Inorganica Chimica Acta, 110 (1985) L7–L10

Crystal and Molecular Structure of (η^5-C_5H_5)$_3$Lu·OC_4H_8

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Received March 5, 1985

The structures of the organolanthanide and yttrium complexes, Cp_3Ln·THF (Cp = η^5-C_5H_5, Ln = La, Pr, Nd, Gd and Y) have been reported [1–4]. Schumann *et al.* prepared the dicyclopentadienyllutetium hydride by reaction of Cp_2LuCl with NaH in tetrahydrofuran [5]. In studying this reaction, we have obtained a product which upon recrystallization in THF at –6 °C afforded colourless transparent prismatic crystals suitable for X-ray structure analysis. Chemical analyses could not be performed due to the minute amount of material available; however, it was identified as Cp_3Lu·THF by means of a single-crystal structure determination.

Experimental

Crystals were sealed in glass capillaries under dried argon; that used for data collection had approximate dimensions of 0.30 × 0.40 × 0.45 mm. The intensity data were collected on a RASA-IIS four-circle diffractometer with graphite-monochromatized Mo Kα_1 radiation (λ = 0.70926 Å) using an $\omega/2\theta$ scan technique, and 2525 unique reflections in the range of $3° < 2\theta < 48°$ were measured. Of these, 1898 reflections with $|F_o| > 3\sigma(|F_o|)$ were considered observed and used for the structure analysis. The crystals belong to monoclinic with space group $P2_1/n$ and a = 8.107(1), b = 24.545(4), c = 8.187(2) Å, β = 101.10(1)°, V = 1598.6(6) Å^3, Z = 4, D_c = 1.84 g cm^{-3}, μ(Mo Kα) = 64.94 cm^{-1}. The unit-cell parameters were determined by a least-squares refinement of the setting angles of 12 reflections with $2\theta > 20°$. Three standard reflections were monitored every 100 reflections to check on crystal stability and no apparent decay in intensity was observed during data collection. The intensity data were reduced with the application of Lorentz and polarization factors and no corrections for absorption were made.

Solution and Refinement

The structure was solved by the heavy-atom Patterson and Fourier synthesis techniques. After the Lu atom was located, all non-hydrogen atoms were determined by Fourier syntheses. The structure was refined using the block-diagonal least-squares method with isotropic thermal parameters and the conventional R index is 0.114. Five more cycles of refinement with anisotropic thermal parameters were carried out and the R ($=\Sigma w||F_o| - |F_c||/\Sigma w|F_o|$, where the weights are w = 1 for $|F_o| \leqslant 55$, $w = [55/|F_o|]^2$ for $|F_o| > 55$) is 0.077. The positions of the H atoms of the Cp rings and THF were calculated using a C–H bond length of 1.08 Å and ideal bond angles. The H atoms were included in the structure-factor calculation and the final R is 0.076 for 1898 observed reflections. 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 calculations were performed on a Burroughs B6935 computer using HBLS and DAPH programs (T. Ashida, 1967) [6]. The final fractional atomic coordinates are listed in Table I and the bond lengths and bond angles are given in Table II.

Results and Discussion

The molecular structure viewed down the b axis, is shown in Fig. 1. The compound, (η^5-C_5H_5)$_3$Lu·THF is isostructural with the derivatives of La, Pr, Nd, Gd and Y. The crystallographic data of the isostructural complexes are listed in Table III. It can be seen that the unit-cell parameters and volumes decrease with increasing atomic number of the lanthanide. This is in agreement with the regular pattern of contraction of the ionic radius of the element. The data for Y were placed between Gd^{3+} and Lu^{3+} for its ionic radius is only 0.03 Å less than Gd^{3+} and 0.05 Å larger than Lu^{3+} [7]. In (η^5-C_5H_5)$_3$Lu·THF, the Lu–C(η^5) bond lengths range from 2.63(4) to 2.74(3) Å and the average is 2.69(4) Å, Lu–O 2.39(2) Å, Lu-centroid average 2.42 Å, which are longer than those reported for the following complexes,

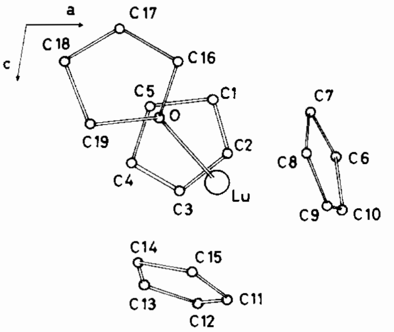

Fig. 1. A view of the molecular structure looking down the b axis.

0020-1693/85/$3.30

TABLE I. Final Fractional Atomic Coordinates $(\times 10^4)$ and Thermal Parameters $(\times 10^4)$.[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Lu	5734(1)	3563(0)	4433(1)	84(1)	15.9(1)	88(1)	−1.3(8)	33(2)	−2.8(8)
C(1)	5191(48)	2771(11)	2013(33)	479(97)	16(5)	143(46)	31(35)	−75(99)	−32(25)
C(2)	5871(39)	2528(13)	3557(36)	263(61)	26(6)	184(51)	22(32)	90(88)	−1(29)
C(3)	4733(28)	2543(11)	4597(36)	108(37)	21(5)	249(57)	−12(23)	−24(70)	9(27)
C(4)	3287(43)	2821(13)	3807(55)	241(67)	18(6)	534(99)	19(33)	−145(99)	−45(43)
C(5)	3641(48)	2970(13)	2221(46)	336(80)	26(7)	314(78)	29(39)	−397(99)	−35(38)
C(6)	8665(34)	3367(12)	3643(42)	163(47)	25(6)	344(75)	22(27)	299(98)	−47(34)
C(7)	7839(29)	3842(17)	2445(36)	101(40)	58(11)	205(53)	−4(34)	208(78)	49(40)
C(8)	7929(31)	4298(13)	3491(40)	142(41)	24(6)	345(72)	−6(27)	124(87)	67(36)
C(9)	8653(35)	4194(12)	4964(41)	193(50)	23(6)	315(69)	−10(28)	214(97)	−44(33)
C(10)	9052(32)	3661(17)	5088(45)	84(39)	54(12)	286(68)	−47(33)	−11(82)	21(45)
C(11)	6488(35)	3942(17)	7558(27)	190(51)	69(12)	49(32)	53(41)	62(64)	−74(32)
C(12)	5681(67)	3431(17)	7586(42)	690(99)	44(11)	190(61)	197(68)	519(99)	102(42)
C(13)	4174(53)	3509(12)	7074(44)	534(99)	23(6)	327(75)	−70(41)	777(99)	−50(34)
C(14)	3917(38)	4011(14)	6512(36)	227(57)	38(8)	182(51)	38(35)	157(87)	−62(33)
C(15)	5352(39)	4329(14)	6790(31)	306(64)	31(7)	136(41)	23(36)	260(86)	−25(29)
C(16)	4150(29)	4302(16)	958(34)	123(39)	41(8)	204(51)	48(32)	53(72)	62(36)
C(17)	2455(45)	4520(19)	93(40)	296(78)	63(15)	194(58)	171(55)	104(99)	54(44)
C(18)	1147(36)	4344(20)	908(38)	169(51)	73(14)	213(60)	49(46)	62(88)	181(52)
C(19)	2137(27)	4290(12)	2744(28)	128(36)	27(6)	159(40)	35(25)	104(63)	43(26)
O	3927(16)	4167(6)	2629(17)	101(22)	21(3)	124(23)	16(13)	106(36)	24(13)

[a] The thermal parameters are defined by $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

TABLE II. Bond Lengths (Å) and Angles (°).

Lu–C(1)	2.75(4)	Lu–C(2)	2.65(3)	Lu–C(3)	2.64(3)
Lu–C(4)	2.67(5)	Lu–C(5)	2.66(4)	Lu–C(6)	2.63(4)
Lu–C(7)	2.67(4)	Lu–C(8)	2.75(3)	Lu–C(9)	2.79(3)
Lu–C(10)	2.65(4)	Lu–C(11)	2.68(4)	Lu–C(12)	2.61(5)
Lu–C(13)	2.71(4)	Lu–C(14)	2.69(4)	Lu–C(15)	2.75(3)
Lu–O	2.39(2)	C(1)–C(2)	1.41(5)	C(2)–C(3)	1.37(4)
C(3)–C(4)	1.40(5)	C(4)–C(5)	1.43(6)	C(5)–C(1)	1.39(6)
C(6)–C(7)	1.59(5)	C(7)–C(8)	1.40(5)	C(8)–C(9)	1.26(5)
C(9)–C(10)	1.35(5)	C(10)–C(6)	1.37(5)	C(11)–C(12)	1.42(7)
C(12)–C(13)	1.23(7)	C(13)–C(14)	1.32(6)	C(14)–C(15)	1.38(5)
C(15)–C(11)	1.39(5)	C(16)–C(17)	1.52(6)	C(17)–C(18)	1.42(7)
C(18)–C(19)	1.57(6)	C(16)–O	1.45(4)	C(19)–O	1.50(3)
Lu–Cent1[a]	2.40	Lu–Cent2	2.42	Lu–Cent3	2.43

C(1)–C(2)–C(3)	111(3)	C(2)–C(3)–C(4)	109(3)
C(3)–C(4)–C(5)	104(4)	C(4)–C(5)–C(1)	111(4)
C(5)–C(1)–C(2)	104(3)	C(6)–C(7)–C(8)	104(3)
C(7)–C(8)–C(9)	113(3)	C(8)–C(9)–C(10)	109(3)
C(9)–C(10)–C(6)	116(4)	C(10)–C(6)–C(7)	98(3)
C(11)–C(12)–C(13)	107(5)	C(12)–C(13)–C(14)	111(4)
C(13)–C(14)–C(15)	114(3)	C(14)–C(15)–C(11)	99(3)
C(15)–C(11)–C(12)	110(4)	C(16)–C(17)–C(18)	111(4)
C(17)–C(18)–C(19)	101(4)	C(18)–C(19)–O	106(3)
C(19)–O–C(16)	108(2)	C(17)–C(16)–O	105(3)
Cent1–Lu–Cent2	120.3	Cent1–Lu–O	97.4
Cent1–Lu–Cent3	118.3	Cent2–Lu–O	99.5
Cent2–Lu–Cent3	114.3	Cent3–Lu–O	100.0

[a] Cent 1 is defined as the centroid of the Cp ring comprised of C(1)–C(5); Cent 2 of C(6)–C(10) and Cent 3 of C(11)–C(15).

TABLE III. Crystallographic Data in the Isostructural Series $Cp_3Ln{\cdot}THF$ (Ln = La, Pr, Nd, Gd, Y, Lu).

Compound	La [1]	Pr [4]^b	Nd [4]^b	Gd [3]	Y [1]	Lu^a
Mol. wt.	405.40	408.3	411.6	424.6	356.30	442.37
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	8.371(4)	8.284(3)	8.254(3)	8.220(4)	8.170(3)	8.107(1)
b (Å)	24.636(5)	24.510(9)	24.467(9)	24.650(9)	24.594(5)	24.545(4)
c (Å)	8.454(3)	8.406(3)	8.364(3)	8.317(4)	8.260(3)	8.187(2)
β (deg)	101.84(3)	101.60(3)	101.42(3)	101.39(3)	101.32(3)	101.10(1)
Cell vol. (Å^3)	1706.4	1671.8	1655.6	1652.0	1627.4	1598.6
Z	4	4	4	4	4	4
Dc (g cm^{-3})	1.58	1.62	1.65	1.71	1.45	1.84

^{a}Present work. ^{b}The data were collected at −60 °C.

TABLE IV. Significant Structure Parameters in Isostructural Series $Cp_3Ln{\cdot}THF$ (Ln = La, Pr, Nd, Gd, Y, Lu).

Compound	Ln^{3+} radii [11] (Å)	Ln^{3+} crystal radii [7] (Å)	Ln–O (Å)	Ln–Cent1 (Å)	Ln–Cent2 (Å)	Ln–Cent3 (Å)	Ln–C (average) (Å)
$Cp_3La{\cdot}THF$ [1]	1.061	1.36	2.57(1)	2.575	2.575	2.576	2.82(4)
$Cp_3Pr{\cdot}THF$ [4]	1.013	1.32	2.56(1)	2.54	2.55	2.51	2.80(2)
$Cp_3Nd{\cdot}THF$ [4]	0.995	1.30	2.54(1)	2.51	2.51	2.51	2.78(2)
$Cp_3Gd{\cdot}THF$ [3]	0.938	1.25	2.494(7)	2.47	2.49	2.49	2.74(3)
$Cp_3Y{\cdot}THF$ [1]	0.88	1.22	2.451(4)	2.438	2.453	2.454	2.71(3)
$Cp_3Lu{\cdot}THF^a$	0.848	1.17	2.39(2)	2.40	2.42	2.43	2.69(4)

^{a}Present work.

$Cp_2Lu{-}CH_2Si(CH_3)_3{\cdot}THF$ with $Lu{-}C(\eta^5) = 2.61(3)$, Lu–O = 2.29(1), Lu–Centroid = 2.35 Å [8]; $Cp_2Lu{-}C_6H_4\text{-}4\text{-}CH_3{\cdot}THF$ with $Lu{-}C(\eta^5) = 2.59(4)$, Lu–O = 2.27(3), Lu-Centroid = 2.32 Å [8]; $Cp_2Lu{-}Bu^t{\cdot}THF$ with $Lu{-}C(\eta^5) = 2.63(1)$, Lu–O = 2.31(2) Å [9]. This deviation is due to steric crowding of the three cyclopentadienyl groups and the THF in the present complex. However, the bond distances in the title compound are reasonable in comparison to the corresponding values in the isostructural complexes of La, Pr, Nd, Gd, Y and that can be clearly illustrated in Table IV. The variation in structural parameters is in accordance with the known regularity of the Ln elements.

The angles of O–Lu–Centroid are 97.4°, 99.5°, 100.0° and Centroid–Lu–Centroid 120.3°, 118.3°, 114.3°, respectively. Therefore the oxygen atom of tetrahydrofuran and the three cyclopentadienyls around Lu give rise to distorted tetrahedral coordination, the dihedral angles between the planes of cyclopentadienyl being 116(2)°, 116(2)°, and 118(2)°, respectively.

The structure determination confirmed that the reaction of Cp_2LuCl and NaH in tetrahydrofuran has produced at least in part, a crystalline product, $Cp_3Lu{\cdot}THF$, but the mechanism is not clear yet. Schumann pointed out that the dicyclopentadienyl lutetium chloride reacted with sodium hydride in tetrahydrofuran in a way not yet clear, to yield tricyclopentadienyl lutetium μ-hydride complex, $[Na(THF)_6][(C_5H_5)_3LuHLu(C_5H_5)_3]{\cdot}(THF)_2$ [10]. We suggest that the solvated tricyclopentadienyl lutetium was afforded either by the decomposition of μ-hydride complex during the course of the reaction, or through partial dismutation of $[Cp_2Lu(\mu\text{-}H)_2]$ according to:

$$[Cp_2Lu(\mu\text{-}H)]_2 \overset{THF}{\rightleftharpoons} Cp_3Lu{\cdot}THF + CpLuH_2(THF)_3$$

Acknowledgements

The authors thank Prof. Ma Zhesheng and Mr. Han Shaoxu (Beijing Graduate School of Wuhan Geological College, Beijing) for intensity data collection.

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