_{max} = 440 nm; 6, λ_{max} = 410, 475 nm). In accordance with the generally accepted interpretation of this phenomena [11], this shift testifies to the increase in the anthracene dianion interaction with the

TABLE 1. Main geometrical parameters of structures 5 and 7

	5A [a]	5B [a]	7
Metal coordination no.	7	7	8
Lu–C(9) (Å)	2.44(1)	2.43(1)	2.473(6)
Lu–C(10) (Å)	2.43(1)	2.46(1)	2.482(6)
Lu–C_{Cp}(average) (Å)	2.59	2.58	2.65
Lu–$Cp_{centroid}$ (Å)	2.31	2.29	2.35
Interplanar angle between the C(1)–C(4) and C(5)–C(8) planes (°)	29.9	38.7	40.1
Cp–Lu–Cp angle (°)	–	–	122.5
The nearest contact between the $C_5H_5^-$ and $C_{14}H_{10}^{2-}$ ligands (Å)	3.31–3.42	3.20–3.21	3.14–3.19
Interplanar angle of the C(11), C(9), C(13) and C(12), C(10), C(14) planes with the C(11)–C(14) plane (°)	32.6 30.8	37.5 35.9	36.9 39.4

[a] Structure 5 contains two independent molecules A and B differing in the orientation of the cyclopentadienyl rings relative to the anthracene dianion.

counter-ion. It is possible that coordination of Lu^{3+} leads to a decrease in the anthracene dianion HOMO energy due to interaction with vacant 5d orbitals of Lu^{3+}.

It has been demonstrated [12] that the change in the chemical shift in the NMR ^{13}C spectra of structurally similar molecules and ions correlates with the value of excessive negative charge on the carbon atoms. The NMR spectroscopy data for 5 and 6 and related compounds are presented in Tables 2 and 3. The values of the differences between the chemical shifts of C-1 and C-2 resonance signals in the spectra of 5 and 6, Li- and Mg- adducts, and anthracene, demonstrate that an excessive negative charge on the anthracene ligand carbon atoms in 5 and 6 is essentially lower than in the case of anthracene adducts with Group I and II metals. The same pattern with the exception of lithium is observed for C(9) resonance signals. However, it should be noted that the above-mentioned correlation for C(9)

and C(10) atoms may not be quite rigorous, as changes in chemical shift values depend not only on the alteration of the negative charge but also on the polarization action of the cation. The latter is strongly dependent on solvation conditions and distortion of the planar anthracene structure on dianion formation which was shown earlier for Li and Mg adducts [16,17].

These considerations seem to be true for the NMR ^1H data (see Table 3). All these results together with electronic absorption spectroscopy data allow us to conclude that coordination of anthracene dianion with Lu^{3+} results in a reduction of the electron density on the anthracenide ligand. On the basis of NMR data, it can be also supposed that the character of the Lu-anthracene bond in 5 and 6 is similar to that proposed for the Mg-anthracene bond in $[Mg(C_{14}H_{10}^{2-})(THF)_3]$ [13], which has been interpreted as a highly polarized covalent bond or a tight ion pair of Mg^{2+} and $C_{14}H_{10}^{2-}$.

This assumption is in agreement with the X-ray data. The degree of the chemical bond covalency may be estimated via alteration of the difference between the M–C(9) or M–C(10) bond length ($d_{M-C(9)}$) and the metal ion radius, r [18,19]. The average $d_{M-C(9)}$ values are 2.339 Å in $[Li(tmeda)]_2[C_{14}H_{10}^{2-}]$ [16], 2.295 Å in $[Mg(C_{14}H_{10}^{2-})(THF)_3]$ (average of two independent molecules) [17], 2.44 Å in compound 5 (average of two independent molecules) and 2.478 Å in compound 7. The metal ion radii are equal: 0.73 Å for Li^+ (coordination number 4) [20], 0.80 Å for Mg^{2+} (coordination number 5) [20]; 1.06 Å for Lu^{3+} (coordination number 7) (estimated on the basis of [20]); 1.117 Å for Lu^{3+} (coordination number 8) [20]. Therefore the differences $(d_{M-C(9)} - r)$ are as follows: 1.61 Å for the Li complex, 1.50 Å for the Mg complex, 1.38 Å for compound 5 and 1.36 Å for compound 7. These data are consistent with increasing M–C(9) bond covalency in the Li–Mg–Lu series. It should be mentioned that the interplanar angle between two side benzene rings of the anthracenide ligand increases in the same order: Li complex, 14.7°; Mg complex, 26.6° and 30.6° (for two independent molecules); complex 5, 29.9° and 38.7° (for two independent molecules); complex 7, 40.1°. The

TABLE 2. NMR $^{13}C\{H\}$ data (THF-d_8, ppm) for lutetiumanthracenide derivatives 5 and 6 and related compounds

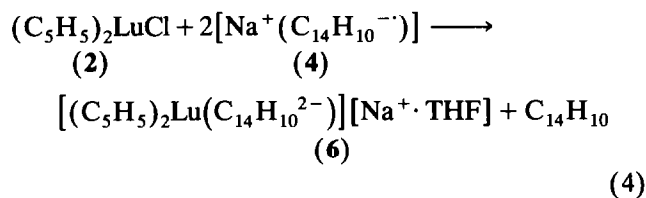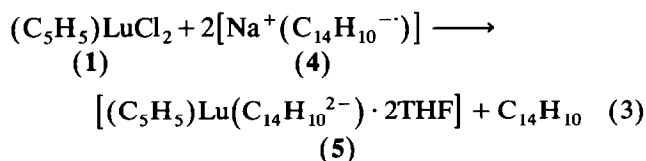|	C-1	C-2	C-9	C-11	C_5H_5	Ref.
$[Li_2^+(C_{14}H_{10}^{2-})]$ [a]	102.4	115.6	76.4	151.4	–	[12]
$[Mg^{2+}(C_{14}H_{10}^{2-})]$	114.1	118.1	57.7	145.9	–	[13]
5	119.4	120.9	66.8	139.0	110.0	–
6	118.3	119.6	62.3	143.4	107.9	–
Anthracene [b]	128.1	125.3	126.2	131.8	–	[12]
9,10-Dihydroanthracene	127.9	126.7	36.7	137.7	–	[13]

[a] Solvent, tetrahydrofuran; [b] Solvent, chloroform.

TABLE 3. NMR ^{1}H data (THF-d_8 δ, ppm) for lutetiumanthracenide derivatives **5** and **6** related compounds

|	H-1	H-2	H-9	C_5H_5	Ref.
$[Na_2^+(C_{14}H_{10}^{2-})]$	2.85m	3.85m	1.55s	–	–
$[Li_2^+(C_{14}H_{10}^{2-})]$	3.36m	4.25m	1.89s	–	[14]
$[Mg^{2+}(C_{14}H_{10}^{2-})]$	5.95m	6.01m	3.51s	–	[13]
5	6.17m	6.33m	3.54s	5.72s	–
6	6.29m	6.42m	3.90s	5.18s	–
Anthracene	7.91m	7.39m	8.31m	–	[15]
9,10-Dihydroanthracene	7.11m	7.25m	3.90s	–	[13]

two last values are even greater than in the case of 9,10-dihydroanthracene (35° [21]).

Evidently, increase in M–C(9) bond covalency and, to a great extent, increase in the interplanar angle is a consequence of the strengthing of the metal polarization action, which increases the localization of the negative charge on C(9) and C(10) carbon atoms of the anthracenide ligand. At the same time, as can be seen from comparison of the structures of **5** and **7**, volumes of other ligands also influence the value of the interplanar angle.

This assumption on the nature of the lutetium–anthracene bond is also confirmed by the fact that reactions (1) and (2) with radical ion adduct **4** lead to **5** and **6**, respectively, and an equimolar amount of anthracene is formed.

$$(C_5H_5)LuCl_2 + 2[Na^+(C_{14}H_{10}^{-\cdot})] \longrightarrow$$
$$\quad (1) \qquad\qquad (4)$$

$$[(C_5H_5)Lu(C_{14}H_{10}^{2-}) \cdot 2THF] + C_{14}H_{10} \quad (3)$$
$$(5)$$

$$(C_5H_5)_2LuCl + 2[Na^+(C_{14}H_{10}^{-\cdot})] \longrightarrow$$
$$\quad (2) \qquad\qquad (4)$$

$$[(C_5H_5)_2Lu(C_{14}H_{10}^{2-})][Na^+ \cdot THF] + C_{14}H_{10}$$
$$(6)$$

$$(4)$$

The formation of trivial exchange reaction products is not observed. Possibly, initially formed radical ionic lutetium complexes quickly transform to **5** or **6** according to scheme (5).

$$2C_{14}H_{10}^{-\cdot} \rightleftharpoons C_{14}H_{10}^{2-} + C_{14}H_{10} \quad (5)$$
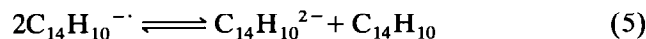
As is known [11], equilibria of the type (5) are being shifted to the right under conditions that are favorable for the appearance of tight contact between counterions. These contacts are typical for tight ion pairs and similar aggregates. The analogous spontaneous formation of polyanions from monoanions on coordination with lanthanide and actinide cations was observed earlier [22] in the case of cycloheptatrienyl trianion formation from the cycloheptadienyl anion by the action of

anhydrous $LnCl_3$ (Ln = Er, Gd) and $AnCl_4$ (An = Th, U) on LiC_7H_8R (R = H, Me, ^nBu) solution. Nevertheless, it should be noted that the cycloheptatrienyl trianion formed is a conjugated aromatic system in contrast to the anti-aromatic anthracene dianion.

It is noteworthy that the equilibrium (5) cannot be shifted to the left even in the presence of excess anthracene (up to 500 mol%) relative to **5** and **6** in THF. This shift may be achieved only by replacement of THF by much the more polar hexamethylphosphoramide (HMPA) solvent. The HMPA action probably greatly weakens the interaction between Lu^{3+} and the anthracene dianion, and dissociation of the complexes **5** and **6** becomes possible with the formation of the anthracene dianion and $[(C_5H_5)_2Lu(HMPA)_n]^+$ and $[(C_5H_5)Lu(HMPA)_m]^{2+}$ cations. When an equimolar mixture of anthracene and **5** or **6** is dissolved in HMPA, the absorption bands of **5** (**6**) disappear in the electronic absorption spectrum and only the spectrum typical for anthracene radical ions is observed.

Thus, the exchange reaction between halogen containing lanthanide complexes and sodium–anthracene adducts may be used as a synthetic method for the preparation of a new type of rare earth organic derivatives, anthracenide-lanthanoid complexes. The use of anthracene dianion as a ligand allows, on the one hand the preparation of stable organometallic compounds, whose stability is probably due to a high negative charge and a suitable angular geometry of the anthracenide ligand; on the other hand, coordination with Lu^{3+} cation stabilizes the unstable anti-aromatic system of the anthracene dianion.

3. Experimental details

All experiments were carried out in sealed Schlenk-type glass apparatus in a vacuum. THF was distilled over $LiAlH_4$ and stored with a small amount of sodium anthracenide in evacuated glass ampoules equipped with teflon stopcocks. Pentane and diglyme were distilled over K/Na alloy. HMPA was kept over CaH_2 in a vacuum for 2 days and then distilled over a fresh

portion of CaH_2 in a high vacuum. THF-d_8 was stirred over the K/Na alloy for 2 days and then distilled and stored a similar way as THF. ^1H and ^{13}C NMR spectra were recorded on a Bruker-250 spectrometer. UV and visible absorption spectra were recorded on a Specord UV-VIS spectrophotometer. Complexes 5 and 6 were analyzed for THF and C_5H_5 content by the method described in [23]. Lutetium was determined by complexonometric titration with a xylenol orange indicator. Compounds 1 and 2 were prepared according to [24] and [25]. A technique described earlier [8] was used for

the preparation of crystal samples suitable for X-ray studies without any contact with the atmosphere.

3.1. The synthesis of $[Na_2^+(C_{14}H_{10}^{2-})]$ (3)

Anthracene (0.086 g, 0.5 mmol) was placed in one of the glass ampoules whose design allowed the UV and visible spectra of the reaction mixture to be registered; 0.5 g of sodium metal were placed in the other ampoule. The apparatus was then evacuated and a sodium mirror was obtained on the ampoule walls by quick heating of sodium. THF (50 ml) was condensed in the

TABLE 4. Atom coordinates ($\times 10^4$) and temperature factors ($\overset{\circ}{A} \times 10^3$)

Atom	x	y	z	U [a]
Lu	3909(1)	7057(1)	−95(1)	16(1)
C(1)	7617(7)	8221(3)	573(3)	28(2)
C(2)	7345(8)	8856(4)	725(4)	34(2)
C(3)	6187(8)	9203(3)	335(4)	35(2)
C(4)	5299(8)	8911(3)	−217(3)	28(2)
C(5)	5296(7)	7355(3)	−1958(3)	25(2)
C(6)	6238(8)	6913(3)	−2259(3)	30(2)
C(7)	7422(7)	6569(3)	−1862(3)	29(2)
C(8)	7660(7)	6674(3)	−1169(3)	23(2)
C(9)	6840(6)	7224(3)	−127(3)	21(2)
C(10)	4521(7)	7899(3)	−899(3)	22(2)
C(11)	6708(6)	7911(3)	40(3)	22(2)
C(12)	5516(7)	8270(3)	−374(3)	23(2)
C(13)	6725(6)	7114(3)	−863(3)	20(2)
C(14)	5523(7)	7468(3)	−1263(3)	20(2)
C(15)	2256(8)	7920(4)	493(4)	42(2)
C(16)	3742(7)	7907(4)	877(3)	28(2)
C(17)	3913(10)	7322(3)	1191(3)	38(2)
C(18)	2520(14)	6964(4)	1014(5)	67(4)
C(19)	1490(10)	7326(5)	588(5)	62(4)
C(20)	1908(7)	6070(3)	−291(3)	22(2)
C(21)	2145(7)	6303(3)	−937(3)	21(2)
C(22)	3757(7)	6168(3)	−1058(3)	23(2)
C(23)	4523(7)	5864(3)	−481(3)	24(2)
C(24)	3370(7)	5804(3)	−12(3)	23(2)
Na	9726(3)	9507(1)	−2332(1)	29(1)
C(25)	8451(10)	11080(4)	−2185(4)	54(3)
C(26)	8076(9)	10405(4)	−1279(4)	37(2)
C(27)	8890(9)	9898(4)	−846(4)	41(2)
C(28)	9830(8)	8823(4)	−888(4)	41(2)
C(29)	9802(8)	8256(4)	−1341(4)	37(2)
C(30)	10616(9)	7893(4)	−2362(4)	48(3)
C(31)	6368(8)	8734(3)	−2540(4)	37(2)
C(32)	7261(9)	9017(3)	−3575(4)	36(2)
C(33)	8290(8)	9502(4)	−3889(3)	35(2)
C(34)	10948(8)	9961(3)	−3719(3)	29(2)
C(35)	12517(8)	9908(4)	−3277(3)	32(2)
C(36)	13588(9)	10058(5)	−2143(4)	55(3)
O(1)	8978(6)	10514(2)	−1832(2)	32(1)
O(2)	8957(6)	9328(2)	−1248(2)	32(1)
O(3)	10450(6)	8436(2)	−1944(3)	35(2)
O(4)	12155(5)	9987(2)	−2599(2)	31(1)
O(5)	9893(5)	9466(2)	−3531(2)	29(1)
O(6)	7193(5)	9203(2)	−2895(2)	32(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5. Bond lengths (Å)

C(1)–C(2)	1.39(1)	C(15)–Lu	2.631(8)	Na–O(2)	2.360(5)
C(1)–C(11)	1.402(8)	C(15)–C(16)	1.385(9)	Na–O(3)	2.434(6)
C(2)–C(3)	1.38(1)	C(15)–C(19)	1.42(1)	Na–O(4)	2.372(5)
C(3)–C(4)	1.403(9)	C(16)–Lu	2.658(7)	Na–O(5)	2.424(5)
C(4)–C(12)	1.400(9)	C(16)–C(17)	1.38(1)	Na–O(6)	2.370(5)
C(5)–C(6)	1.394(9)	C(17)–Lu	2.638(7)	C(25)–O(1)	1.43(1)
C(5)–C(14)	1.406(9)	C(17)–C(18)	1.40(1)	C(26)–C(27)	1.49(1)
C(6)–C(7)	1.399(9)	C(18)–Lu	2.62(1)	C(26)–O(1)	1.422(9)
C(7)–C(8)	1.398(9)	C(18)–C(19)	1.37(1)	C(27)–O(2)	1.447(9)
C(8)–C(13)	1.393(9)	C(19)–Lu	2.62(1)	C(28)–C(29)	1.50(1)
C(9)–Lu	2.473(6)	C(20)–Lu	2.662(6)	C(28)–O(2)	1.436(9)
C(9)–C(11)	1.488(9)	C(20)–C(21)	1.418(9)	C(29)–O(3)	1.428(9)
C(9)–C(13)	1.487(8)	C(20)–C(24)	1.400(8)	C(30)–O(3)	1.43(1)
C(10)–Lu	2.482(6)	C(21)–Lu	2.641(6)	C931)–O(6)	1.433(9)
C(10)–C(12)	1.488(8)	C(21)–C(22)	1.418(8)	C(32)–C(33)	1.51(1)
C(10)–C(14)	1.476(9)	C(22)–Lu	2.679(6)	C(32)–O(6)	1.426(8)
C(11)–C(12)	1.437(8)	C(22)–C(23)	1.412(8)	C(33)–O(5)	1.448(8)
C(13)–C(14)	1.422(8)	C(23)–Lu	2.687(6)	C(34)–C(35)	1.501(9)
		C(23)–C(24)	1.418(9)	C(34)–O(5)	1.437(8)
		C(24)–Lu	2.678(6)	C(35)–O(4)	1.434(8)
		Na–O(1)	2.451(6)	C(36)–O(4)	1.430(9)

TABLE 6. Bond angles (°)

C(9)–Lu–C(10)	67.1(2)	C(21)–C(20)–C(24)	107.6(5)
C(2)–C(1)–C(11)	121.6(6)	C(20)–C(21)–C(22)	108.3(5)
C(1)–C(2)–C(3)	120.1(6)	C(21)–C(22)–C(23)	107.6(5)
C(2)–C(3)–C(4)	119.5(6)	C(22)–C(23)–C(24)	107.8(5)
C(3)–C(4)–C(12)	121.8(6)	C(20)–C(24)–C(23)	108.7(5)
C(6)–C(5)–C(14)	121.3(5)	O(1)–Na–O(2)	69.8(2)
C(5)–C(6)–C(7)	119.5(6)	O(1)–Na–O(3)	137.1(2)
C(6)–C(7)–C(8)	120.0(6)	O(2)–Na–O(3)	69.0(2)
C(7)–C(8)–C(13)	121.1(5)	O(1)–Na–O(4)	89.2(2)
Lu–C(9)–C(11)	92.0(3)	O(2)–Na–O(4)	126.7(2)
Lu–C(9)–C(13)	92.6(3)	O(3)–Na–O(4)	106.1(2)
C(11)–C(9)–C(13)	112.0(5)	O(1)–Na–O(5)	118.7(2)
Lu–C(10)–C(12)	92.9(4)	O(2)–Na–O(5)	163.2(2)
Lu–C(10)–C(14)	92.8(4)	O(3)–Na–O(5)	104.2(2)
C(12)–C(10)–C(14)	111.7(5)	O(4)–Na–O(5)	69.5(2)
C(1)–C(11)–C(9)	125.1(5)	O(1)–Na–O(6)	100.1(2)
C(1)–C(11)–C(12)	118.6(6)	O(2)–Na–O(6)	94.6(2)
C(9)–C(11)–C(12)	116.3(5)	O(3)–Na–O(6)	94.6(2)
C(4)–C(12)–C(10)	126.0(5)	O(4)–Na–O(6)	138.0(2)
C(4)–C(12)–C(11)	118.3(5)	O(5)–Na–O(6)	70.2(2)
C(10)–C(12)–C(11)	115.5(5)	C(27)–C(26)–O(1)	108.9(6)
C(8)–C(13)–C(9)	124.2(5)	C(26)–C(27)–O(2)	108.1(5)
C(8)–C(13)–C(14)	119.4(5)	C(29)–C(28)–O(2)	108.0(5)
C(9)–C(13)–C(14)	116.4(5)	C(28)–C(29)–O(3)	108.7(6)
C(5)–C(14)–C(10)	124.7(5)	C(33)–C(32)–O(6)	107.1(5)
C(5)–C(14)–C(13)	118.8(5)	C(32)–C(33)–O(5)	107.0(5)
C(10)–C(14)–C(13)	116.4(5)	C(35)–C(34)–O(5)	108.0(5)
C(16)–C(15)–C(19)	107.1(7)	C(34)–C(35)–O(4)	107.1(5)
C(15)–C(16)–C(17)	108.3(6)	C(25)–O(1)–C(26)	111.1(6)
C(16)–C(17)–C(18)	108.8(7)	C(27)–O(2)–C(28)	112.3(5)
C(17)–C(18)–C(19)	107.8(8)	C(29)–O(3)–C(30)	110.7(6)
C(15)–C(19)–C(18)	108.1(8)	C(35)–O(4)–C(36)	111.8(5)
		C(33)–O(5)–C(34)	112.9(5)
		C(31)–O(6)–C(32)	110.8(5)

first ampoule and the apparatus was sealed. The anthracene solution formed was transferred onto the sodium mirror and stirred for about 1 day until the absorption bands of free anthracene and its radical ions disappeared in the visible spectrum. The disodium anthracenide solution obtained had the only absorption band in the visible spectrum (λ_{max} = 600 nm). The resulting solution was filtered, collected in the first ampoule and sealed.

3.2. The synthesis of [Na$^+$($C_{14}H_{10}^-$)] (4)

Anthracene (0.086 g, 0.5 mmol) was added to 0.5 mmol of 3 in THF (50 ml) with stirring. The visible spectrum of the resulting solution showed only the presence of the radical anion form of sodium-anthracenide.

3.3. The synthesis of [(C_5H_5)Lu($C_{14}H_{10}^{2-}$) · 2THF] (5)

Compound 3 (0.5 mmol) in THF (50 ml) was added to 1 (0.256 g, 0.5 mmol) in THF (20 ml). The solution turned red-orange and NaCl precipitated. The precipitate was removed and the solution was evaporated in a vacuum. After recrystallization of residue from THF, 0.23 g (83%) of 5 was obtained as red-orange crystals. Anal. Found: C_5H_5, 12.7; Lu, 30.0. [(C_5H_5)Lu(C_{14}-H_{10}^{2-}) · 2C$_4$H$_8$O] calc.: C_5H_5, 11.6; Lu, 31.1%.

3.4. The synthesis of [(C_5H_5)$_2$Lu($C_{14}H_{10}^{2-}$)][Na$^+$·THF] (6)

Compound 3 (1.5 mmol) in THF (50 ml) was added to 2 (0.511 g, 1.5 mmol) in THF (20 ml). The solution immediately turned dark-orange and NaCl precipitated. The precipitate was removed and the solution evaporated in a vacuum. The residue was dried in a dynamic vacuum of 2 · 10^{-2} Torr during 2 h at room temperature and 6 (0.611 g, 66%) was obtained as a glassy mass. Dissolution of 6 in diglyme and subsequent slow addition of pentane resulted in the formation of 7 as large orange-red needle-shaped crystals. Anal. Found: C_5H_5, 23.0; Lu, 32.4; THF, 9.7. [(C$_5$-H$_5$)$_2$Lu($C_{14}H_{10}^{2-}$)][Na$^+$·THF] calc.: C_5H_5, 22.5; Lu, 30.3; THF, 12.5°.

3.5. X-ray crystal structure determination

Crystal data for 7: LuNaC$_{36}$H$_{48}$O$_6$, M_r = 774.7, monoclinic, space group $P2_1/c$ at 143 K: a = 8.326(4), b = 21.005(7), c = 20.045(8) Å, β = 96.18(4)°, V = 3485(3) Å^3, Z = 4, D_c = 1.476 Mg m^{-3}, μ(MoK$_\alpha$) = 28.87 cm^{-1}, F(000) = 1576; 5608 independent reflections with $F > 4\sigma(F)$ were collected with a Siemens P3/PC diffractometer at 143 K (λ(MoK$_\alpha$) = 0.71069 Å, graphite monochromator, $2\theta < 47°$). The structure was solved by direct methods and refined by the least-squares technique in anisotropic approximation to R =

0.043, R_W = 0.041, GOF = 1.75. Weighting scheme $\omega^{-1} = \sigma^2(F)$. The DIFABS programme [26] was used to correct the intensities for absorption. The H atoms at the C(9) and C(10) atoms of the anthracene dianion central cycle were located as the highest peaks in the difference electron density map. The other H atoms were placed in the calculated positions and included in the calculations with fixed positional and isotropic thermal parameters U_{iso} = 0.08 Å^2. All calculations were carried out with the SHELX PLUS programs. Atomic coordinates, bond lengths and bond angles are listed in Tables 4–6.

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