

Dicationic Methyl Complexes of the Rare-Earth Elements

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The reactions of $Ln(\text{AlMe}_4)_3$ ($Ln = \text{Ho}, \text{Tm}$) with the crown ether [12]crown-4 yield dicationic methyl rare-earth metal complexes $[Ln\text{Me}([12]\text{crown-4})_2][\text{AlMe}_4]_2$ ($Ln = \text{Ho}$ (**1**), Tm (**2**)). The reaction of $\text{La}(\text{AlMe}_4)_3$ with [18]crown-6 in thf affords $[\text{LaMe}([18]\text{crown-6})(\text{thf})_2][\text{AlMe}_4]_2$ (**3**). The compounds have been characterized by X-ray diffraction, **1** and **3** additionally by elemental analyses as well as by ^1H and ^{27}Al , and **3** also by ^{13}C NMR spectroscopy.

Key words: Lanthanoides, Crown Ethers, Alkyl Complexes, Structure, NMR

Introduction

Over the last few decades investigations in alkyl compounds of the rare-earth metals gain more interest [1–5]. Their potential application as precursors in various catalytic processes has stimulated research in the development of neutral as well as ionic alkyl compounds. Amongst others, isoprene polymerization is the main process where rare-earth metal alkyl compounds can be employed as catalysts. For instance, neutral complexes such as $[(L)Ln(\text{CH}_2\text{SiMe}_3)_2(\text{thf})_{0-1}]$ ($L = (2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N} = \text{C}(\text{Me})\text{C}(\text{=CH}_2)\text{N}-\text{C}_6\text{H}_3-2,6\text{-}^i\text{Pr}_2$, (*S,S*)-bis(oxazolinyphenyl)amido or [2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3\text{N} \text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\text{N}]_2$ -(*m*-phenylene)) are known to be catalytically active towards isoprene polymerization [6–8]. Activation of neutral alkyl complexes can be initiated by addition of aluminum alkyls, mostly Al^iBu_3 , and/or tritylium salts ($[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$), so that a cationic species is generated as the active catalytic species [5, 6, 8–11].

However, it has been shown that addition of three equivalents of THF to the tris(tetramethylaluminates) of the rare-earth metals, $Ln(\text{AlMe}_4)_3$, leads to elimination of AlMe_3 and formation of the trimethyl compounds $[Ln\text{Me}_3]_n$ [12, 13]. Excess of THF affords monocationic dimethyl complexes $[Ln\text{Me}_2(\text{thf})_5][\text{AlMe}_4]$ ($Ln = \text{Y}, \text{Ho}, \text{Sm}$) [14, 15]. The addition of chelate ligands like crown ethers or

triaminals to THF solutions of the rare-earth metal complexes $Ln(\text{AlMe}_4)_3$ leads to a replacement of THF by these ligands. The composition of the products depends on the size of the ligand and the metal ion. Smaller ligands cause non-solvated sandwich-like complexes, including $[(12)\text{crown-4}]_2Ln\text{Me}[\text{AlMe}_4]_2$ and $[(\text{TRTAC})_2\text{YMe}_2][\text{AlMe}_4]$ ($\text{TRTAC} = 1,3,5$ -trialkyl-1,3,5-triazacyclohexane) [14–16], whereas only one of the bigger ligands can coordinate to the rare-earth metal ion with the ligand sphere saturated with THF molecules as observed for $[(15)\text{crown-5}]\text{YMe}(\text{thf})_2[\text{AlMe}_4]_2$ [16].

Results and Discussion

Solid-state structures of compounds 1–3

We have now observed that treatment of $Ln(\text{AlMe}_4)_3$ ($Ln = \text{Ho}, \text{Tm}$) in THF with the small crown ether [12]crown-4 leads to the compounds $[Ln\text{Me}([12]\text{crown-4})_2][\text{AlMe}_4]_2$ ($Ln = \text{Ho}$ (**1**), Tm (**2**)). Hereby **1** was obtained in only 19% yield, and only a few pale-green crystals suitable for X-ray diffraction experiments but not for further characterization were obtained for **2**. These ionic compounds contain two $[\text{AlMe}_4]^-$ anions and a cation with sandwich-like coordination of two crown ether ligands for the lanthanoid ion bearing a further methyl group (Fig. 1). The structures of **1** and **2** in

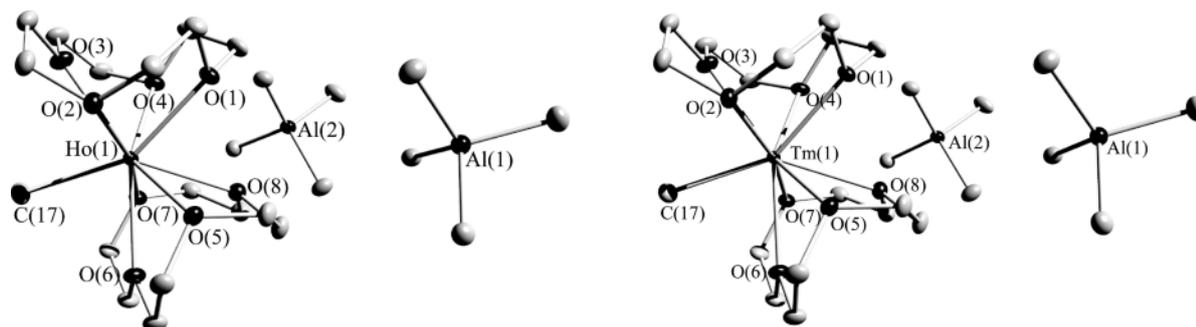


Fig. 1. Molecular structures of compound **1** (left) and **2** (right) in the crystalline state. Displacement ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths and angles (Å, deg) of $[LnMe([12]crown-4)_2][AlMe_4]_2$ ($Ln = Ho$ (**1**), Tm (**2**)).

Ln	Ho (1)	Tm (2)
Distances		
$Ln(1)-C(17)$	2.401(2)	2.388(2)
$Ln(1)-O(1)$	2.468(2)	2.453(1)
$Ln(1)-O(2)$	2.490(2)	2.478(1)
$Ln(1)-O(3)$	2.537(2)	2.528(1)
$Ln(1)-O(4)$	2.455(1)	2.449(1)
$Ln(1)-O(5)$	2.404(1)	2.395(1)
$Ln(1)-O(6)$	2.501(1)	2.489(1)
$Ln(1)-O(7)$	2.434(1)	2.423(1)
$Ln(1)-O(8)$	2.536(2)	1.526(2)
Angles		
$O(1)-Ln(1)-O(3)$	79.6(1)	79.5(1)
$O(2)-Ln(1)-O(4)$	110.4(1)	110.9(1)
$O(5)-Ln(1)-O(7)$	117.9(1)	118.5(1)
$O(6)-Ln(1)-O(8)$	70.2(1)	70.4(1)
$O(3)-Ln(1)-C(17)$	72.9(1)	73.2(1)
$O(6)-Ln(1)-C(17)$	74.0(1)	74.0(1)

the crystalline state are isostructural to that of the yttrium analog $[YMe([12]crown-4)_2][AlMe_4]_2$ [16]. Selected bond lengths and angles are listed in Table 1. The bond lengths of **1** are slightly shorter than those of the yttrium compound, but the angles show nearly the same values. Compound **1** shows a Ho–C bond of 2.401(2) Å. For comparison: the bond length in the dicationic methyl holmium compound $[HoMe(thf)_6][BPh_4]_2$ at 2.378(4) Å is somewhat shorter, whereas the related monocationic methyl holmium compound $[HoMe_2(thf)_5][AlMe_4]$ reveals longer bonds of 2.464(6) and 2.449(6) Å [15, 17].

Due to the smaller radius of the thulium ion, in **2** the ligands approach the central atom more closely causing decreased bond lengths and marginally wider angles.

The reaction of $La(AlMe_4)_3$ with [18]crown-6 yields $[LaMe([18]crown-6)(thf)_2][AlMe_4]_2$ (**3**). This ligand is much bigger than [12]crown-4, and only one coordinates to the lanthanum ion. Crystals of this compound were also suitable for X-ray diffraction experiments revealing a structure isostructural to the praseodymium analog $[PrMe([18]crown-6)(thf)_2][AlMe_4]_2$ [16]. Selected bond lengths and angles of **3** are listed in Table 2. In this compound the crown ether surrounds the central metal in a flat-boat manner. To one side of the boat one THF molecule and to the other side one THF molecule and a methyl group are orientated (Fig. 2). The La–C bond of compound **3** is 2.540(2) Å long, somewhat longer than in the dicationic methyl complex $[LaMe(thf)_6][BPh_4]_2$ in which the lanthanum atom adopts a coordination number of seven with a La–C bond length of 2.456(6) Å [18]. The La–O bond lengths are in the range between 2.597(2) (La(1)–O(2)) and 2.668(2) Å (La(1)–O(3)), which is in good agreement with the lengths of the La–O bonds in $[LaMe(thf)_6][BPh_4]_2$ (2.497(3)–2.679(2) Å) [18]. Generally, the bigger lanthanum ion causes longer

Table 2. Selected bond lengths and angles (Å, deg) of $[LaMe([18]crown-6)_2(thf)_2][AlMe_4]_2$ (**3**).

Distances		Angles	
La(1)–C(13)	2.540(2)	O(8)–La(1)–O(1)	97.3(1)
La(1)–O(1)	2.605(2)	O(8)–La(1)–O(2)	72.0(1)
La(1)–O(2)	2.597(2)	O(8)–La(1)–O(3)	69.1(1)
La(1)–O(3)	2.668(2)	O(8)–La(1)–O(4)	94.2(1)
La(1)–O(4)	2.626(2)	O(8)–La(1)–O(5)	77.0(1)
La(1)–O(5)	2.637(2)	O(8)–La(1)–O(6)	72.4(1)
La(1)–O(6)	2.666(2)	O(8)–La(1)–O(7)	142.2(1)
La(1)–O(7)	2.613(2)	O(8)–La(1)–C(13)	143.1(1)
La(1)–O(8)	2.642(2)	O(7)–La(1)–C(13)	74.4(1)

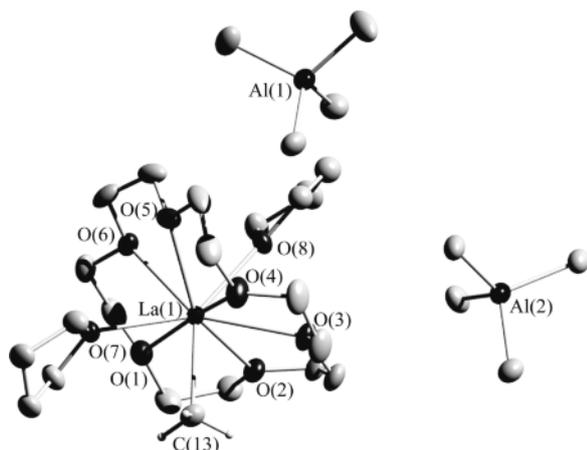


Fig. 2. Molecular structure of compound **3** in the crystalline state. Displacement ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

bonds than observed in the praseodymium compound. By contrast, the angles in **3** and $[\text{PrMe}([\text{18}] \text{crown-6})(\text{thf})_2][\text{AlMe}_4]_2$ are found to be very similar [16].

NMR spectroscopy of compounds **1** and **3**

The pronounced paramagnetic nature of the holmium ion causes extreme chemical shifts and line broadening in the NMR spectra of its compounds. Consequently, the ^1H NMR spectrum of compound **1** exhibits three resonances, one signal at 3.68 ppm is assigned to the crown ether, while one at -0.92 and a very broad one at -6.26 ppm are caused by the metal-bound methyl groups. The assignment of the resonances of the methyl groups by an $^1\text{H}/^{27}\text{Al}$ HMBC experiment failed, which is obviously a result of signal broadening and/or missing of the $^{27}\text{Al}-^1\text{H}$ coupling due to paramagnetism. Nevertheless, the holmium compound **1** behave like the compound $[\text{HoMe}_2(\text{thf})_5][\text{AlMe}_4]_2$ featuring also holmium- and aluminum-bound methyl groups [15]. Recent NMR studies of this compound have shown two signals in the high-field region of the ^1H NMR spectrum, one at -0.83 ppm ($[\text{AlMe}_4]^-$) and a very broad one at -13.93 ppm for the holmium-bound methyl groups. So the broad signal at -6.26 ppm in the ^1H NMR spectrum of **1** belongs most certainly to the holmium-bound methyl group.

As for $\text{Ho}(\text{AlMe}_4)_3$ and $[\text{HoMe}(\text{thf})_6][\text{AlMe}_4]$, no ^{13}C NMR signals could be observed for compound **1**.

In the ^{27}Al NMR spectrum of **1** one signal for the anion can be observed at 182 ppm (at -80°C).

The ^1H NMR spectrum of compound **3** reveals a multiplet at 4.12 ppm formed by two overlapping components, caused by protons of the crown ether hydrogen atoms in axial and equatorial positions. The signal of the lanthanum-bound methyl group is observed at -0.97 ppm, whereas the signal at -1.29 ppm is assigned to the aluminum-bound methyl groups. The related yttrium compound $[\text{YMe}([\text{18}] \text{crown-6})(\text{thf})][\text{AlMe}_4]_2$ shows very similar shifts: -0.98 ppm for the yttrium-bound and -1.30 for the aluminum-bound methyl groups (at 173 K) [16]. In the ^{13}C NMR spectrum, the crown ether causes a broader signal at 70.6 ppm. The resonances for the coordinated THF molecules are observed in the anticipated regions, whereas the aluminum-bound methyl groups result in a broad signal at -4.20 ppm and the lanthanum bound methyl groups at -9.20 ppm. The ^{27}Al NMR signal of the anion in compound **3** is observed at -155 ppm, which is in good agreement with that of related compounds [16].

Experimental Section

All operations were performed under an inert atmosphere of argon using modified Schlenk line or glove box techniques. THF was distilled from potassium, pentane was distilled from LiAlH_4 . The solvents were degassed three times and stored in a glove box under argon. NMR spectra were recorded using Bruker AV 300, Bruker DRX 500, Bruker Avance III 500, and Bruker Avance 600 spectrometers. Elemental analyses were carried out for compound **1** using a EuroEA elemental analyzer and for compound **3** using a Leco CHN 932 instrument.

Preparation of $[\text{HoMe}([\text{12}] \text{crown-4})_2][\text{AlMe}_4]_2$ (**1**)

$\text{Ho}(\text{AlMe}_4)_3$ (190 mg, 0.45 mmol) was dissolved in cold THF (15 mL, -30°C) and stirred overnight at room temperature. $[\text{12}] \text{Crown-4}$ (0.15 mL, 0.9 mmol) was added to the yellow solution, and the mixture was again stirred overnight. The solution was concentrated in a vacuum to a volume of ca. 8 mL and layered with pentane to initiate crystallization. Yellow crystals were obtained after one day. Yield 60 mg (19%). $M_r = 706.61$, found C 41.54, H 8.15%; $\text{C}_{25}\text{H}_{59}\text{O}_8\text{Al}_2\text{Ho}$ requires C 42.49, H 8.42%. ^1H NMR (500 MHz, $[\text{D}_8]\text{THF}$, 25°C): $\delta = 3.68$ (s, $[\text{12}] \text{crown-4}$), -0.92 ($\text{Al}(\text{CH}_3)_4$), -6.26 (HoCH_3). ^{27}Al NMR (130 MHz, $[\text{D}_8]\text{THF}$, -80°C): $\delta = 182$ (s).

Table 3. Crystal data and numbers pertinent to data collection and structure refinement of compounds **1**–**3**.

Compound	1	2	3
Empirical formula	C ₂₅ H ₅₉ O ₈ Al ₂ Ho	C ₂₅ H ₅₉ O ₈ Al ₂ Tm	C ₂₉ H ₆₇ O ₈ Al ₂ La
<i>M_r</i>	706.61	710.61	736.70
Crystal size, mm	0.32 × 0.25 × 0.11	0.30 × 0.28 × 0.10	0.27 × 0.14 × 0.10
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	11.00149(13)	11.0130(14)	11.8798(1)
<i>b</i> , Å	20.8596(2)	20.898(3)	14.7828(2)
<i>c</i> , Å	14.40475(17)	14.4340(14)	21.9504(3)
β, deg	95.5118(11)	95.386(12)	92.2564(9)
<i>V</i> , Å ³	3290.41(7)	3307.3(7)	3851.87(8)
<i>Z</i>	4	4	4
<i>D</i> _{calcd.} , Mg m ⁻³	1.43	1.43	1.27
μ, mm ⁻¹	2.5	2.8	1.2
θ range, deg	2.7–30.0	3.1–30.0	2.9–30.0
Refl. collected/unique	69723/9592	108097/9647	78022/11226
<i>R</i> _{int}	0.0410	0.0345	0.055
Refl. with <i>I</i> > 2σ(<i>I</i>)	8831	8357	9255
Refined param.	334	334	369
<i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0191/0.0449	0.0176/0.0325	0.0296/0.0659
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0220/0.0465	0.0260/0.0343	0.0414/0.0706
Δρ _{max} /min, e Å ⁻³	1.28/–0.55	0.63/–0.52	0.84/–0.79
CCDC no.	966037	966038	966039

Preparation of [LaMe([18]crown-6)(thf)₂][AlMe₄]₂ (**3**)

La(AlMe₄)₃ (99 mg, 0.25 mmol) was dissolved in pentane (20 mL). A solution of [18]crown-6 (66 mg, 0.25 mmol) in pentane (2 mL) was added leading to immediate precipitation. The reaction mixture was stirred for 15 min and filtered. The solid residue was dried *in vacuo*, dissolved in THF (10 mL) and layered with pentane to initiate crystallization. Crystals were obtained after 30 min. Yield 31 mg (17%). *M_r* = 736.70, found C 47.33, H 9.08%; C₂₉H₆₇O₈Al₂La requires C 47.28, H 9.17%. – ¹H NMR (300 MHz, [D₈]THF, 28 °C): δ = 4.12 (m, 24H, [18]crown-6), 3.61 (s, 8H, OCH₂CH₂), 1.77 (s, 8H, OCH₂CH₂), –0.97 (s, 3H, LaCH₃), –1.29 (br s, 12H, Al(CH₃)₄). – ¹³C NMR (75 MHz, [D₈]THF, 28 °C): δ = 70.62 ([18]crown-6), 68.3 (OCH₂CH₂), 26.4 (OCH₂CH₂), –4.20 (Al(CH₃)₄), –9.20 (LaCH₃). – ²⁷Al NMR (130 MHz, [D₈]THF, 25 °C): δ = –155 (s).

Crystal structure determinations

Suitable single crystals were selected, coated with paratone oil and mounted onto the diffractometers. Data collection at 100.0(1) K was performed for compound **1** on a SuperNova Atlas diffractometer, and for **2** and **3** on a Nonius Kappa CCD diffractometer by using monochromated MoK_α radiation (λ = 0.71073 Å). For structure solution and refinement, SHELXS/L-97 was used [19]. Crystal and refinement details, as well as CCDC numbers are provided in Table 3.

CCDC 966037–966039 (**1**–**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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