

The first example of a dinuclear anionic lanthanocene complex: [K(18-crown-6){(C₁₃H₈)CPh₂(C₅H₄)Nd(BH₄)₂}]₂·C₄H₈O₂

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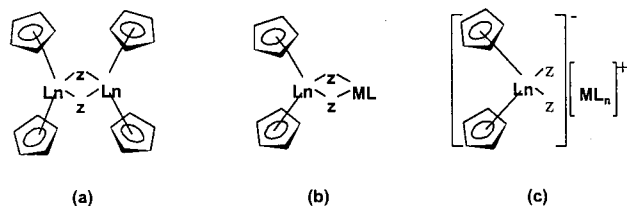
Abstract

The first dinuclear anionic lanthanocene compound is described. By reaction of [Nd(BH₄)₃(THF)₃] with K₂[FluCPh₂Cp] in THF solution in the presence of 18-crown-6 ether we got an anionic complex [K(18-crown-6){(C₁₃H₈)CPh₂(C₅H₄)Nd(BH₄)₂}]₂·C₄H₈O₂. The crystal structure of this complex was determined and indicated that this anionic compound crystallized in a binuclear fashion. It consists of three parts: the two discrete anions of {(C₁₃H₈)CPh₂(C₅H₄)Nd(BH₄)₂}⁻ moiety is connected by the cation of [K(18-crown-6)]⁺·C₄H₈O₂ through a weak η² interaction of the Flu moieties with the K⁺ cations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dinuclear anionic lanthanocene compounds; 18-Crown-6 ether; Crystal structures

1. Introduction

The metallocene(III) chlorides and borohydrides of Group 3 elements are key intermediates to many of the organometallic complexes, which could be conveniently converted into new derivatives by further reaction of the Cl and BH₄ groups with anionic reagents or protic substrates [1]. The molecular structures of these compounds fall into three classes: (a) homometallic complexes of formula [Ln(η-Cp*)₂(μ-Z)]₂, (b) the heterometallic compounds [Ln(η-Cp*)₂(μ-Z)₂ML] and (c) the anionic complexes [ML]⁺[Ln(η-Cp*)₂Z]⁻. Un-



Scheme 1. L = neutral ligand; Z = monoanionic ligand; M = alkali metal, etc.

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like compounds of classes (a) and (b), this anionic complexes exist as discrete cation and anion pairs [Ln = a Group 3 metal; Cp* denotes a general substituted or unsubstituted cyclopentadienyl ligand] (Scheme 1).

Until now a large number of lanthanocene chlorides have been structurally characterized as classes (a) [2] or (b) [3]. Only in recent years few crystal data on class (c) compounds have been reported in the literature (e.g. [As(C₆H₅)₄][Cp''₂NdCl₂] (Cp'' = (Me₃Si)₂C₅H₃) [4], [Li(THF)₄][(Flu)CPh₂(Cp)LnZ₂] (Flu = fluorenyl C₁₃H₈; Cp = cyclopentadienyl C₅H₄; Z = Cl or BH₄) [5], and [Li(THF)₄][Cp''₂LnCl₂] [6], while all of these compounds are mononuclear. In this work, we report on the first dinuclear example of this anionic lanthanocene complex with the Lewis basic 18-crown-6 macrocycle as the neutral donor ligand [K(18-crown-6){(Flu)CPh₂(Cp)Nd(BH₄)₂}]₂·C₄H₈O₂ (**1**).

2. Results and discussion

2.1. Synthesis

This anionic complex [K(18-crown-6){(C₁₃H₈)CPh₂-

Table 1
X-ray diffraction data collection parameters for complex **1**

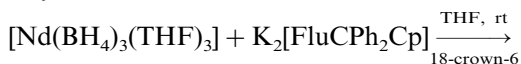
Formula	C ₄₇ H ₅₈ Nd(BH ₄) ₂ KO ₇
F _w	915.91
Crystal system	Monoclinic
Space group	P2 ₁ /a (no. 14)
Unit cell dimensions	
<i>a</i> (Å)	15.530(3)
<i>b</i> (Å)	20.217(2)
<i>c</i> (Å)	14.106(1)
β (°)	92.60(1)
<i>V</i> (Å ³)	4424.0(9)
<i>T</i> (K)	293
<i>Z</i>	4
μ (Mo–Kα) (cm ⁻¹)	13.15
Reflections collected	7096
Independent reflections	6786
<i>R</i>	0.037
<i>R</i> _w ^a	0.045

$$^a R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2]^{0.5}.$$

Table 2
Selected bond lengths (Å) and bond angles (°) for complex **1**

<i>Bond lengths</i>			
K–O(1)	2.754(6)	Nd–B(2)	2.623(7)
K–O(2)	2.805(6)	Nd–H(23)	2.47
K–O(3)	2.740(5)	Nd–H(24)	2.40
K–O(4)	2.696(5)	Nd–H(25)	2.41
K–O(5)	2.881(5)	Nd–H(27)	2.48
K–O(6)	2.757(6)	Nd–H(28)	2.39
K–O(7)	2.78(1)	Nd–H(29)	2.52
K–C(3)	3.403(7)	Nd–C(1)	2.817(5)
K–C(4)	3.322(7)	Nd–C(6)	2.938(6)
B(1)–H(23)	0.97	Nd–C(7)	2.915(6)
B(1)–H(24)	1.20	Nd–C(12)	2.781(5)
B(1)–H(25)	1.20	Nd–C(13)	2.752(5)
B(1)–H(26)	1.15	Nd–C(15)	2.701(5)
B(2)–H(27)	1.07	Nd–C(16)	2.691(5)
B(2)–H(28)	1.22	Nd–C(17)	2.741(6)
B(2)–H(29)	1.03	Nd–C(18)	2.753(6)
B(2)–H(30)	1.07	Nd–C(19)	2.718(5)
Nd–B(1)	2.641(8)		
<i>Bond angles</i>			
B(1)–Nd–B(2)	100.2(3)	C(14)–C(15)–C(16)	126.0(5)
C(12)–C(13)–C(14)	126.0(5)	C(14)–C(15)–C(19)	125.0(5)
C(13)–C(14)–C(15)	103.1(4)	C(20)–C(14)–C(26)	102.3(4)
C(1)–C(13)–C(14)	126.7(5)		

(C₅H₄)Nd(BH₄)₂}]₂·C₄H₈O₂ (**1**) was synthesized directly by the reaction of [Nd(BH₄)₃(THF)₃] [7] with K₂[FluCPh₂Cp] [8] in THF containing 18-crown-6 ether in yields of 20%.



By slow diffusion of hexane into the concentrated THF solution, we got the slightly green single crystals suitable for X-ray diffraction. This compound obtained

is highly sensitive to air and moisture and decomposed immediately in contact with air after a short time. However, it can be stored under argon at room temperature for several months without decomposition.

2.2. Molecular structure

Crystal data and details of data collection and structure refinement of **1** are listed in Table 1. Table 2 lists selected bond distances and angles.

The solid state structure of the complex **1** investigated by single crystal structure analysis revealed that it is built up by the unit [K(18-crown-6){(C₁₃H₈)CPh₂(C₅H₄)Nd(BH₄)₂}]₂ as the fundamental group, meanwhile two units are bridged by the bidentate ligand and 1,4-dioxane. The similar tendency to build up binuclear complexes bridged by bidentate ligands DME or dioxane was observed for the related organometallic heavier alkali metal derivatives of potassium or rubidium, as [{RbFlu(18-crown-6)}₂(dioxane)] [9], [{RbFlu(18-crown-6)}₂(DME)] [9], or [{KFlu(18-crown-6)}₂(DME)] [10].

The significant difference between complex **1** and the above mentioned alkali metal complexes is the consistency of the anion. In those alkali metal complexes, cyclopentadienyl, indenyl, fluorenyl, or pentamethylcyclopentadienyl is involved as the carbanion [9]. However, in **1**, it is the discrete tetrahedral anion of {FluCPh₂CpNd(BH₄)₂}⁻ moiety (Fig. 1), whose structure is almost identical to that of complex [Li(THF)₄][(C₁₃H₈)CPh₂(C₅H₄)Ln(BH₄)₂] reported in our previous work [5]. In the anion, the Nd ion is bonded to the cyclopentadienyl ring and fluorenyl ring in η⁵ fashion, and coordinated by two BH₄ ligands in symmetric geometry. The average Nd–C (Cp-ring) distance of 2.722 Å is comparable to the corresponding values of 2.78 and 2.667(3) Å in [As(C₆H₅)₄][Cp'₂NdCl₂] [4] and [Li(THF)₄][Cp''₂LnCl₂] [6], respectively, if Shannon's ionic radii are taken into account [11]. The longer Nd–C (Flu-ring) distances ranging from 2.752(5) to 2.938(6) Å, mean value 2.841 Å, can be explained by the inclined stereorigid planar fluorenyl ligation. The B(1)–Nd–B(2) angle of 100.2(3)° in **1** is larger than the value 99.3(1)° of ∠Cl(1)–Nd–Cl(2) in [As(C₆H₅)₄][Cp'₂NdCl₂] [4], but smaller than that of 103.11(3)° in [Li(THF)₄][Cp'₂ErCl₂] [6], perhaps due to crystal packing forms. The angle at the diphenylmethylene carbon C(13)–C(14)–C(15) = 103.1(4)° is larger than those of previously reported Group 4 metallocenes having a C₅H₄CR₂C₁₃H₈ (R = Me, Ph) chelating ligand system [12].

The most remarkable structural feature of the complex (Fig. 2) is the mode of attachment of the tetrahedral BH₄ ligands. The two boron atoms have almost same ligation geometry. Each of them is linked to the metal center via a μ³-hydrogen bridging the B and the

Nd atoms. This ‘ate’ coordination type of the borohydride ligand has only been known in the uranium compounds [13]. The two Nd–B distances (Nd–B(1) = 2.641(8) Å, Nd–B(2) = 2.623(7) Å) which are compared with that of 2.664(25) Å determined in the monomeric neodymium borohydride complex (C₅H₄CH₂-CH₂OMe)₂Nd(BH₄) [14] are shorter than that of dimeric neodymium complexes (e.g. 2.875(6) and 2.941(6) in {(COT)Nd(BH₄)(THF)}₂ [15]). The short distances are characteristics of tridentate BH₄ ligands. The six Nd–Hb bond distances for the tridentate groups do not differ significantly (Nd–Hb = 2.41, 2.40, 2.47, 2.39, 2.48, 2.52 Å, respectively). While the two Nd–B–Ht angles are almost linear (Nd–B(1)–Ht = 171.5, Nd–B(2)–Ht = 177.1°). The tetrahedral BH₄ groups are strongly distorted from its ideal H–B–H angles of 109°28′. The bond distances of B–Hbs are not obviously longer than those of the B–Hts, even though

there is the interaction of B–Hbs with the electrophilic Nd metal.

The coordination sphere of the potassium cation of this complex is quite similar to that of the Rb in the complex [{RbFlu(18-crown-6)}₂(dioxane)] [9]. The K⁺ ion is coordinated by the six oxygen atoms of the 18-crown-6 ligand and by one oxygen atom of the bidentate ligand 1,4-dioxane. The best plane through the oxygen atoms of the crown ether is always arranged parallel to the best plane through the 13 carbon atoms of the fluorenyl ring for all potassium and rubidium derivatives. For the complex 1, an angle of 127.5° between the O6-plane and C13-plane was found. The six K–O (18-crown-6) bond lengths range from 2.695(5) to 2.881(5) Å, the value of the K–O (dioxane) bond lengths is 2.78(1) Å, which are shorter when compared to that of the recently published complex [{RbFlu(18-crown-6)}₂(dioxane)] (the mean value of

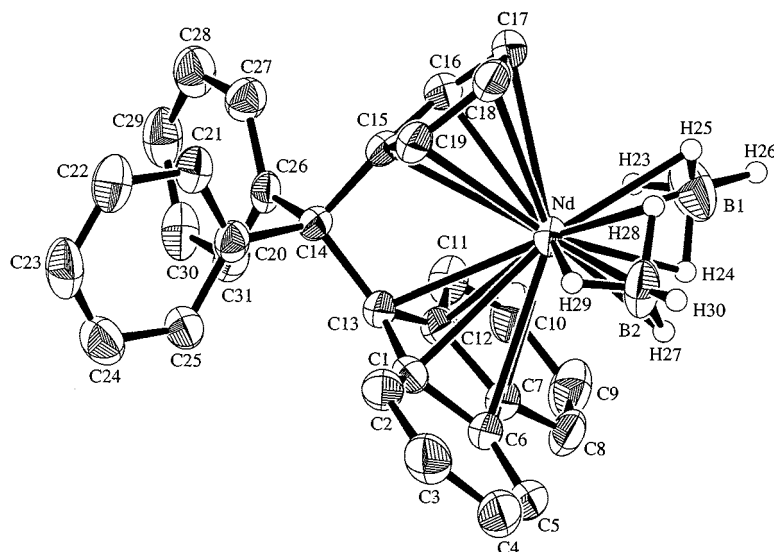


Fig. 1. ORTEP drawing of the {FluCPh₂CpNd(BH₄)₂}⁻ anion.

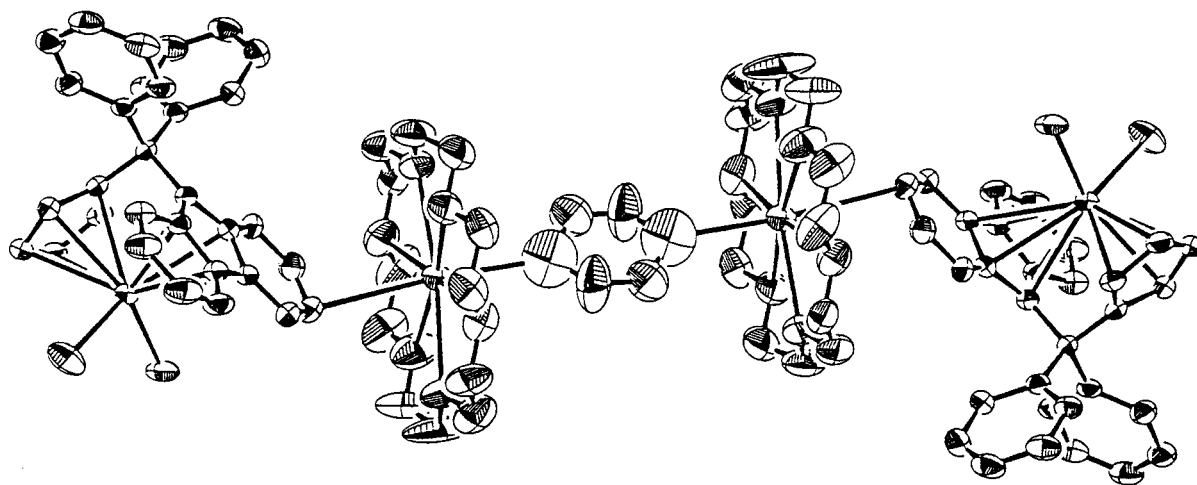


Fig. 2. ORTEP plot of the molecular structure of complex 1.

Rb–O (18-crown-6) is 2.917 Å, the Rb–O (dioxane) distance is 3.077(4) Å [9]). The shorter K–O distances in **1** can be explained by the weak η^2 interaction of the anionic moiety with the K⁺ cation observed in this compound. The alkali metal cations are located above the bond between the carbon atoms of C₃ and C₄, which is one bond of the six-membered ring of the fluorenyl moiety. The K–C₃ and K–C₄ lengths are 3.322(7) and 3.403(7) Å. The other K–C (1, 2, 5, 6) are much longer (out of 4.00 Å). Similar η^2 interaction of K⁺ ion with molecules of benzene has been reported in complexes [K(18-crown-6)(η^2 -C₆H₆)₂][(LaCp^{tt})₂(μ - η^6 : η^6 -C₆H₆)]·2C₆H₆ (Cp^{tt} = η^5 -C₅H₃Bu₂-1,3) [16] and {KCPh₃(PMDTA)} (PMDTA = (*N,N,N',N'',N'''*-pentamethyl-diethylenetriamine)) [17]. The reason for this finding must be that the anion structure of complex **1** is a discrete tetrahedral [(Flu)CPh₂(Cp)Ln(BH₄)₂][−] moiety not a simple fluorenyl carboanion (Flu[−]) as in above mentioned alkali metal complexes. So different bonding type of the anions to the cations will be observed.

3. Experimental

3.1. General procedure

All operation involving organometallics were carried out under an inert atmosphere of argon using standard Schlenk techniques. THF was distilled under argon from sodium benzophenone ketyl prior to use. Lanthanide borohydrate compounds [7] was prepared according to the procedures in literature and the reactant fluorene was purchased from Aldrich. K₂[(C₁₃H₈)CPh₂(C₅H₄)] [8] was synthesized using the method described in literature for related compounds. KH was washed carefully with *n*-hexane. 18-Crown-6 was purchased from Aldrich and used without further purification. Mass spectra were recorded on a Hp 5989A spectrometer (*T* = 50–400°C, 1.3 kV). Elemental analysis was performed by the Analytical Laboratory of the Shanghai Institute of Organic Chemistry.

3.2. Synthesis of [K(18-crown-6){(C₁₃H₈)-CPh₂(C₅H₄)Nd(BH₄)₂}]₂·C₄H₈O₂ (**1**)

To a suspension of Nd(BH₄)₃(THF)₃ (0.85 g, 1.85 mmol) in 15 ml THF at the presence of 18-crown-6 was added dropwise a solution of K₂[(C₁₃H₈)CPh₂(C₅H₄)] (0.05 M, 37 ml, in THF) with vigorous stirring at −78°C under argon. The mixture was slowly warmed to room temperature and stirred for another 4 h. The precipitate was separated and resultant clear solution was concentrated to 10 ml and slowly diluted with hexane. Orange crystals of this complex were formed

after keeping overnight. (0.35 g, 20.7%). Anal. Found: C, 59.39; H, 6.56. Calc. for C₄₅H₅₈NdB₂KO₇: C, 59.24; H, 6.19%. MS (EI) (70 eV, 50–400°C): *m/z* 770 (12.03, [M – KBH₄ – THF]⁺), 165 (100, [C₁₃H₉]⁺).

3.3. X-ray structure determination

Single crystals were sealed in thin-walled glass capillaries under an atmosphere of argon. Crystal data and experimental details are given in Table 1, while selected bond lengths and bond angles for complex are listed in Table 2. X-ray diffraction data were collected at a room temperature using the ω –2 θ scan technique to a maximum 2 θ value of 50.0°. The intensities of three representative reflections were measured after every 200 reflections. Over the course of data collection, the standards decreased by 0.9%. A linear correction factor was applied to the data to account for this phenomenon. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom Patterson methods [18] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically [19]. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation [20].

4. Conclusions

The crown ether 18-crown-6, as a Lewis base complex ligand, has been widely used in potassium organometallic chemistry. In this paper, we have obtained, for the first time, the binuclear organolanthanocene compound with the hexadentate ligand 18-crown-6. The Flu moiety is not η^6 bonded to the K⁺ cations, and a weak η^2 interaction of the K⁺ cations with the Flu moiety in this complex is observed.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 154520 for compound **1**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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