

THE FORMATION AND X-RAY CRYSTAL STRUCTURE OF $(\eta^5\text{-C}_5\text{H}_5)_2\text{LuCl} \cdot \text{OC}_4\text{H}_8$

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Summary

LuCl_3 reacts with two equivalents of sodium cyclopentadienide in THF followed by crystallization from this solvent at 5°C to afford $(\text{C}_5\text{H}_5)_2\text{LuCl} \cdot \text{OC}_4\text{H}_8$. The product has been characterized by its proton NMR and mass spectra, elemental analysis and by single crystal X-ray diffraction studies. The complex $(\text{C}_5\text{H}_5)_2\text{LuCl} \cdot \text{OC}_4\text{H}_8$ crystallizes in the monoclinic space group $P2_1/n$ with the unit cell parameters, a 8.116(2), b 12.670(2), c 14.376(1) Å, β 105.61(1)°, V 1423.7 Å³, $Z = 4$, D_c 1.925 g cm⁻³. The structure was solved by heavy-atom Patterson techniques and the least-squares refinement has led to a final R value of 0.097 based on 2253 independent observed reflections. The THF molecule is coordinated to the lutetium atom at a Lu–O bond length of 2.27(1) Å. The Lu–C(η^5) bond distances average 2.56 Å. The compound $(\eta^5\text{-C}_5\text{H}_5)_2\text{LuCl} \cdot \text{OC}_4\text{H}_8$ is a neutral monomer.

Introduction

The di(η^5 -cyclopentadienyl)lutetium chloride was first prepared by Dubeck et al. in 1963 [1]. However, to our knowledge its crystal structure has not been reported. The crystal structures of its four analogues which exist as chlorine-bridged dimers, namely $[(\text{C}_5\text{H}_5)_2\text{Sc}(\mu\text{-Cl})_2]$ [2], $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Yb}(\mu\text{-Cl})_2]$ [3], $[\text{Cp}_2^{\text{L}}\text{Yb}(\mu\text{-Cl})_2]$ and $[\text{Cp}_2^{\text{L}}\text{Pr}(\mu\text{-Cl})_2]$ [4] ($\text{Cp}^{\text{L}} = 1,3((\text{CH}_3)_3\text{Si})_2\text{C}_5\text{H}_3$)), has been reported in the literature. Here we wish to report * the formation and X-ray crystal structure determination of monomeric $(\eta^5\text{-C}_5\text{H}_5)_2\text{LuCl} \cdot \text{OC}_4\text{H}_8$.

Results and discussion

The $(\eta^5\text{-C}_5\text{H}_5)_2\text{LuCl}$ complex was prepared according to the method of Dubeck et al. [1]. Although the synthesis was carried out in THF, the solvent-free product

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was obtained by vacuum sublimation. Molecular weight measurements in THF solution indicated that $(C_5H_5)_2LuCl$ was a monomer. However, in benzene solution it was a dimer. The mass spectra of $(C_5H_5)_2LuCl$ have been measured and the results are listed in Table 1. This complex exhibits a parent molecular ion at 680, showing that it is a dimer in solid state. Major peaks for $(C_5H_5)_2LuCl^+$, $C_5H_5Lu^+$, $C_5H_6^+$ and $C_5H_5^+$ fragments are also observed. The proton NMR spectra of $(C_5H_5)_2LuCl$ in THF solution exhibit singlet resonances at 5.58 ppm assignable to equivalent cyclopentadienyl ring hydrogens. The crystals suitable for X-ray diffraction studies could be obtained by recrystallization of $(C_5H_5)_2LuCl$ from THF solution at 5°C. The product was proved to be a THF adduct, $(\eta^5-C_5H_5)_2LuCl \cdot OC_4H_8$. The crystal structure of the title compound shows that the molecular unit is a monomer which is coordinated with THF and does not contain the chlorine bridge. The monomeric structure of dicyclopentadienyl lutetium chloride with coordinated THF is the first example in the series of dicyclopentadienyl lanthanide chlorides.

The molecular structure and atom numbering of $(C_5H_5)_2LuCl \cdot OC_4H_8$ are shown in Fig. 1. The bond lengths and angles of the title compound are presented in Table 2. The Lu–C(η^5) bond distances range from 2.48(5) to 2.60(2) Å and average 2.56 Å. This is shorter than the value previously reported by us for $(C_5H_5)_3Lu \cdot OC_4H_8$, 2.69(4) Å [5]. The Lu–O bond distance, 2.27(1) Å is also significantly shorter than the 2.39 Å in $(C_5H_5)_3Lu \cdot OC_4H_8$, probably due to the decrease of steric crowding in the present structure in which chlorine atom replaces the bulky cyclopentadienyl. A comparison of bond lengths and angles of organolutetium complexes is listed in Table 3. In $(C_5H_5)_2LuCl \cdot OC_4H_8$, the Lu–C(η^5), Lu–O and Lu–centroid distances are also a little shorter than those for the following complexes, $Cp_2LuCH_2Si(CH_3)_3 \cdot OC_4H_8$, $Cp_2LuC_6H_4-4-CH_3 \cdot OC_4H_8$ and $Cp_2LuBu^1 \cdot OC_4H_8$ (Cp = C_5H_5). The Lu–Cl distance of 2.50(1) Å in the title compound is longer than the Lu–C(σ) distances 2.38(2) and 2.35(4) Å for $Cp_2LuCH_2Si(CH_3)_3 \cdot OC_4H_8$ and $Cp_2LuC_6H_4-4-CH_3 \cdot OC_4H_8$ [6], respectively. However, Lu–Cl distance 2.50(1) Å is close to the value of Lu–C(σ) 2.47(2) Å for $Cp_2LuBu^1 \cdot OC_4H_8$ [7], as a result of several factors.

TABLE 1
MASS SPECTRA OF $[(C_5H_5)_2LuCl]_2^a$

<i>m/e</i>	Rel. intensity	Assignment
680	6.00	$[(C_5H_5)_2LuCl]_2$
646	1.21	$[(C_5H_5)_2Lu \begin{array}{c} \diagup Cl \\ \diagdown \end{array} Lu(C_5H_5)_2 + 1]^+$
615	31.29	$(C_5H_5)Lu \begin{array}{c} \diagup Cl \\ \diagdown \end{array} Lu(C_5H_5)_2^+$
340	1.77	$(C_5H_5)_2LuCl^+$
305	100.00	$(C_5H_5)_2Lu^+$
275	12.69	$(C_5H_5)LuCl^+$
240	2.90	$(C_5H_5)Lu^+$
66	60.94	$C_5H_6^+$
65	34.08	$C_5H_5^+$

^a Recorded at *EI*, *T* 50–300°C, *EM* = 1.3 kV.

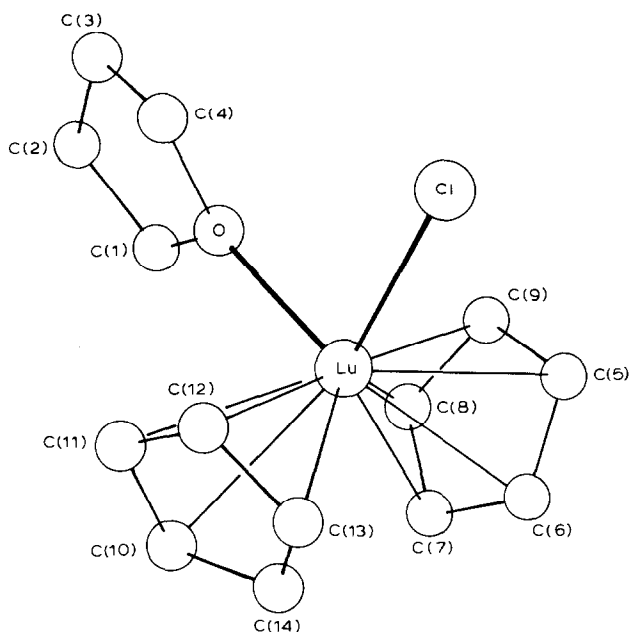


Fig. 1. Molecular structure and atom numbering scheme for $(\eta^5\text{-C}_5\text{H}_5)_2\text{LuCl}\cdot\text{OC}_4\text{H}_8$.

Evans suggested that because of the difference of Ln–Cl bond type, the effective chloride radius appears to be evidently different, for example, the four values for an effective radius of a chloride attached to these metals in a terminal fashion are in

TABLE 2
BOND LENGTHS (Å) AND ANGLES (°)

Lu–Cl	2.50(1)	Lu–O	2.27(1)	Lu–C(5)	2.60(2)
Lu–C(6)	2.57(3)	Lu–C(7)	2.60(3)	Lu–C(8)	2.57(4)
Lu–C(9)	2.58(3)	Lu–C(10)	2.57(4)	Lu–C(11)	2.58(3)
Lu–C(12)	2.55(4)	Lu–C(13)	2.48(5)	Lu–C(14)	2.51(4)
C(1)–O	1.42(3)	C(1)–C(2)	1.51(4)	C(2)–C(3)	1.48(5)
C(3)–C(4)	1.44(6)	C(4)–O	1.48(4)	C(5)–C(6)	1.38(4)
C(6)–C(7)	1.40(4)	C(7)–C(8)	1.35(5)	C(8)–C(9)	1.40(5)
C(9)–C(5)	1.42(4)	C(10)–C(11)	1.33(5)	C(11)–C(12)	1.39(5)
C(12)–C(13)	1.30(6)	C(13)–C(14)	1.17(6)	C(10)–C(14)	1.37(6)
Lu–Cent(1)	2.30	Lu–Cent(2)	2.28		
C(1)–C(2)–C(3)	105(3)	C(2)–C(3)–C(4)	108(3)		
C(3)–C(4)–O	107(3)	C(2)–C(1)–O	109(2)		
C(1)–O–C(4)	108(2)	C(6)–C(5)–C(9)	107(2)		
C(5)–C(6)–C(7)	109(2)	C(6)–C(7)–C(8)	108(3)		
C(7)–C(8)–C(9)	110(3)	C(5)–C(9)–C(8)	107(3)		
C(11)–C(10)–C(14)	105(4)	C(10)–C(11)–C(12)	106(3)		
C(11)–C(12)–C(13)	106(3)	C(12)–C(13)–C(14)	111(4)		
C(10)–C(14)–C(13)	112(4)	Cl–Lu–O	91.6(4)		
Cl–Lu–Cent(1)	108	Cl–Lu–Cent(2)	108		
O–Lu–Cent(1)	106	O–Lu–Cent(2)	107		
Cent(1)–Lu–Cent(2)	129				

TABLE 3

COMPARISON OF BOND LENGTHS (Å) AND ANGLES (°) FOR ORGANOLUTETIUM COMPLEXES

Complex	Lu-O	Lu-C(η) (av.)	Lu-centroid (av.)	Lu-Cl or Lu-C(σ)	Cp(1)- Lu-Cp(2)	Reference
Cp ₃ Lu·OC ₄ H ₈	2.39(2)	2.69(4)	2.42			5
Cp ₂ LuCl·OC ₄ H ₈	2.27(1)	2.56	2.29	2.50(1)	128.9	this work
Cp ₂ LuCH ₂ Si(CH ₃) ₃ ·OC ₄ H ₈	2.29(1)	2.61(3)	2.35	2.38(2)	130.2	6
Cp ₂ LuC ₆ H ₄ -4-CH ₃ ·OC ₄ H ₈	2.27(3)	2.59(4)	2.32	2.35(4)	128.8	6
Cp ₂ LuBu ^t ·OC ₄ H ₈	2.31(2)	2.63(1)	2.36	2.47(2)	125.6	7

the range of 1.62–1.70 Å, 1.63 Å for [Yb[CH(SiMe₃)₂]₃Cl]⁻ [8]; 1.67 Å for (C₅Me₅)₂YbCl(Me₂PCH₂PMe₂) [9]; 1.67 Å for [Cp^t₂NdCl₂]⁻ [10], and 1.70 Å for (C₅Me₅)₂Y(μ-Cl)YCl(C₅Me₅)₂ [11]. However, the effective chloride radius in cyclopentadienyl homometallic bridged dimers is considerably longer being in the range of 1.78–1.80 Å. For example, those in [(CH₃C₅H₄)₂Yb(μ-Cl)]₂ [3], [Cp^t₂Yb(μ-Cl)]₂ [4] and [Cp^t₂Pr(μ-Cl)]₂ [4] are 1.78, 1.79 and 1.80 Å, respectively. The effective chloride radius of (C₅H₅)₂LuCl·OC₄H₈ calculated from its structure data is 1.65 Å, in agreement with Lu-Cl bond in a terminal fashion. Furthermore, the structure of title compound indicates moderate steric crowding and thus the compound is stable based on the cone packing model [12].

The angles of Cl-Lu-O, Cl-Lu-cent(1), Cl-Lu-cent(2), O-Lu-cent(1) and O-Lu-cent(2) are 91.6(4), 108.4, 108.1, 106.4, and 107.2° respectively, while that of cent(1)-Lu-cent(2) is 128.9°. Therefore the oxygen atom of tetrahydrofuran, one chlorine atom and two cyclopentadienyls around Lu give rise to distorted tetrahedral coordination. The coordination number of lutetium atom is eight.

Experimental

All operations were performed in an atmosphere of prepurified argon using Schlenk techniques or in a glovebox. Tetrahydrofuran was refluxed and distilled over either finely divided LiAlH₄ or blue sodium benzophenone under argon immediately prior to use. Anhydrous lutetium chloride was prepared from the hydrate by a literature method [13]. Metal analyses were accomplished by using direct complexometric titration with disodium EDTA [13]. Proton NMR spectra were recorded on an EM 360L (60 MHz) spectrometer and referenced to external Me₄Si. Mass spectra were recorded on a Finnigan 4021 spectrometer.

Preparation of (η⁵-C₅H₅)₂LuCl·OC₄H₈

A solution of cyclopentadienylsodium (0.027 mol) in 15 ml of THF at room temperature was added to a dispersion of 3.84 g (0.014 mol) of anhydrous lutetium trichloride in 25 ml of THF at 0°C. The resulting pale orange suspension was stirred overnight at room temperature. The solvent was then removed under vacuum leaving a yellow powder. This was placed in a Schlenk-type sublimator and sublimed at 200–240°C/10⁻³ Torr. The yield of (η⁵-C₅H₅)₂LuCl was 67%. Anal. Found: Lu, 51.18; Cl, 10.32 C₁₀H₁₀LuCl calcd.: Lu, 51.37; Cl, 10.41%. The greenish-white crystals were slightly soluble in THF at room temperature, but extremely soluble in

warm THF. Colourless transparent prismatic crystals suitable for X-ray crystallographic studies were grown by allowing the warm THF solution to cool slowly to 5°C.

X-ray data collection

The crystals were sealed in thin-wall glass capillaries under dried argon and the size of crystal for data collection was approximately $0.2 \times 0.4 \times 0.5$ mm.

The intensity data were measured on a CAD-4 four-circle diffractometer with graphite monochromatized Cu- K_{α} radiation (λ 1.5418 Å) and 2562 independent reflections in the range of $2\theta \leq 140^{\circ}$ were collected. Of these the 2253 reflections with $|F_0| > 3\sigma(|F_0|)$ were considered observed and used for the structure solution and refinement. The crystals belong to monoclinic with space group $P2_1/n$ and a 8.116(2), b 12.670(2), c 14.376(1) Å, β 105.61(1)°, V 1423.7 Å³, $Z = 4$, D_c 1.925 g cm⁻³, $\mu(\text{Cu-}K_{\alpha})$ 146.9 cm⁻¹. The intensity data corrections were made for LP and absorption factors.

Structure solution and refinement

The structure was solved by the heavy-atom Patterson and Fourier synthesis techniques. After the Lu atom was located, the positions of all non-hydrogen atoms were revealed by subsequent Fourier syntheses. The structure was refined by the block-diagonal least-squares techniques with isotropic thermal parameters and the R index is 0.127. The further refinements with anisotropic thermal parameters were carried out. All hydrogen atoms were first located by using a C-H bond length of 1.08 Å and ideal bond angles and then included in another two circles of refinement. The final R ($= \sum w ||F_0| - |F_0|| / \sum w |F_0|$, where the weights are $w = 1$ for $|F_0| \leq 50$, $w = [50/|F_0|]^2$ for $|F_0| > 50$) is 0.097 for the 2253 observed reflections. The calculations were performed on a VAX-11/780 computer using HBLS

TABLE 4

FINAL FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^2$)

Atom	x	y	z	B_{eq}
Lu	10017(1)	925(1)	6986(0)	124(2)
Cl	8870(9)	-912(4)	6701(5)	403(22)
O	9186(15)	1060(9)	8366(7)	180(39)
C(1)	9679(28)	1823(17)	9108(11)	313(76)
C(2)	8577(38)	1684(26)	9798(18)	544(128)
C(3)	7498(38)	753(33)	9432(19)	654(157)
C(4)	7625(37)	535(30)	8473(18)	599(136)
C(5)	12901(26)	-46(19)	7149(15)	340(81)
C(6)	12953(26)	865(19)	6628(18)	359(89)
C(7)	13046(29)	1738(21)	7237(23)	498(112)
C(8)	12974(29)	1377(30)	8110(20)	617(135)
C(9)	12888(28)	270(26)	8091(16)	462(106)
C(10)	8870(41)	2733(18)	6296(28)	788(138)
C(11)	7504(34)	2231(25)	6408(17)	548(119)
C(12)	7225(39)	1405(23)	5750(27)	757(139)
C(13)	8449(56)	1457(34)	5321(16)	880(193)
C(14)	9340(40)	2185(33)	5591(28)	850(191)

and DAPH programs (T. Ashida, 1967) [14]. Neutral atomic scattering factors for C, H, O, Lu and anomalous dispersion for Lu were taken from International Tables for X-ray crystallography (1974). The final atomic coordinates and thermal parameters are given in Table 4.

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