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X-ray crystal structure of the tetra(*tert*-butyl)erbate anion and attempts to prepare tetravalent organolanthanide complexes

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Abstract

The new $[Li(DME)_3^+]$ salt of the previously-known tetra(*tert*-butyl)erbate(III) anion $[Er(t\text{-}Bu)_4^-]$ has been prepared and structurally characterized. The erbium(III) center is ligated by four *tert*-butyl groups in an approximately tetrahedral arrangement. The C–Er–C angles between the *tert*-butyl groups range from 108.8(3)° to 111.2(3)° and the Er–C distances range from 2.352(6) to 2.395(6) Å. The lithium cation is surrounded by three DME molecules, which form a distorted octahedral coordination sphere. Attempts to oxidize the analogous terbate complex $[Li(DME)_3][Tb(t\text{-}Bu)_4]$ and its cerium analog to electrically neutral tetra(alkyl)lanthanide(IV) compounds are described.

Keywords: Lanthanide; Organolanthanide; Crystal structure; Tetravalent; Oxidation; Lithium salt; Erbium; Organoerbium; *tert*-Butyl

1. Introduction

In recent years there has been renewed interest in organometallic compounds of the lanthanide elements, whose structures, physical properties, and chemical reactivities often differ significantly from organometallic compounds of the d-block transition metals [1–3]. Although the +3 oxidation state dominates throughout the series, it has long been known that certain lanthanide elements – especially Sm^{II}, Eu^{II}, and Yb^{II} – have stable divalent oxidation states, and certain others – especially Ce^{IV} – have stable tetravalent states [4,5]. Recently, the inorganic and organometallic chemistry of lanthanide(II) ions has expanded considerably, and now includes compounds of La^{II}, Ce^{II}, Pr^{II}, Nd^{II}, Dy^{II}, and Tm^{II} [6,7]. In contrast, there have been fewer advances in the inorganic and organometallic chemistry of lanthanide(IV) ions. This class of compounds continues to be dominated by inorganic derivatives of cerium(IV) [8,9]; few organocerium(IV) compounds have been described, and few tetravalent compounds of any kind are known for the other lanthanide elements [10–13]. The only known formally tetravalent organolanthanide complexes are bis(cyclooctatetraene) cerium(IV) and related derivatives, and even these are best regarded as complexes of cerium(III) bearing partly oxidized C_8H_8 ligands [14–17].

We became interested in the possibility of preparing electrically neutral tetra(alkyl)lanthanide(IV) compounds, which are currently unknown, by oxidation of tetra(alkyl)lanthanate(III) compounds. Of $[LnR_4^-]$ compounds in which R is an alkyl group, the only ones that have been isolated are those with $R = t$-butyl [18–20], CH_2SiMe_3 [21,22], or $CH(SiMe_3)_2$ [21]; also known are aryl and alkynyl compounds with $R =$ phenyl [23], 2,6-dimethylphenyl [24], or *tert*-butylethynyl [25]. In this work, we report the X-ray crystal structure of $[Li(DME)_3]$-$[Er(t\text{-}Bu)_4]$ (**1**) and describe our attempts to oxidize the terbate complex $[Li(DME)_3][Tb(t\text{-}Bu)_4]$ (**2**).

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2. Results and discussion

2.1. Syntheses of tetra(tert-butyl)metallate complexes of lanthanide elements

The preparation of the salt $[Li(THF)_4][Er(t\text{-}Bu)_4]$ has been reported previously [19]. In our hands, the reported preparation proceeded as described, but we were not able to obtain analytically pure material. Instead, we obtained materials with low carbon and hydrogen analyses that retained chloride. Attempts to prepare the terbium analog $[Li(THF)_4][Tb(t\text{-}Bu)_4]$ gave similar results.

In order to obtain crystalline and analytically pure samples, we have investigated the corresponding $[Li(DME)_3^+]$ salt, where DME is 1,2-dimethoxyethane. Thus, slow addition of a pentane solution of *tert*-butyllithium to a suspension of anhydrous erbium trichloride in DME/pentane at −78 °C, followed by warming to room temperature gives a pink solution, from which pink crystals of $[Li(DME)_3][Er(t\text{-}Bu)_4]$ (**1**) can be obtained by layering a saturated ether solution with pentane and cooling to −20 °C. The material so obtained is analytically pure. The corresponding Tb complex $[Li(DME)_3][Tb(t\text{-}Bu)_4]$ (**2**) can be made similarly, but the cerium analog could not be successfully isolated by the same route.

The IR spectrum of the erbium complex **1** shows ν_{CH} bands due to the *tert*-butyl groups at 2753, 2724, and 2667 cm^{-1}. In comparison, for the $[Li(THF)_4^+]$ salt of this same anion, Evans et al. reported similar bands at 2760, 2730, 2670 and 2620 cm^{-1} [19]. The low frequencies of these C–H modes are characteristic of *tert*-butyl groups [26,27], and are not consequences of CH_3–Li or agostic interactions, as verified by the X-ray structure (see below). The IR spectrum of the terbium analog **2** is essentially identical to that of **1**. ^1H NMR spectra of paramagnetic **1** and **2** contain broad resonances for the *tert*-butyl groups at δ −11 and −76.6, respectively.

2.2. Molecular structure of [Li(DME)$_3$][Er(t-Bu)$_4$] (1)

General crystallographic data, selected bond lengths and angles for **1** are listed in Tables 1 and 2, respectively; views of one of the cations and one of the anions are given in Fig. 1. In the asymmetric unit there are two anions, one full cation, and two half-cations. Except for some disordering of the *tert*-butyl groups on Er(2), the two crystallographically inequivalent anions have very similar metric parameters. The DME ligands about one of the lithium centers are also disordered, but again the coordination geometries of all three independent cations are very similar.

The erbium(III) center in **1** is ligated by four *tert*-butyl groups in an approximately tetrahedral arrangement. The C–Er–C angles between the *tert*-butyl groups range from 108.4(3)° to 111.2(3)° and the Er–C distances range from 2.352(6) to 2.395(6) Å. These values are similar to those seen for the $[Lu(t\text{-}Bu)_4^-]$ anion [18], in which the C–Lu–C angles range from 107.3° to 109.8° and the Lu–C distances range from 2.32(2) to 2.43(2) Å. In $Cp_2Lu(t\text{-}Bu)(THF)$ [28], the Lu–C distance to the *tert*-butyl group was much longer at 2.47(2) Å, probably because the coordination number of this compound is higher.

Each lithium cation in **1** is surrounded by three DME molecules, which form a distorted octahedral coordination

Table 1
Crystal Data for $[Li(DME)_3][Er(t\text{-}Bu)_4]$ (**1**)

Empirical formula	$C_{28}H_{66}ErLiO_6$
Formula weight	673.01
Temperature (K)	193(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	27.309(9)
b (Å)	19.177(6)
c (Å)	27.818(9)
(β) (°)	94.614(6)
V (Å^3)	14521(8)
Z	16
ρ (Mg/m^3)	1.231
Absorption coefficient (mm^{-1})	2.343
F(000)	5648
Crystal size (mm)	0.08 × 0.14 × 0.14
θ Range for data collection (°)	1.92–25.38
Reflections collected	74312
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	72825/649/625
Goodness-of-fit on F^2	0.907
$R^a[I > 2\sigma(I)]$	0.0955
wR_2^b (all data)	0.2459
Largest peak and hole (e Å^{-3})	2.689 and −1.158

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \{\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°) for $[Li(DME)_3][Er(t\text{-}Bu)_4]$ (**1**)

Distances			
Er(1)–C(1)	2.378(6)	C(9)–C(11)	1.493(14)
Er(1)–C(5)	2.352(6)	C(9)–C(12)	1.480(14)
Er(1)–C(9)	2.395(6)	C(13)–C(14)	1.477(14)
Er(1)–C(13)	2.378(6)	C(13)–C(15)	1.501(14)
C(1)–C(2)	1.509(14)	C(13)–C(16)	1.488(14)
C(1)–C(3)	1.500(14)	Li(1)–O(41)	2.089(14)
C(1)–C(4)	1.491(14)	Li(1)–O(42)	2.077(14)
C(5)–C(6)	1.471(14)	Li(1)–O(51)	2.144(15)
C(5)–C(7)	1.485(14)	Li(1)–O(52)	2.083(15)
C(5)–C(8)	1.478(14)	Li(1)–O(61)	2.113(14)
C(9)–C(10)	1.497(14)	Li(1)–O(62)	2.066(15)
Angles			
C(1)–Er(1)–C(5)	108.8(3)	O(42)–Li(1)–O(51)	90.5(6)
C(1)–Er(1)–C(9)	109.3(3)	O(42)–Li(1)–O(52)	163.4(8)
C(1)–Er(1)–C(13)	109.6(3)	O(42)–Li(1)–O(61)	93.8(6)
C(5)–Er(1)–C(9)	111.2(3)	O(42)–Li(1)–O(62)	100.26(6)
C(5)–Er(1)–C(13)	108.4(3)	O(51)–Li(1)–O(52)	77.4(5)
O(41)–Li(1)–O(42)	77.7(5)	O(51)–Li(1)–O(61)	91.2(6)
O(41)–Li(1)–O(51)	100.5(6)	O(51)–Li(1)–O(62)	164.8(7)
O(41)–Li(1)–O(52)	93.2(6)	O(52)–Li(1)–O(61)	97.8(6)
O(41)–Li(1)–O(61)	165.5(8)	O(52)–Li(1)–O(62)	93.9(6)
O(41)–Li(1)–O(62)	92.3(6)	O(61)–Li(1)–O(62)	77.6(5)

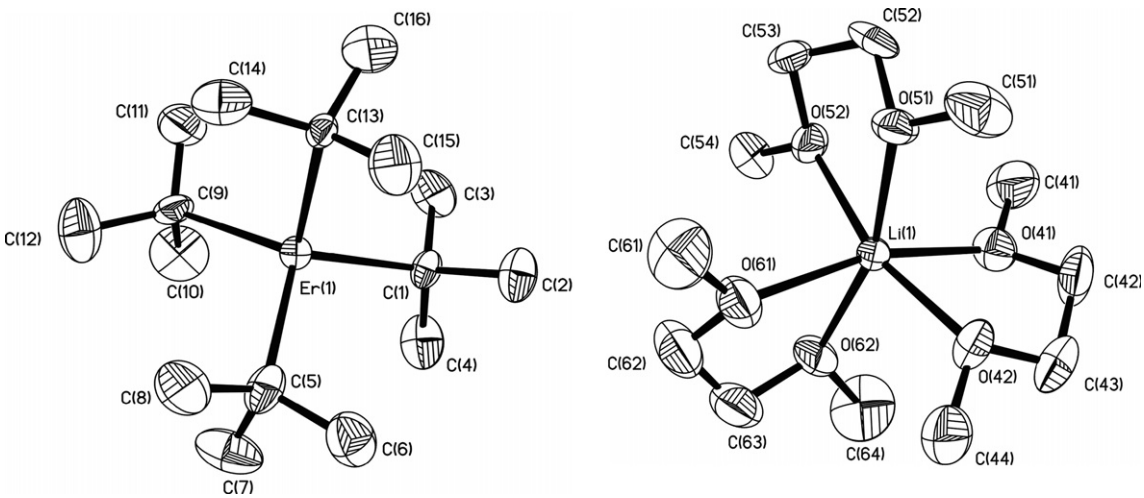

Fig. 1. Molecular structure of $[Li(DME)_3][Er(t\text{-}Bu)_4]$ (**1**); anion at left, cation at right.

sphere. The Li–O distances, which lie between 2.07(2) and 2.14(2) Å, agree with the 2.07(1)–2.17(1) Å range found in $[Li(DME)_3][(Cp_3Sm)_2(\mu\text{-}Cl)]$ [29] and the 2.12(1) Å value in $[Li(DME)_3][Zr(SCMe_3)_5]$ [30]. Some $[Li(DME)_3^+]$ cations are known in which the Li–O distances vary over a wider range: from 2.03(2) to 2.37(2) Å in $[Li(DME)_3][(C_5H_4Me)La(NPh_2)_3]$ [31] and from 2.07(2) to 2.34(2) Å in $[Li(DME)_3][Cp_2Nd(NPh_2)_2]$ [32]. The O–Li–O angles in **1** range from 77.4(5)° to 77.7(5)°, a range that is consistent with previous values for this cation.

Colorless crystals of the terbium analog **2** were also obtained by diffusion of pentane into an ether solution at −20 °C. The crystals were twinned and the diffraction data set, which approximated to cubic symmetry, could not be solved.

2.3. Attempts to prepare tetra(alkyl)lanthanide(IV) species

Alkyl groups are reasonably strongly donating and are well-known to stabilize higher oxidation states of transition metals [33]. Among alkyl groups, *tert*-butyl substituents are among the most strongly donating [34]. In addition, because four *tert*-butyl groups are able to saturate the coordination sphere of a Ln^{3+} metal – as the existence of $[Ln(t\text{-}Bu)_4^-]$ anions shows – they should also be able to saturate the coordination sphere of a somewhat smaller Ln^{4+} metal center. Such Ln^{4+} centers are still large enough to accommodate four *tert*-butyl substituents, as shown by the existence of a tetra(*tert*-butyl) complex of an even smaller ion: the Cr^{4+} center in $Cr(t\text{-}Bu)_4$ [35].

Of all the lanthanide elements, cerium has the most accessible tetravalent oxidation state and is the natural starting point for efforts to prepare a tetra(alkyl) derivative. Although we were unable to isolate pure salts of the tetra(*tert*-butyl)cerate(III) ion (see above), we attempted to prepare this species and oxidize it *in situ*. After treatment of $CeCl_3$ with 4 equivalents of *tert*-butyllithium in THF/ pentane at −78 °C, the mixture was exposed to dry O_2 at −40 °C. No color change occurred. Filtration and removal of the solvent gave an oily liquid, from which no organometallic species could be isolated.

The significance of this result is unclear, in part because the organocerium(III) starting material was not isolated but prepared *in situ*. To complement this result, we investigated whether pure samples of the anionic terbium(III) compound $[Li(DME)_3][Tb(t\text{-}Bu)_4]$ (**2**) react with oxidants to generate $Tb(t\text{-}Bu)_4$. Terbium (along with Pr) has the most accessible +4 oxidation state after cerium, its stability deriving in part from its f^7 electronic configuration.

Injection of 4 equivalents of dioxygen into solutions of **2** immediately caused a color change from colorless to yellow. When this reaction was followed by NMR spectroscopy, the broad ^1H NMR resonance at δ −76.6 due to the starting material disappeared after the addition of oxygen. Two new resonances appeared at δ 0.88 and 4.62, which are due to *iso*-butane (1.67 mol/mol Tb), and *iso*-butene (0.80 mol/mol Tb), respectively [36–38]; these assignments were confirmed by GC analysis. No new NMR resonances appeared that could be ascribed to an organolanthanide product. Similar addition of O_2 to the erbium complex **1** caused an exotherm but did not result in a change in the solution color. The broad ^1H NMR peak at δ −11 due to the starting material disappeared after dioxygen was added, but no peaks due to new organolanthanide species were apparent.

We also examined the action of one-electron chemical oxidants on the terbium compound **2**. Addition of silver acetate or silver chloride to a solution of **2** in diethyl ether resulted in the immediate precipitation of silver metal and a color change similar to that seen upon the addition of oxygen. Neither of these reactions resulted in the formation of pentane-soluble organolanthanide species. Addition of one equivalent of 1,1′-dimethylferrocenium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate to **2** in diethyl ether caused the solution to change color from blue (the color of the ferrocenium salt) to yellow (the color of dimethylferrocene),

but again there was no evidence from the NMR spectra of the formation of a new organolanthanide species.

The present studies suggest that Ln(*t*-butyl)$_4$ species, if they exist, are not readily obtained by direct oxidation of their [Ln(*t*-butyl)$_4^-$] analogs with common oxidizing agents, possibly because the alkyl groups are more easily oxidized than the metal center.

3. Experimental

All syntheses were carried out under an argon atmosphere, using a glove box and Schlenk techniques. Solvents were dried over Na/benzophenone and distilled under nitrogen immediately before use. The starting materials $ErCl_3$ and $TbCl_3$ (99.9% pure, Alfa-Aesar), pentane solutions of *tert*-butyllithium (Aldrich), and oxygen gas (S. J. Smith) were used as received. Microanalyses were performed by the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Nicolet Impact 410 instrument as Nujol mulls between KBr plates. The gas chromatographs were recorded on an Agilent 6890/5973 GCMS equipped with FID and TCD detectors; the inlet temperature was 250 °C, the oven temperature was 275 °C, the carrier gas was He (20.0 mL/min), and the separations were carried out on a 30 m long, 0.32 mm diameter, 1.5 μm thick carbon PLOT column with a deactivated SiO_2 guard column (J&W Scientific). The ^{1}H NMR data were collected on a Varian Unity U400 instrument at 400 MHz. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to tetramethylsilane.

3.1. Tris(1,2-dimethoxyethane)lithium tetra(tert-butyl)erbate, [Li(DME)$_3$][Er(t-Bu)$_4$] (1)

To a slurry of $ErCl_3$ (0.30 g, 1.10 mmol) suspended in 1,2-dimethoxyethane (9 mL) and pentane (5 mL) at −78 °C was added a solution of *tert*-butyllithium (2.82 mL of a 1.7 M solution in pentane, diluted to 35 mL with pentane) dropwise over 90 min. The mixture was stirred for two hours at −78 °C and then slowly warmed to room temperature. After two hours at room temperature, the mixture had separated into a colorless layer (pentane and DME), a pink suspension (crude product), and a white powder (LiCl). The colorless layer was carefully decanted and the solid was washed with pentane (30 mL) and extracted with diethyl ether (2 × 30 mL). The bright pink extract was filtered, concentrated to about 30 mL, layered with pentane (~10 mL), and cooled to −20 °C. The pink prisms were isolated and dried in vacuum. Yield: 0.3 g (40%). Mp: 105 °C (dec). *Anal.* Calc. for $C_{28}H_{66}LiO_6Er$: C, 49.9; H, 9.88; Li, 1.03; Er, 24.9. Found: C, 49.1; H, 9.69; Li, 1.02; Er, 24.1%. ^{1}H NMR (d_8-THF): δ −11 (s, fwhm = 680 Hz, *t*-Bu), δ 3.2 (br, DME). IR (cm^{-1}): 2753 s, 2724 s, 2667 s, 2615 w, 1267 m, 1194 m, 1127 m, 1085 s, 1031 m, 870 s, 784 s.

3.2. Tris(1,2-dimethoxyethane)lithium tetra(tert-butyl)terbate, [Li(DME)$_3$][Tb(t-Bu)$_4$] (2)

The procedure is the same as that for the preparation of **1** except that the reagents used were $TbCl_3$ (0.30 g, 1.13 mmol) and *tert*-butyllithium (2.9 mL of a 1.7 M solution in pentane). The product was isolated as colorless prisms. Yield: 0.31 g (41%). Mp: 80 °C (dec). *Anal.* Calc. for $C_{28}H_{66}LiO_6Tb$: C, 50.6; H 10.0; Li, 1.04; Tb, 23.9. Found. C, 49.8; H, 9.78; Li, 1.02; Tb, 23.4%. ^{1}H NMR (d_8-THF): δ −76.6 (s, fwhm = 300 Hz, *t*-Bu) δ 3.3 (s, MeO), 3.4 (s, OCH_2). IR (cm^{-1}): 2752 s, 2722 s, 2668 s, 1246 s, 1195 s, 1130 s, 1088 s, 1030 m, 985 m, 871 s, 777 s.

3.3. Attempts to oxidize tetra(tert-butyl)terbate, [Li(DME)$_3$][Tb(t-Bu)$_4$] (2)

Colorless crystals of **2** (0.31 g, 0.47 mmol) were dissolved in diethyl ether (30 mL) and O_2 gas (45 mL, 1.85 mmol) was injected by syringe into the solution at room temperature. The solution color changed from colorless to yellow and a small amount of a flocculent precipitate formed. An aliquot was removed for analysis by GCMS, which showed the presence of *iso*-butene and *iso*-butane, in addition to peaks for the solvent and 1,2-dimethoxyethane.

In a separate experiment, a sample of **2** was placed in a 5 mm diameter NMR tube capped with a rubber septum, and the crystals were dissolved in d_8-THF (1 mL) to give a colorless solution. O_2 gas was bubbled into the solution until the solution color became yellow. ^{1}H NMR spectra were taken before and after the introduction of O_2. ^{1}H NMR (d_8-THF): δ 0.88 (s, CH*Me*$_3$), δ 4.62 (s, *CH*$_2$=CMe$_2$). The methine peak of *iso*-butane and the methyl peak of iso-butene were obscured by the resonance at δ 1.72 due to the solvent; peaks at δ 3.44 and 3.28 due to 1,2-dimethoxyethane were also present. By assuming that the 1,2-dimethoxyethane peaks corresponded to 3 mol/(mol Tb), the peak integrations suggested that 1.67 mol of *iso*-butane and 0.80 mol of *iso*-butene were formed per mol of Tb.

3.4. X-ray crystallographic studies [39]

Pink crystals of [Li(DME)$_3$][Er(*t*-Bu)$_4$] (**1**) were grown by diffusion of pentane into a diethyl ether solution at −20 °C. The crystal was twinned but the twinning was non-merohedral, and the two partially overlapping diffraction patterns were indexed separately. Systematic absences for *hkl* ($h + k \neq 2n$), and *h0l* ($l \neq 2n$) were consistent with the space groups *Cc* and *C*2/*c*. The structure was solved in *Cc* and later symmetrized to *C*2/*c*, which is correct space group. No corrections for crystal decay were necessary and, owing to the twinning, no absorption correction was applied. Systematically absent reflections were deleted.

The structure was solved using direct methods by using the SHELXTL software package. The correct positions for the

erbium atoms were deduced by direct-methods from an E-map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were fixed in "idealized" positions and their displacement parameters were tied to those of the attached non-hydrogen atom. The $Li(DME)_3$ cation centered on Li(3) was disordered about the two-fold axis. The disorder involved overlapping atoms, and was modeled in terms of three complete DME molecules, the atoms of which were assigned site occupancy factors of exactly 0.5. In addition, two of the *tert*-butyl groups on Er(2) were disordered over two rotameric conformations. The site occupancy factors for these groups were initially refined, but later set equal to exactly 0.5.

At this point, it became clear that several classes of reflections were affected by the twinning. Reflections with $|l| = 0$, 1, 11, 12, 13, 14, 24, 25, and 26 were systematically more intense than calculated. For reflections with these values of l, the calculated intensity was set equal to the formula $I_{calc} = xI_{hkl} + (1 - x)I_{h'k'l'}$, where $h' = -h - \mathrm{rnd}(l/6)$, $k' = -k$, and $l' = l$, and x is the volume fraction of the major twin individual; "rnd" indicates that the quotient $l/6$ was rounded to the nearest integer. About 100 of the reflections with $|l| = 1$, 11, and 14 were not modeled well by this function ($F^2 > 4.5F^2$), evidently because the two reciprocal lattices were sometimes distinguishable and only one reflection had been measured; such reflections were either reassigned calculated intensities based solely on the major twin, or deleted from the reflection file. The intensities of symmetry-equivalent reflections were *not* averaged, and 72 825 unique reflections were used in the least-squares refinement. The twin ratio refined to 0.682(1) for the major twin individual.

Similarity constraints were imposed on the Li–O, C–O, and C–C distances of the disordered DME ligands attached to Li(3), on the C–C distances in the disordered *tert*-butyl groups on Er(2), and on the displacement parameters of adjacent atoms. In the final cycle of least squares, anisotropic displacement factors were refined for all erbium and for all ordered oxygen carbon atoms; isotropic displacement parameters were refined for the lithium atoms and all disordered oxygen and carbon atoms. Hydrogen atoms were placed in idealized positions (for methyl protons, they were placed in positions staggered with respect to the substituents on the vicinal atom). The displacement parameters for methylene hydrogens were set equal to 1.2 times U_{eq} for the attached carbon; those for methyl hydrogens were set to 1.5 times U_{eq}. Successful convergence was indicated by the maximum shift/error of −0.009 for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final Fourier difference map (2.69 e $Å^{-3}$) was located 1.2 Å from Er(2). A final analysis of variance between observed and calculated structure factors showed that the intensities of many of the reflections with $|l| = 1$, 11, and 14 (and some with $|l| = 2$) were still not modeled well; otherwise, there were no systematic errors.

4. Supplementary material

CCDC 635390 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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