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The First Structurally Characterized Organolanthanoid Compound with an Anthracene Dianion Ligand. Synthesis and Structure (at 143 K) of η^5-$(C_5H_5)Lu(C_{14}H_{10}{}^{2-})\cdot 2thf$ (thf = tetrahydrofuran)

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The interaction of η^5-$(C_5H_5)LuCl_2$ with $Na^+{}_2(C_{14}H_{10}{}^{2-})$ or $Na^+(C_{14}H_{10}{}^{\cdot -})$ has led to the formation of η^5-$(C_5H_5)Lu(C_{14}H_{10}{}^{2-})\cdot 2thf$ (thf = tetrahydrofuran), containing anthracene dianion as a ligand and the structure of the new complex has been established by a low-temperature X-ray diffraction study at 143 K.

The synthesis of 4f-element complexes with new types of ligands is a problem of great interest in the field of organolanthanoid chemistry. Our attention was attracted to the dianions of aromatic hydrocarbons because of their well-known ability to form complexes with metals of Groups 1[1] and 2.[2]

We have reported previously[3] the formation of an anionic Lu^{III} complex with anthracene dianion, $Na[Lu(C_5H_5)_2(C_{14}H_{10}]\cdot C_4H_8O$, prepared by reaction of $[(C_5H_5)_2LuCl\cdot thf]$ (thf = tetrahydrofuran) with disodium anthracenide. Here we describe the reaction of cyclopentadienyllutetium dichloride **1** with disodium anthracenide **2**, as a route for the synthesis of neutral organolanthanoid complexes with an anthracene dianion ligand [reaction (1)].

$$\underset{\mathbf{1}}{\eta^5\text{-}(C_5H_5)LuCl_2} + \underset{\mathbf{2}}{Na_2(C_{14}H_{10}{}^{2-})} \rightarrow \eta^5\text{-}(C_5H_5Lu(C_{14}H_{10}{}^{2-}) + 2NaCl \qquad (1)$$

The interaction of **1** with an equimolar amount of **2** in thf at room temperature leads to $C_5H_5Lu(CL_{14}H_{10}{}^{2-})\cdot 2C_4H_8O$ **3** in 83% yield.† **3** was obtained after recrystallization from thf as red–orange crystals that are extremely air- and moisture-sensitive.

The molecular structure of **3** was determined by a low-temperature X-ray study. Transparent and well-formed crystals of **3** became cloudy and decomposed on exposure to air for a few seconds, even under a layer of absolute pentane. When the crystals were transferred to the Kel-F fine capillary, they rapidly decomposed because of interaction with traces of moisture and oxygen adsorbed on the capillary walls. Therefore, in order to prepare samples for X-ray experiments we

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† ^1H NMR spectrum of **3** ($[^2H_8]$thf): δ 6.33 (m, 4H), 6.17 (m, 4H), 3.54 (s, 2H), 5.72 (s, 5H).

Complex **3** was analysed for C_5H_5 content by the method of ref. 4. Lutetium analyses were carried out by direct complexometric titration with disodium EDTA and xylenol orange indicator. Calc. for $C_5H_5Lu(C_{14}H_{10})\cdot 2C_4H_8O$: C_5H_5, 11.6%; Lu, 31.1%; found: C_5H_5, 12.7%; Lu, 30.0%.

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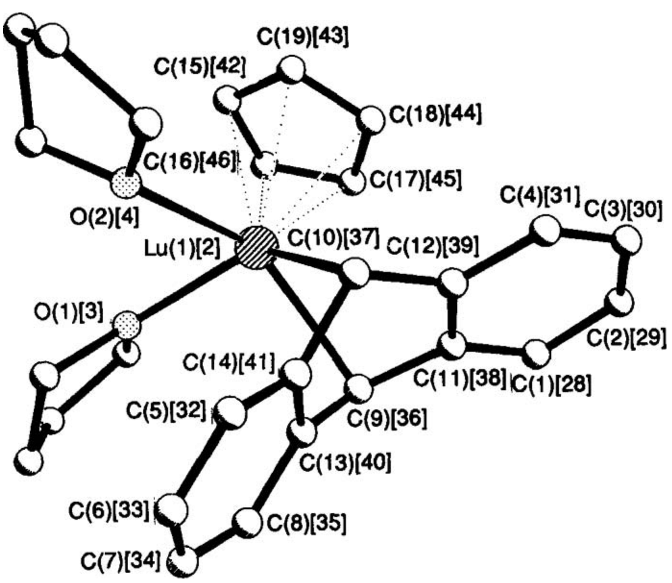

Fig. 1 The molecular structure of $[C_5H_5Lu(C_{14}H_{10})\cdot 2C_4H_8O]$ (the atom numbering scheme for the second complex is given in brackets). Main bond distances (Å) and bond angles (°) (average values for the two independent complexes): Lu(1)—C(9) 2.44(1), Lu(1)—C(10) 2.45(1), Lu(1)—O(1) 2.34(1), Lu(1)—O(2) 2.30(1), C(9)—C(11) 1.46(2), C(9)—C(13) 1.47(2), C(10)—C(12) 1.45(1), C(10)—C(14) 1.48(2), C(11)—C(12) 1.42(2), C(13)—C(14) 1.45(2); C(9)—Lu—C(10) 67.9(4), O(1)—Lu—O(2) 78.3(2), C(12)—C(10)—C(14) 114.5(9), C(11)—C(9)—C(13) 114.7(9), C(9)—C(13)—C(14) 116.4(9), C(10)—C(14)—C(13) 116.1(9), C(10)—C(12)—C(11) 116.5(9), C(9)—C(11)—C(12) 116.4(9)

devised a method which completely excluded any contact between a single crystal and the atmosphere. Vaseline, which had previously been dried over K–Na alloy and distilled *in vacuo*, was vacuum-transferred to a Schlenk-tube containing crystals of **3** and the system was filled with pre-purified argon. After these manipulations both the crystals and the Vaseline were transferred in air to a Petri dish. A crystal, protected by a layer of Vaseline, was selected for X-ray investigation with a thin glass rod lubricated by Anusol viscous grease and placed on the diffractometer goniometer into a stream of cold nitrogen (– 130 °C). The Vaseline became frozen, covering the crystal with a thin layer and protecting it from the atmosphere.

According to the X-ray data,‡ there are two independent $[C_5H_5Lu(C_{14}H_{10}{}^{2-})\cdot 2C_4H_8O]$ complexes in the crystal with very similar geometries, consisting of a Lu atom coordinated by an anthracene dianion, a cyclopentadienyl anion and two thf molecules. The distances between the Lu atom and the C atoms of the C_5H_5-anion are 2.36(1)–2.54(1) Å. The Lu–O distances [2.29(1)–2.36(1) Å] are typical for Lu^{3+} compounds with coordinated thf.[6]

The most interesting feature of the structure studied is the conformation of the coordinated anthracene dianion. In both the independent complexes, due to Lu—C(9,10) and Lu(2)—C(36,37) bond formation these dianions are bent along the C(9)···C(10) and C(36)···C(37) axes and their two planar (within 0.029 Å) symmetrical parts intersect with interplanar angles of 38.7° and 29.9°, respectively. Thus the central ring of the anthracene ligand has lost its aromatic character and acquired a boat conformation with bend angles of 35.8° and 37.5°. The coordination of the C atoms bound to Lu is close to a distorted tetrahedron (the C—C—H bond angles are in the range 113–118°). The fused benzene rings of the coordinated anthracene are situated at essentially different distances from the lutetium atom: the mean bond distances Lu(1)—C(11,12) and Lu(1)—C(13,14) are 3.01–3.04 Å and 2.72 Å, respectively. The most probable reason for this inequality is steric interaction, the distances between the cyclopentadienyl C(17,18) atoms and the anthracene C(11,12) atoms being shortened to 3.45 Å and 3.32 Å, respectively (twice the van der Waals radius of a carbon atom of 3.42 Å).[7] The coordination of the Lu atoms in the two independent molecules is similar, but there are some essential differences. The distances between the carbon atoms of cyclopentadienyl ligand and those of the nearest aromatic ring of anthracene in the second complex are shorter than those in the first one [C(39)···C(44) 3.20 Å, C(38)···C(45) 3.63 Å]. This difference results in a decrease in the interplanar angle between the aromatic rings of the coordinated dianion. The Lu(2)—C(38,39) distances are 0.15 Å shorter than Lu(1)—C(11,12). In both complexes some additional interaction of the anthracene dianion with the Lu atom seems to exist. The distances Lu(1)—C(13,14) and Lu(2)—C(40,41) are in the range 2.71–2.73 Å and so are only a little longer than the Lu—C bonds in some structurally characterized organolanthanoids.[8] This elongation can be explained in terms of deformations of the complex because of steric repulsion between the cyclopentadienyl and anthracene ligands. It should be noted that the structural data obtained for **3** are in good agreement with those obtained previously for $[Mg(thf)_3(C_{14}H_{10})]$[9] and $[Mg(thf)_3(C_{14}H_8Me_2)]$,[10] possessing a similar structure.

It is interesting that reaction of **1** with the anthracene radical-anion in $(C_{14}H_{10}{}^{\cdot-})Na^+$ **4** leads to a lutetium complex with an anthracene dianion ligand [reaction (2)] and not with this radical-anion as would be expected in the case of a trivial exchange reaction between **1** and **4**

$$\eta^5\text{-}(C_5H_5)LuCl_2 + 2(C_{14}H_{10}{}^{\cdot-})Na^+ \rightarrow \eta^5\text{-}(C_5H_5)Lu(C_{14}H_{10}{}^{2-}) + C_{14}H_{10} + 2NaCl \qquad (2)$$

$$2C_{14}H_{10}{}^{\cdot-} \rightleftarrows C_{14}H_{10}{}^{2-} + C_{14}H_{10} \qquad (3)$$

The disproportionation equilibrium (3) is known[1] to exist in solutions of anthracene adducts. This is shifted to the right when the interaction between the radical-anion and the metal cation increases.

The formation of dianion complex **3** *in reaction* (2) *testifies* to the strong interaction of the Lu^{3+} ion with anthracene dianion and is in agreement with a strong shortwave shift of the absorption band in the visible spectrum of **3** (λ_{max} = 440 nm) as compared with **2** (λ_{max} = 600 nm).[1]

The earlier results[3] and the present work demonstrate that the exchange reaction between lanthanoid halides and sodium anthracene adducts may be used as a convenient method for the preparation of a new type of organolanthanoid complex with anthracene dianion ligands.

In conclusion, it should be mentioned that the anthracene dianion, owing to its high negative charge and large size, satisfies well both of the two basic principles of organolanthanoid stability: optimization of electrostatic interactions and saturation of the coordination sphere of the metal.

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‡ *Crystal data* for **3**: $LuC_{27}H_{31}O_2$, $M = 562.3$, monoclinic, space group $P2_1/c$, at 143 K, $a = 17.220(5)$ Å, $b = 15.553(4)$ Å, $c = 18.478(5)$ Å, $\beta = 112.68(2)°$, $V = 4507(3)$ Å^3, $Z = 8$ (two independent formula units), $\rho_c = 1.658(1)$ Mg m^{-3}, μ(Mo-Kα) = 44.0 cm^{-1}, $F(000) = 2240.2576$ Unique reflections with $F_0 > 4\sigma(F_0)$ were collected of the total of 2681 independent reflections with a Siemens P3/PC diffractometer at 150 K [λ(Mo-Kα) = 0.71069 Å, graphite monochromator, $2\theta < 40°$]. The structure was solved by the heavy-atom method and refined by the least-squares method in anisotropic approximation to $R = 0.024$, $R_w = 0.024$, GOF = 4.47, using a weighting scheme $\omega^{-1} = \sigma^2(F)$. DDIFABS[5] was used to correct the intensities for absorption. The H atoms at carbon atoms of the central ring of the anthracene dianion C(9,10,36,37) were located as the highest peaks of the difference electron density map. The other H atoms were placed in calculated positions and included in the calculations with fixed positional and isotopic thermal parameters $U_{iso} = 0.08$ Å^2. All calculations were carried out using the SHELX PLUS programs. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1992, Issue No. 1.

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