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Syntheses and crystal structures of bis(tetrahydrofurfurylindenyl) lanthanocene chlorides $(C_4H_7OCH_2C_9H_6)_2LnCl$ (Ln = Nd, Sm, Dy, Ho, Er, Yb)

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Abstract

Reaction of anhydrous lanthanide trichlorides with tetrahydrofurfuryl indenyl lithium in THF afforded bis(tetrahydrofurfurylindenyl) lanthanocene chlorides complexes $(C_4H_7OCH_2C_9H_6)_2LnCl$, Ln = Nd (**1**), Sm (**2**), Dy (**3**), Ho (**4**), Er (**5**), Yb (**6**). The X-ray crystallographic structures of all the six complexes were determined and these indicate that they are unsolvated nine-coordinate monomeric complexes with a *trans* arrangement of both the sidearm and indenyl rings in the solid state. They belong to the same crystal system (orthorhombic) and space group ($P2_12_12_1$) with the same structure. Especially, they are more stable to air and moisture than the corresponding unsubstituted indenyl lanthanide complexes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tetrahydrofurfurylindenyl; Synthesis; Lanthanide chlorides; Crystal structures

1. Introduction

It is well known that lanthanide alky and hydride compounds are the efficient catalysts for many organic reactions [1], especially polymerization of polar monomers [2] and non-polar monomers [3]. As the precursors of the lanthanide alky and hydride compounds, indenyl complexes, $(C_9H_7)_2LnCl$, attract increasing interests in organolanthanide chemistry. Owing to the lanthanide contraction and coordination unsaturation, $(C_9H_7)_2LnCl$ complexes (especially, the lighter lanthanide chlorides) are not easily synthesized, even with bulky substituent on the indenyl ring [4]. Recently, considerable efforts have been devoted to exploring the organometallic chemistry of metallocene with donor-functionalized side chains [5], because the donor-functionalized side chains can increase the stability of highly reactive organolanthanide complexes by forming the intramolecular chelating coordination with the central metal, and for the lighter lanthanides complexes, the enhanced stability facilitates the synthesis of the desired complexes. Most of the ligands used are those with ether- or amino-substituted cyclopentadienyl groups. Compared with transition-metal complexes, the indenyl ligand has not been widely used in the organometallic chemistry of lanthanocenes. Few ether-substituted indenyl ligands of lanthanocenes were reported, such as $(CH_3OCH_2CH_2C_9H_6)_2LnCl$ [6] and $[O(CH_2CH_2C_9H_6)_2]LnCl\cdot THF$ [7]. All the complexes are still sensitive to air and moisture, whether in solid or solution phase. Here, we report the synthesis of new tetrahydrofurfuryl substituted indenyl lanthanide chlorides complexes $(C_4H_7CCH_2C_9H_6)_2LnCl$ (Ln = Nd (**1**), Sm (**2**), Dy (**3**), Ho (**4**), Er (**5**), and Yb (**6**) and the X-ray crystal

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structure of all the six complexes, these crystals can be exposed to air for several hours without decomposition.

2. Results and discussion

2.1. Synthesis

The indene derivative $C_4H_7OCH_2C_9H_7$ was prepared directly from the reaction of tetrahydrofurfuryl chloride with indenyl potassium at 0 °C in 63% yield. After deprotonation of the indene derivative with *n*-butyllithium in hexane, followed by centrifugation and washing with hexane, the white precipitation was dissolved in THF to give a clear orange–yellow solution. Reaction of the solution with a stoichiometric amount of anhydrous lanthanide chlorides (Ln = Nd, Sm, Dy, Ho, Er and Yb) in THF, followed by centrifugation and removal of the solvent and extraction with mixed solvents (toluene–THF), crystals of the corresponding complexes were obtained in moderate yields (Scheme 1) after keeping at −10 °C for several days. These complexes are readily dissolved in THF, only soluble in toluene on heating and insoluble in hexane. All complexes in solution are air and moisture sensitive, but their crystals can be kept for long time in air.

2.2. Molecular structure

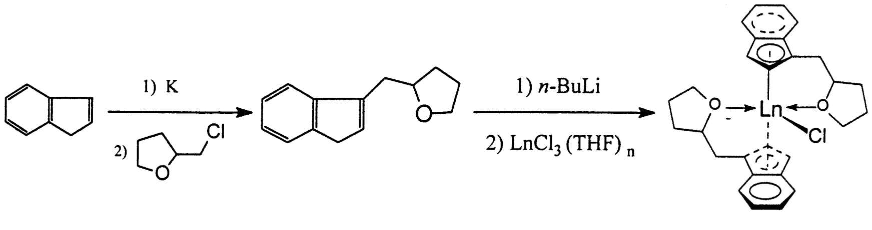
The IR spectra of all the six complexes showed similar pattern and displayed the characteristic absorption peaks of aromatic group at about 3030, 1600, 750 cm^{-1}, η^5-indenyl moieties at about 3060, 1430, 1290, 1030, 780 cm^{-1}, and C–O–C band at 1060, 870, 840 cm^{-1}. The EIMS data of these complexes displayed characteristic fragments, such as $[M]^+$, $[M-Cl]^+$, $[M-L]^+$ $[C_4H_7O]^+$, etc.

All complexes belong to the same crystal system (orthorhombic) and space group ($P2_12_12_1$) with similar crystal data. So, they are isostructural, and the representative ORTEP drawing of **2** is shown Fig. 1. Although the compounds crystallize from the mixed solutions (include THF), they remain unsolvated nine-coordinate monomeric complexes in solid state. The central metal atom is coordinated by two indenyl, two oxygens of tetrahydrofurfuryl and one chlorine to form a distorted trigonal bipyramid. Two oxygen atoms lie at both apices, and the chlorine, the central metal atom and the two centroids of cyclopentadienyl rings of indene form the equatorial plane.

The distances between the metal ion and η^5-indenyl groups of these complexes are unexceptional. Compared with the bond lengths within this series of complexes (include Y and Gd [8]), the bond distances Ln–Centroid, Ln–Cl and Ln–O (Table 2) follow a trend, going from Nd (**1**) to Yb (**6**): the smaller the ionic radii [9], the shorter the bond length. This trend is also consistent with the lanthanide contraction, and 'gadolinium break phenomenon' [10] is not found.

The angles of Cent(1)–Ln–Cent(2) (from 128.3 to 129.3°), Cent(1)–Ln–Cl (from 118.2 to 115.1°) and Cent(2)–Ln–Cl (from 113.5 to 115.6°), and the angles O(1)–Ln–O(2)(from 161.3 to 159.66°) show large deviation from the ideal trigonal bipyramid geometry. The angles of C(1)–C(10)–C(11) (from 116.3 to 112.9°) and C(15)–C(24)–C(25) (from 112.1 to 112.4°) are larger than the angle of normal tetrahedron, which illustrate the existence of intramolecular tension to some degree. The existence of two positions of C(11) in complex **5** also prove the above notation. As the radii of Yb^{3+} is the smallest of this series, and the angles of C(1)–C(10)–C(11) and C(15)–C(24)–C(25) are smaller than other complexes, indicating that the intramolecualr tension of complex **6** is the highest. With decrease of the metal radii, the differences between O(1)–Ln–Cl and O(2)–Ln–Cl, Cent(1)–Ln–Cl and Cent(2)–Ln–Cl, and C(1)–C(10)–C(11) and C(15)–C(24)–C(25) decrease.

The slip parameter Δ_{M-C} [11], which quantify the η^5-η^3 slippage within indenyl metal complexes, ranging from 0.0895(0.0588) Å for Nd (**1**) to 0.1648(0.0828) Å for Yb (**6**), is not beyond the range of metal-ionic η^5-bonding the indenyl ligands. Although it is not a rectilinear trend, the slip distortion gradually increases with the decrease of the radii size of the metals. Compared with some other representative lanthanide complexes of indenyl ligand bearing pendant O-donors, $(CH_3OCH_2CH_2C_9H_6)_2LnCl$ (Ln = La 0.05(0.05), Nd



Ln = Nd(**1**), Sm(**2**), Dy(**3**), Ho(**4**), Er(**5**), Yb(**6**)

Scheme 1.

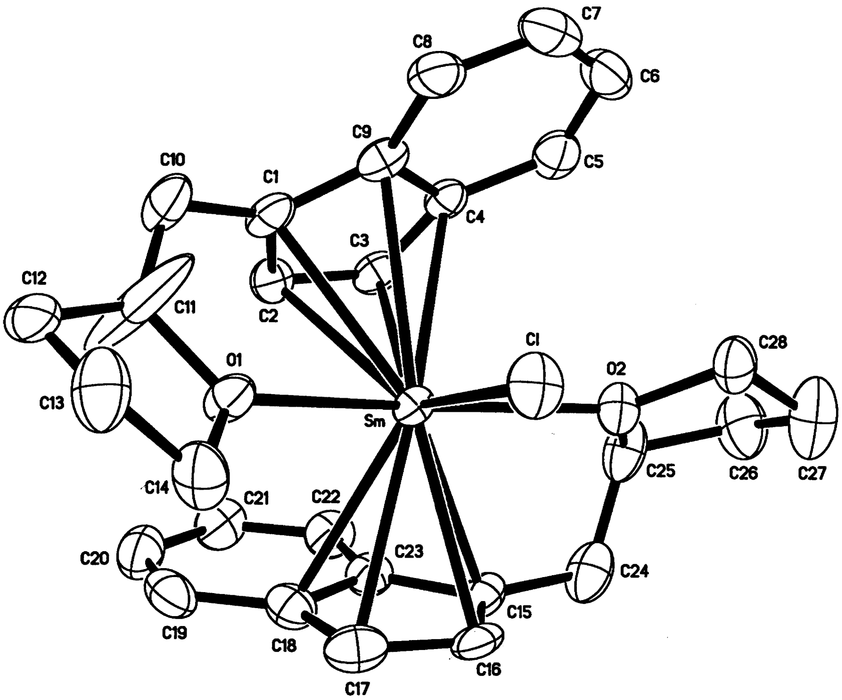


Fig. 1. ORTEP diagram of the molecular structure $(C_6H_7OCH_2C_9H_6)_2SmCl$.

0.093 (0.084), Gd 0.116 (0.110), Y 0.130 (0.150) Å) [6] and $[O(CH_2CH_2C_9H_6)_2]$ LnCl·THF (Ln = Nd 0.103 (0.043), Gd 0.126 (0.038), Ho 0.147 (0.050) Å [7], it is concluded that the space coordination environment of tetrahydrofurfurylindenyl is less crowded than the above two ligands. The dihedral angle of indene planes (from 51.5 to 52.4°) is smaller than the corresponding complex of $(CH_3OCH_2CH_2C_9H_6)_2LnCl$ (Ln = Nd, 53.78, Gd 53.68, Y 51.80°) [6], which also support the above conclusion.

3. Conclusion

Using the tetrahydrofurfurylindenyl ligand, six stable lanthanocene chlorides complexes have been synthesized and their X-ray structures were characterized. The investigation results indicate that the side chain oxygen atom displace THF to coordinate with the central metal to form bisindenyl-type complexes. These stable lanthanocene chlorides facilitate the synthesis of a lot of derivatives, such as lanthanide alky and hydride complexes, etc.

4. Experimental

4.1. General procedures

All manipulations involving orgnaometallics were carried out under an inert atmosphere of argon using standard Schlenk techniques. After drying over 4A molecular sieves, tetrahydrofuran, toluene and hexane were distilled under argon from sodium–potassium alloy with benzophenone ketyl prior to use. Tetrahydrofurfuryl chloride [12] and anhydrous lanthanide chlorides [13] were prepared according to published procedures; the reactants *n*-butyllithium and indene were purchased from Aldrich, the latter being distilled before use. The analysis of rare earth metals and chlorine were accomplished using direct complexmetric titration with disodium EDTA and the Volhard method, respectively. Carbon and hydrogen analysis were carried out by the combustion method. IR spectra were recorded on a Bio-Rad FTS135 spectrometer in the form of KBr pellets. Mass spectra were recorded on a LGQ spectrometer. ^{1}H-NMR was recorded on a Varian Unity-400(400 MHz) spectrometer,

4.2. Preparation of tetrahydrofurfurylindene and tetrdhydrofurfurylindenyl lithium

A solution of indene (23.2 g, 200 mmol in 60 ml THF) was added dropwise to a stirred suspension of potassium metal in 250 ml THF (8.5 g, excess) at 0 °C, and the mixture was stirred for another 6 h at room temperature (r.t.), until no gas was given off. After centrifugation, a clear yellow solution was obtained, then cooled to 0 °C and tetrahydrofurfuryl chloride (24.1 g, 200 mmol) was added slowly. The resultant red–brown mixture was allowed to warm to r.t. and stirred for 4 h, then refluxed for 8 h. After cooling to r.t., the reaction was quenched with water. The organic phase was separated and aqueous part was extracted with Et_2O (2 × 100 ml). The combined organic solutions were dried overnight with anhydrous $MgSO_4$. Removal of the solvent, followed by distillation under reduced pressure gave a pale yellow liquid (yield: 25.2 g, 63%), boiling point (b.p.) 76–80 °C, 0.1 mm Hg. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.46–7.18 (m, 4H, aromatic), 6.31 (t, 1H, $J = 1.2$ Hz, CH, indene), 4.26 (m, 1H, CH, C_4H_7O), 3.85 (m, 2H, CH_2, C_4H_7O), 3.35 (d, 2H, $J = 1.2$ Hz, CH_2, indene), 2.79 (d AB, 2H, CH_2), 1.88(t 2H, $J = 1.2$ Hz, CH_2, C_4H_7O), 1.60(m, 2H, CH_2, C_4H_7O). EI mass spectrum: *m/z* 200 (48%, $[M^+]$), 71 (100%, $[C_4H_7O]^+$).

To a solution of *n*-butyllithium (1.6 M in hexane, 30 ml) in 30 hexane was added dropwise $C_4H_7OCH_2C_9H_7$ (9.6 g, 0.048 mmol in 20 ml hexane) with rigorous stirring at 0 °C. The resulting mixture was stirred for 1 h, then warmed to r.t. and stirred overnight. After centrifugation, the white precipitation was washed with hexane (2 × 20 ml), the 90 ml THF was added to obtain a clear orange yellow solution in 75% yield.

4.3. Synthesis of bis(tetrahydrofurfurylindenyl) neodymium chloride (1)

A THF solution(15 ml) of tetrahydrofurfurylindenyl lithium (0.006 mmol) was added slowly to a suspension of $NdCl_3$ (0.746 g, 0.003 mmol in 20 ml THF) at low temperature (−60 to −78 °C). The reaction mixture was allowed to warm to r.t. and stirred for 24 h. After centrifugation the solvent was evaporated in vacuo. The residue was extracted with 30 ml toluene–THF (4:1) and kept at −10 °C. Green crystals were obtained in 68% yield. Anal. Calc. for $C_{28}H_{30}O_2ClNd$: Nd, 24.97; Cl, 6.14; C, 58.16; H, 5.19. Found: Nd, 25.12; Cl, 6.25; C, 58.98; H, 5.26%. EIMS *m/z* (fragment, relative intensity %): 575 ($[M]^+$, 29), 539 ($[M-Cl]^+$, 13), 376 ($[M-L]^+$ 60), 142 ($[Nd]^+$, 15), 71 ($[C_4H_7O]^+$, 100). IR (cm^{-1}): 3063(w), 3035(m), 1601(m), 1426(m), 1336(s), 1296(m), 1069(m), 1027(s), 957(m), 945(s), 869(w), 838(w), 788(s), 749(s), 442(s).

4.4. Synthesis of bis(tetrahydrofurfurylindenyl) samarium chloride (2)

The procedure was similar to that for **1**. Red crystals were obtained in 82% yield. Anal. Calc. for $C_{26}H_{30}O_2ClSm$: Sm, 25.75; Cl, 6.08; C, 57.55; H, 5.14. Found: Sm, 25.92; Cl, 6.17; C,57.67; H, 5.29%. EIMS *m/z* (fragment, relative intensity %): 585 ($[M]^+$, 2), 549 ($[M-Cl]^+$, 9), 386 ($[M-L]^+$, 12), 151 ($[Sm]^+$, 7), 71 ($[C_4H_7O]^+$, 100). IR (cm^{-1}): 3060(w), 3036(m), 1608(m), 1427(m), 1337(s), 1297(m), 1068(m), 1027(s), 957(m), 945(s), 868(w), 838(m), 790(s), 750(s), 442(s).

Table 1
Details of the crystal data and structure refinement for complexes **1**–**6**

Complex	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{28}H_{30}O_2ClNd$	$C_{28}H_{30}O_2ClSm$	$C_{28}H_{30}O_2ClDy$	$C_{28}H_{30}O_2ClHo$	$C_{28}H_{30}O_2ClEr$	$C_{28}H_{30}O_2ClYb$
Formula weight	578.21	584.32	596.47	598.90	601.23	607.01
Crystal dimensions (mm)	0.50 × 0.32 × 0.24	0.26 × 0.22 × 0.21	0.52 × 0.40 × 0.38	0.25 × 0.22 × 0.19	0.42 × 0.38 × 0.31	0.26 × 0.26 × 0.16
Color	Green	Red	Light yellow	Yellow	Pink	Green
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group (number)	$P2_12_12_1$, 19	$P2_12_12_1$, 19	$P2_12_12_1$, 19	$P2_12_12_1$, 19	$P2_12_12_1$, 19	$P2_12_12_1$, 19
a (Å)	10.432(3)	10.398(2)	10.472(3)	10.4207(7)	10.4263(2)	10.4665(6)
b (Å)	14.822(5)	14.746(3)	14.815(6)	14.7264(6)	14.7400(3)	14.7204(5)
c (Å)	15.441(4)	15.221(3)	15.142(5)	14.9983(7)	15.0209(3)	14.9288(8)
Volume (Å^3)	2387.5(13)	2333.8(8)	2349.2(13)	2301.6(2)	2308.47(8)	2300.1(2)
Z	4	4	4	4	4	4
D_{calc} (g cm^{-1})	1.609	1.663	1.686	1.728	1.730	1.753
Absorption coefficient (mm^{-1})	2.309	2.654	3.318	3.577	3.775	4.206
$F(000)$	1164	1172	1188	1192	1196	1204
θ Range for data collection (°)	1.90–24.98	1.92–24.78	1.92–25.02	2.38–27.48	2.39–27.45	2.39–27.48
Reflections collected	3207	5313	5621	5234	5249	5274
Independent reflections	2910	5313	4137	5234	5249	5274
Data/restraints/parameters	2910/0/289	5313/0/289	4137/0/289	5234/0/289	5249/1/288	5274/0/289
Goodness-of-fit on F^2	0.869	1.053	0.924	0.899	0.961	0.638
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0437$, $wR_2 = 0.0868$	$R_1 = 0.0261$, $wR_2 = 0.0569$	$R_1 = 0.0328$, $wR_2 = 0.0833$	$R_1 = 0.0317$, $wR_2 = 0.0404$	$R_1 = 0.0173$, $wR_2 = 0.0393$	$R_1 = 0.0226$, $wR_2 = 0.0226$
R indices (all data)	$R_1 = 0.0596$, $wR_2 = 0.0912$	$R_1 = 0.0305$, $wR_2 = 0.0771$	$R_1 = 0.0364$, $wR_2 = 0.0850$	$R_1 = 0.0393$, $wR_2 = 0.0414$	$R_1 = 0.0187$, $wR_2 = 0.0396$	$R_1 = 0.0271$, $wR_2 = 0.0306$
$\rho_{max/min}$ (e Å^{-3})	0.844 and −0.888	1.339 and −1.139	0.918 and −0.535	0.961 and −1.202	0.615 and −0.449	0.991 and −1.170

*4.5. Synthesis of bis(tetrahydrofurfurylindenyl) dysprosium chioride (**3**)*

The procedure was similar to that for **1**. Light yellow crystals were obtained in 54% yield. Anal. Calc. for $C_{28}H_{30}O_2ClDy$: Dy, 27.27; Cl, 5.96; C, 56.38; H, 5.03. Found: Dy, 27.50; Cl, 6.17; C.56.91; H, 5.16%. EIMS *m/z* (fragment, relative intensity %): 596 ($[M]^+$, 1.2), 563 ($[M-Cl]^+$, 6), 397 ($[M-L]^+$, 7), 164 ($[Dy]^+$, 3), 71 ($[C_4H_7O]^+$, 100). IR (cm^{-1}): 3060(w), 3037(m), 1600(w), 1428(m), 1338(s), 1290(w), 1068(m), 1027(s). 958(m), 945(s), 791(s), 749(s), 441 (m).

*4.6. Synthesis of bis(tetrahydrofurfuryfindenyl) holmium chloride (**4**)*

The procedure was similar to that for **1**. Yellow crystals were obtained in 38% yield. Anal. Calc. for $C_{28}H_{30}O_2ClHo$: Ho, 27.56; Cl, 5.93; C, 56.15; H, 5.01. Found: Ho, 27.80; Cl, 6.07; C, 56.53; H, 5.28%. EIMS *m/z* (fragment, relative intensity %): 599 ($[M]^+$, 10), 564 ($[M-Cl]^+$, 11), 400 ($[M-L]^+$, 9), 165 ($[Ho]^+$, 3.5), 71 ($[C_4H_7O]^+$, 100). IR (cm^{-1}): 3063(w), 3037(m), 1603(w), 1428(w), 1338(s), 1297(w), 1068(m), 1027(s), 958(m), 945(s),877(w), 838(w), 790(s), 749(s), 441 (m).

*4.7. Synthesis of bis(tetrahydrofurfurylindenyl) erbium chloride (**5**)*

The procedure was similar to that for **1**. Pink crystals were obtained in 33% yield. Anal. Calc. for $C_{28}H_{30}O_2ClEr$: Er, 27.84; Cl, 5.91; C, 55.93; H, 4.99. Found: Er, 27.97; Cl, 6.11; C, 56.15; H, 5.07%. EIMS *m/z* (fragment, relative intensity %): 601 ($[M]^+$, 1.5), 566 ($[M-Cl]^+$, 16), 402 ($[M-L]^+$, 21), 166 ($[Er]^+$, 4.5), 71 ($[C_4H_7O]^+$, 100). IR (cm^{-1}): 3060(w), 3037(m), 1602(w), 1429(w), 1338(s), 1296(w), 1068(m), 1027(s), 958(m), 945(s), 878(w), 838(w), 790(s), 749(s), 442(m).

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1**–**6**

Complex	Nd(**1**)	Sm(**2**)	Gd [8]	Dy(**3**)	Y [8]	Ho(**4**)	Er(**5**)	Yb(**6**)
Ln^{3+} radius (Å) [9]	1.163	1.132	1.095	1.083	1.075	1.072	1.062	1.042
Bond lengths								
Ln–Cl	2.678(3)	2.647(2)	2.6181(11)	2.595(2)	2.5879(7)	2.5784(12)	2.5695(8)	2.5447(8)
Ln–O(1)	2.508(8)	2.480(4)	2.451(3)	2.453(5)	2.416(2)	2.416(4)	2.421(2)	2.402(3)
Ln–O(2)	2.504(7)	2.481(4)	2.459(3)	2.441(5)	2.420(2)	2.422(4)	2.419(2)	2.401(3)
Ln–C(1)	2.751(9)	2.711(5)	2.696(4)	2.663(6)	2.660(3)	2.655(4)	2.658(3)	2.632(3)
Ln-C(2)	2.730(10)	2.688(5)	2.672(4)	2.642(6)	2.627(3)	2.635(5)	2.610(3)	2.582(3)
Ln–C(3)	2.793(11)	2.733(6)	2.737(4)	2.686(7)	2.684(3)	2.682(5)	2.675(3)	2.654(4)
Ln–C(4)	2.857(11)	2.822(6)	2.828(4)	2.837(7)	2.820(3)	2.821(5)	2.800(3)	2.812(4)
Ln–C(9)	2.838(9)	2.812(5)	2.802(4)	2.787(6)	2.769(3)	2.770(5)	2.778(3)	2.763(4)
Δ_{M-C}(ring 1) [a]	0.0895	0.1063	0.1133	0.1483	0.1375	0.1382	0.1413	0.1648
Ln–Cent(1) [b]	2.518	2.473	2.467	2.441	2.429	2.428	2.421	2.406
Ln–C(15)	2.767(11)	2.760(6)	2.723(4)	2.703(7)	2.685(3)	2.686(5)	2.688(3)	2.671(4)
Ln–C(16)	2.760(10)	2.733(5)	2.703(4)	2.660(7)	2.643(3)	2.641(5)	2.640(3)	2.612(4)
Ln–C(17)	2.755(11)	2.755(6)	2.706(4)	2.699(7)	2.672(3)	2.681(6)	2.669(3)	2.654(4)
Ln–C(18)	2.828(10)	2.810(6)	2.769(4)	2.759(7)	2.761(3)	2.749(5)	2.738(3)	2.733(3)
Ln–C(23)	2.811(10)	2.806(6)	2.764(4)	2.760(7)	2.749(3)	2.725(5)	2.743(3)	2.724(3)
Δ_{M-C}(ring 2)	0.0588	0.0587	0.0558	0.0722	0.0883	0.0677	0.0748	0.0828
Ln–Cent(2)	2.509	2.498	2.454	2.433	2.421	2.415	2.411	2.391
Bond angles								
O(1)–Ln–Cl	81.49(18)	80.58(10)	80.43(8)	80.23(14)	79.88(5)	80.09(9)	79.94(6)	79.63(7)
O(2)–Ln–Cl	79.84(18)	79.80(10)	79.58(8)	80.15(13)	79.88(5)	80.03(8)	79.73(6)	80.04(6)
O(1)–Ln–O(2)	161.3(2)	160.4(1)	160.01(10)	160.37(17)	159.75(6)	160.10(11)	159.66(8)	159.66(8)
C(1)–C(10)–C(11)	116.3(11)	117.9(6)	114.9(4)	114.2(7)	113.1(3)	112.2(5)	112.4(3) [c]	112.9(4)
C(15)–C(24)–C(25)	112.1(9)	112.4(5)	112.2(4)	113.2(7)	112.3(3)	113.9(4)	111.5(3)	112.4(3)
Cl–Ln–Cent(l)	113.2	117.6	116.9	116.0	115.9	116.0	115.6	115.1
Cl–Ln–Cent(2)	113.5	113.3	114.4	115.3	115.3	115.1	115.5	115.6
O(1)–Ln–Cent(1)	89.3	90.4	90.8	91.4	91.9	91.8	91.8	92.3
O(1)–Ln–Cent(2)	99.2	99.4	98.9	98.2	98.2	98.0	98.3	97.9
O(2)–Ln–Cent(1)	99.6	99.1	98.5	97.7	97.5	97.6	97.5	96.8
O(2)–Ln–Cent(2)	S8.2	87.9	89.1	89.6	90.0	89.7	89.9	90.4
Cent(1)–Ln–Cent(2)	128.3	129.0	128.7	128.7	123.7	128.9	128.9	129.3
Dihedral angle of idene planes	52.4	52.0	52.0	52.0	51.5	51.5	52.3	52.0

[a] Δ_{M-C} was calculated by subtracting the average values of the Ln–C (4,9 or 18,23) bond length of the bridging-carbon atoms from those of the remaining three carbon Ln–C(1,2,3 or15,16,17) bond length in the indene ring.

[b] Ring 1 and ring 2 indicate C(1)–C(4) and C(9), C(15)–C(18) and C(23), respectively; Cent(1) and Cent(2) are the centroids of ring 1 and ring 2.

[c] There are two positions of C(11) of complex **5**.

4.8. Synthesis of bis(tetrahydrofurfurylindenyl) ytterbium chtoride (6)

The procedure was similar to that for **1**. Green crystals were obtained in 52% yield. Anal. Calc. for $C_{28}H_{30}O_2ClYb$: Yb, 28.53; Cl, 5.85; C, 55.40; H, 4.95. Found: Yb, 28.73; Cl, 6.01; C, 56.04; H, 5.09%. EIMS *m*/*z* (fragment, relative intensity %): 608 ($[M]^+$, 8), 571 ($[M-Cl]^+$, 16), 408 ($[M-L]^+$, 13), 172 ($[Yb]^+$, 2), 71 ($[C_4H_7O]^+$, 100). IR (cm^{-1}): 3060(w), 3037(m), 1610(w), 1428(w), 1338(m), 1297(w), 1067(s), 1027(m), 959(m), 945(m), 877(w), 838(w), 772(s), 746(m), 441 (m).

4.9. X-ray structure determination

Single crystals were sealed in thin-walled glass capillaries under argon. Data was collected on a Siemens P4 diffractometer (complexes **2** and **3**) or Rigaku Rapid diffractometer (complexes **1** and **4**–**6**) with graphite-monochromated Mo–K_α ($\lambda = 0.071073$ Å) radiation using the $\omega - 2\theta$ technique at 293 K. Crystal data and experimental details are listed in Table 1, while selected bond lengths and bond angels are given in Table 2. The crystal structures were solved by direct method and refined on F^2 by full-matrix least-squares methods, expanded using Fourier techniques [14]. All hydrogen atoms were added according to theoretical models with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in refinement. All calculations were performed using the SHELXS-97 crystallographic software package [15].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 184168–184175 for compounds **1**–**6** and $(C_4H_7OCH_2C_9H_6)_2LnCl$ (Ln = Y, Gd), respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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