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Synthetic and Structural Studies of a Series of Soluble Cerium(IV) Alkoxide and Alkoxide Nitrate Complexes[1]

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The reactions of $(NH_4)_2Ce(NO_3)_6$ (CAN) with 2–8 equiv of $NaOCMe_3$ in THF and in *tert*-butyl alcohol have been studied. A series of ceric alkoxide complexes of general formula $Ce(OCMe_3)_a(NO_3)_b(\text{solvent})_cNa_d$ ($a = 1–6$; $b = 0–3$; $c = 2, 4$; $d = 0, 2$; $a + b = 4 + d$) have been identified as well as $Ce_2(OCMe_3)_9Na$ and $Ce_3(OCMe_3)_{10}O$. Interconversion of these complexes by treatment with $NaOCMe_3$ or NH_4NO_3 has also been studied. CAN reacts with 3 equiv of $NaOCMe_3$ in THF to form $Ce(OCMe_3)(NO_3)_3(THF)_2$ (**1**). In *tert*-butyl alcohol this reaction forms the $HOCMe_3$ solvate $Ce(OCMe_3)(NO_3)_3(HOCMe_3)_2$ (**1′**). **1** reacts with 1 equiv of $NaOCMe_3$ and CAN reacts with 4 equiv of $NaOCMe_3$ to form $Ce(OCMe_3)_2(NO_3)_2(THF)_2$ (**2**). In *tert*-butyl alcohol solvent, **1′** reacts with $NaOCMe_3$ to form $Ce(OCMe_3)_2(NO_3)_2(HOCMe_3)_2$ (**2′**). **2′** crystallizes from a concentrated toluene solution at −34 °C in space group $P\bar{1}$ (No. 2; C_i^1) with $a = 10.7548$ (56) Å, $b = 11.0853$ (49) Å, $c = 12.4403$ (56) Å, $\alpha = 72.760$ (34)°, $\beta = 88.190$ (39)°, $\gamma = 69.050$ (35)°, $V = 1318.0$ (11) Å^3, and $Z = 2$ for $D_{calcd} = 1.41$ g cm^{-3}. Least-squares refinement of the model based on 4935 observed reflections converged to $R_F = 7.7\%$. If each NO_3 ligand is taken to occupy just one coordination site, the structure of **2′** is that of a distorted octahedron in which identical ligands are trans to each other. $Ce(OCMe_3)_3(NO_3)(THF)_2$ (**3**) can be prepared from **2** or **2′** and $NaOCMe_3$ or from CAN and 5 equiv of $NaOCMe_3$. $Ce(OCMe_3)_4(THF)_2$ (**4**) is prepared from **3** and $NaOCMe_3$ or from CAN and 6 equiv of $NaOCMe_3$. The reaction of **4** with 2 equiv of $NaOCMe_3$ or reaction of CAN with 8 equiv of $NaOCMe_3$ forms $Ce(OCMe_3)_6Na_2(THF)_4$ (**5**). **5** crystallizes from dimethoxyethane (DME) at −34 °C as $Ce(OCMe_3)_6Na_2(DME)_2$ (**5′**) in space group $Pna2_1$ with $a = 20.5337$ (36) Å, $b = 10.9557$ (23) Å, $c = 19.4128$ (38) Å, $V = 4367.1$ (15) Å^3, and $Z = 4$ for $D_{calcd} = 1.22$ g cm^{-3}. Least-squares refinement of the model based on 9092 observed reflections converged to $R_F = 4.9\%$. **5′** contains a distorted-octahedral arrangement of $OCMe_3$ groups around cerium. Each sodium ion is coordinated by one DME ligand and a facial set of three $OCMe_3$ groups of the $Ce(OCMe_3)_6^{2-}$ octahedron. The reaction of **4** with $^1/_2$ equiv of $NaOCMe_3$ forms $Ce_2(OCMe_3)_9Na$ (**6**). Both **4** and **6** in toluene slowly form $Ce_3(OCMe_3)_{10}O$ (**7**). Complex **5** reacts with 5 equiv of NH_4NO_3 to form **1** in quantitative yield.

Introduction

The Ce(IV) ion is a powerful oxidizing agent that has been studied with a variety of substrates.[2–5] Full utilization of Ce(IV) in oxidations has been limited (a) by the small number of conveniently obtained Ce(IV) reagents, (b) by the limited solubility of these Ce(IV) reagents, and (c) by the fact that one cannot readily control selectivity in these oxidations. When selective Ce(IV) oxidations are observed, it is usually due to a fortuitous combination of substrate, solvent, and the most commonly used reagent, ceric ammonium nitrate (CAN).[6]

Recent developments in organoyttrium and organolanthanide chemistry have shown that the chemistry of these metals can be precisely controlled by varying the steric environment around the metal.[7–9] Similar control of Ce(IV) oxidations may be possible if a wider range of soluble Ce(IV) reagents can be identified. Steric control in the organometallic reactions of yttrium and the lanthanides has in large part been accomplished by using cyclopentadienyl ligands, C_5R_5 (R = H, alkyl). Since cyclopentadienyl ligands can reduce Ce(IV),[10–12] they may not be the best coligands in this case. Alkoxide ligands are likely to be good alternatives to cyclopentadienide coligands,[13,14] and therefore, we have extended our study of yttrium and lanthanide alkoxides[14–16] to Ce(IV).

Ce(IV) alkoxide complexes have been known for many years.[17–21] However, their preparation has not been easy and no X-ray structural data had been published in the literature.[22] Recently, simplified procedures for making Ce(IV) alkoxides from readily available CAN have been reported (eq 1 and 2; R = Me, Et, *i*-Pr, *n*-octyl).[23,24]

$$(NH_4)_2Ce(NO_3)_6 + 4ROH + 4NH_3 \rightarrow Ce(OR)_4 + 6NH_4NO_3 \quad (1)$$

$$(NH_4)_2Ce(NO_3)_6 + 4ROH + 6NaOMe \rightarrow Ce(OR)_4 + 6NaNO_3 + 2NH_3 + 6MeOH \quad (2)$$

We were interested in exploring this approach to make Ce(IV) *tert*-butoxide complexes for comparison with the results of our yttrium and lanthanide *tert*-butoxide investigations.[14,15] In those studies, we found that yttrium and lanthanum form polymetallic species such as $La_3(OR)_9(THF)_2$ and $Y_3(OR)_8Cl(THF)_2$ as the

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main species instead of simple monometallic species such as $Ln(OR)_3$ when R = CMe_3. Monometallic species have been crystallographically identified only with sterically bulky alkoxides as in $Ln[OC_6H_3(CMe_3)_2\text{-}2,6]_3$ (Ln = Y,[25] Ce[26]).

Since Ce(IV) and Y(III) have similar radial sizes (0.97 and 1.019 Å, respectively, for 8-coordination[27]), comparison of their alkoxide chemistry could show the effect of the difference in charge. Since Ce(IV) is also similar in size to U(IV) (1.00 Å for 8-coordination[27]), for which crystallographically characterized *tert*-butoxide complexes are known,[28-30] lanthanide vs actinide comparisons could also be made. Accordingly, we report here the synthesis of a series of hexane-soluble Ce(IV) alkoxide and alkoxide nitrate complexes and the reaction chemistry that connects them in the CAN/$NaOCMe_3$ reaction system.

Results

Synthesis. Ceric ammonium nitrate reacts with 2–8 equiv of $NaOCMe_3$ to form a series of ceric alkoxide complexes of general formula $Ce(OCMe_3)_a(NO_3)_b(\text{solvent})_cNa_d$ (a = 1–6; b = 0–3; c = 2, 4; d = 0, 2; $a + b = 4 + d$). Scheme I summarizes the reaction chemistry observed in THF. *tert*-Butyl alcohol can be used as a solvent in place of THF, but the reactions are not as clean and give lower yields.

Scheme I

$$(NH_4)_2Ce(NO_3)_6 + 2NaOCMe_3 \rightarrow \text{“}Ce(NO_3)_4(THF)_2\text{”} + 2NH_3 + 2NaNO_3 + 2HOCMe_3 \tag{a}$$

$$(NH_4)_2Ce(NO_3)_6 + 3NaOCMe_3 \rightarrow \underset{1}{Ce(OCMe_3)(NO_3)_3(THF)_2} + 2NH_3 + 3NaNO_3 + 2HOCMe_3 \tag{b}$$

$$(NH_4)_2Ce(NO_3)_6 + 4NaOCMe_3 \rightarrow \underset{2}{Ce(OCMe_3)_2(NO_3)_2(THF)_2} + 2NH_3 + 4NaNO_3 + 2HOCMe_3 \tag{c}$$

$$(NH_4)_2Ce(NO_3)_6 + 5NaOCMe_3 \rightarrow \underset{3}{Ce(OCMe_3)_3(NO_3)(THF)_2} + 2NH_3 + 5NaNO_3 + 2HOCMe_3 \tag{d}$$

$$(NH_4)_2Ce(NO_3)_6 + 6NaOCMe_3 \rightarrow \underset{4}{Ce(OCMe_3)_4(THF)_2} + 2NH_3 + 6NaNO_3 + 2HOCMe_3 \tag{e}$$

$$(NH_4)_2Ce(NO_3)_6 + 8NaOCMe_3 \rightarrow \underset{5}{Ce(OCMe_3)_6Na_2(THF)_4} + 2NH_3 + 6NaNO_3 + 2HOCMe_3 \tag{f}$$

$$2(NH_4)_2Ce(NO_3)_6 + 13NaOCMe_3 \rightarrow \underset{6}{Ce_2(OCMe_3)_9Na} + 4NH_3 + 12NaNO_3 + 4HOCMe_3 \tag{g}$$

With the exception of the cerium product of reaction a (see Scheme I), all of the cerium products have been characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy, and IR spectroscopy. X-ray crystallography has been used to identify the products of reactions c (as the *tert*-butyl alcohol solvate $Ce(OR)_2(NO_3)_2(HOR)_2$ (**2′**)), f (as the DME solvate $Ce(OR)_6Na_2(DME)_2$ (**5′**)), and g. Further confirmation of the results in Scheme I is available in Scheme II, which shows that the same products can be obtained in a stepwise manner with use of the same overall alkoxide to cerium stoichiometries. Hence, the mono-, di-, and tetraalkoxides **1**, **2**, and **4**, respectively, can be used as precursors just as CAN is used in Scheme I. NH_4NO_3 can be similarly used to replace alkoxide by nitrate, e.g., in the conversion of **5** to **1** (eq o).

Scheme II

$$\underset{1}{Ce(OR)(NO_3)_3(THF)_2} + aNaOR \rightarrow \underset{\substack{2\ (a = 1),\ 3\ (a = 2),\\ 4\ (a = 3)}}{Ce(OR)_{1+a}(NO_3)_{3-a}(THF)_2} + aNaNO_3 \tag{h}$$

$$\underset{1}{Ce(OR)(NO_3)_3(THF)_2} + 5NaOR \rightarrow \underset{5}{Ce(OR)_6Na_2(THF)_4} + 3NaNO_3 \tag{i}$$

$$2\underset{1}{Ce(OR)(NO_3)_3(THF)_2} + 7NaOR \rightarrow \underset{6}{Ce_2(OR)_9Na} + 6NaNO_3 \tag{j}$$

$$\underset{2}{Ce(OR)_2(NO_3)_2(THF)_2} + bNaOR \rightarrow \underset{3\ (b = 1),\ 4\ (b = 2)}{Ce(OR)_{2+b}(NO_3)_{2-b}(THF)_2} + bNaNO_3 \tag{k}$$

$$\underset{4}{Ce(OR)_4(THF)_2} + 2NaOR \rightarrow \underset{5}{Ce(OR)_6Na_2(THF)_4} \tag{l}$$

$$2\underset{4}{Ce(OR)_4(THF)_2} + NaOR \rightarrow \underset{6}{Ce_2(OR)_9Na} \tag{m}$$

$$\text{“}Ce(NO_3)_4(THF)_2\text{”} + 4NaOR \rightarrow \underset{4}{Ce(OR)_4(THF)_2} + 4NaNO_3 \tag{n}$$

$$\underset{5}{Ce(OR)_6Na_2(THF)_4} + 5NH_4NO_3 \rightarrow \underset{1}{Ce(OR)(NO_3)_3(THF)_2} + 5ROH + 2NaNO_3 + 5NH_3 \tag{o}$$

$$R = CMe_3$$

The first step in Scheme I, reaction a, has the least documentation since the product is an oil that has no NMR-observable ligand protons or carbon atoms (except coordinated THF). The observed evolution of NH_3 and the formation of a precipitate with a weight consistent with that expected for 2 equiv of $NaNO_3$ supports reaction a as written. Further evidence for the "$Ce(NO_3)_4(THF)_x$" product is that it reacts with 4 equiv of $NaOCMe_3$ to form $Ce(OCMe_3)_4(THF)_2$ (**4**; reaction n). We cannot exclude the possibility that some ammonium salts are also formed in reaction a, e.g., $(NH_4)_xCe(NO_3)_4(OCMe_3)_x(THF)_y$. However, the main initial step in the CAN/$NaOCMe_3$ system appears to be an acid–base reaction in which 2 equiv of $NaOCMe_3$ reacts with the NH_4^+ ions of CAN to form NH_3 and $HOCMe_3$. $NaNO_3$ is also produced.

Subsequent addition of $NaOCMe_3$ to this system replaces NO_3 groups by $OCMe_3$ and forms additional $NaNO_3$. This gives, sequentially, the monoalkoxide $Ce(OCMe_3)(NO_3)_3(THF)_2$ (**1**), the dialkoxide $Ce(OCMe_3)_2(NO_3)_2(THF)_2$ (**2**), the trialkoxide $Ce(OCMe_3)_3(NO_3)(THF)_2$ (**3**), and the tetraalkoxide $Ce(OCMe_3)_4(THF)_2$ (**4**). When all four NO_3^- groups of CAN are replaced, additional $OCMe_3^-$ groups attach to cerium to make the anionic complexes $Ce(OCMe_3)_6Na_2(THF)_4$ (**5**) and $Ce_2(OCMe_3)_9Na$ (**6**). The latter complex is analogous to the uranium alkoxide $U_2(OCMe_3)_9K$.[30]

As shown in Scheme III, both $Ce(OCMe_3)_4(THF)_2$ and $Ce_2(OCMe_3)_9Na$ slowly convert to $Ce_3(OCMe_3)_{10}O$ (**7**) in toluene. The trimetallic cerium complex is analogous to the uranium alkoxide oxide $U_3(OCMe_3)_{10}O$.[26,29]

Scheme III

$$\underset{4}{Ce(OCMe_3)_4(THF)_2} \xrightarrow[\text{2–3 days, room temp}]{\text{toluene}} \underset{7}{Ce_3(OCMe_3)_{10}O} \tag{p}$$

$$\underset{6}{Ce_2(OCMe_3)_9Na} \xrightarrow[\text{2 weeks, room temp}]{\text{toluene}} \underset{7}{Ce_3(OCMe_3)_{10}O} \tag{q}$$

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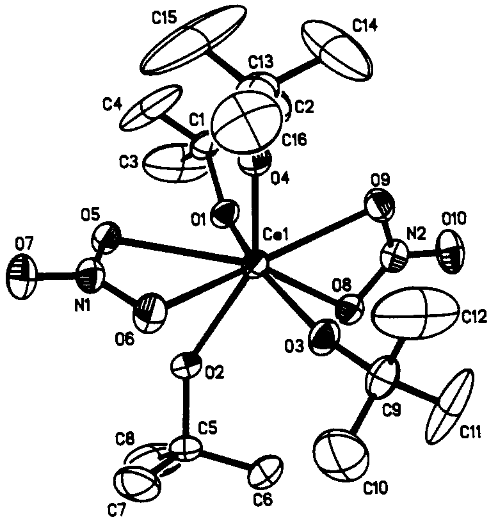

Figure 1. ORTEP plot of $Ce(OCMe_3)_2(NO_3)_2(HOCMe_3)_2$ (**2′**) with probability ellipsoids at 30%.

Table I. Selected Bond Distances (Å) and Angles (deg) for $Ce(OCMe_3)_2(NO_3)_2(HOCMe_3)_2$ (**2′**)

Ce(1)–O(1)	2.521 (5)	Ce(1)–O(5)	2.593 (5)
Ce(1)–O(2)	2.529 (5)	Ce(1)–O(6)	2.515 (6)
Ce(1)–O(3)	2.026 (5)	Ce(1)–O(8)	2.583 (5)
Ce(1)–O(4)	2.023 (5)	Ce(1)–O(9)	2.529 (6)
O(1)–C(1)	1.489 (9)	O(6)–N(1)	1.277 (9)
O(2)–C(5)	1.481 (9)	O(7)–N(1)	1.207 (8)
O(3)–C(9)	1.419 (10)	O(8)–N(2)	1.260 (8)
O(4)–C(13)	1.398 (11)	O(9)–N(2)	1.254 (8)
O(5)–N(1)	1.258 (8)	O(10)–N(2)	1.235 (8)
O(1)–Ce(1)–O(2)	71.8 (2)	O(4)–Ce(1)–O(9)	79.0 (2)
O(1)–Ce(1)–O(3)	149.9 (2)	O(5)–Ce(1)–O(6)	50.0 (2)
O(1)–Ce(1)–O(4)	99.3 (2)	O(5)–Ce(1)–O(8)	137.1 (2)
O(1)–Ce(1)–O(5)	75.7 (2)	O(5)–Ce(1)–O(9)	142.6 (2)
O(1)–Ce(1)–O(6)	124.1 (2)	O(6)–Ce(1)–O(8)	143.5 (2)
O(1)–Ce(1)–O(8)	69.3 (2)	O(6)–Ce(1)–O(9)	155.7 (2)
O(1)–Ce(1)–O(9)	77.3 (2)	O(8)–Ce(1)–O(9)	49.8 (2)
O(2)–Ce(1)–O(3)	98.9 (2)	Ce(1)–O(1)–C(1)	138.5 (5)
O(2)–Ce(1)–O(4)	150.4 (2)	Ce(1)–O(2)–C(5)	138.0 (5)
O(2)–Ce(1)–O(5)	70.1 (2)	Ce(1)–O(3)–C(9)	168.9 (6)
O(2)–Ce(1)–O(6)	77.5 (2)	Ce(1)–O(4)–C(13)	170.2 (7)
O(2)–Ce(1)–O(8)	75.8 (2)	Ce(1)–O(5)–N(1)	94.9 (4)
O(2)–Ce(1)–O(9)	124.1 (2)	Ce(1)–O(6)–N(1)	98.2 (4)
O(3)–Ce(1)–O(4)	101.4 (3)	Ce(1)–O(8)–N(2)	94.9 (4)
O(3)–Ce(1)–O(5)	129.1 (2)	Ce(1)–O(9)–N(2)	97.7 (4)
O(3)–Ce(1)–O(6)	79.3 (2)	O(5)–N(1)–O(6)	116.8 (6)
O(3)–Ce(1)–O(8)	80.7 (2)	O(5)–N(1)–O(7)	121.7 (7)
O(3)–Ce(1)–O(9)	85.6 (2)	O(6)–N(1)–O(7)	121.5 (7)
O(4)–Ce(1)–O(5)	80.4 (2)	O(8)–N(2)–O(9)	117.6 (6)
O(4)–Ce(1)–O(6)	85.4 (2)	O(8)–N(2)–O(10)	122.0 (7)
O(4)–Ce(1)–O(8)	128.6 (2)	O(9)–N(2)–O(10)	120.4 (7)

X-ray Crystal Structures. The structure of $Ce(OCMe_3)_2(NO_3)_2(HOCMe_3)_2$ (**2′**) is shown in Figure 1, and selected bond distances and angles are given in Table I. The cerium atom in this complex is surrounded by eight oxygen atoms. However, rather than describing this complex in terms of eight-coordinate geometries, we shall follow the common practice of considering each of the small-bite NO_3 ligands as occupying one coordination site.[31-36] Hence, we will consider the cerium atom to be six-coordinate. As we shall see, this is reasonable in terms of the bond length and coordination number discussions that follow. The simplest view of **2′** as a six-coordinate species is as an octahedron significantly distorted by the difference in the three types of ligands.

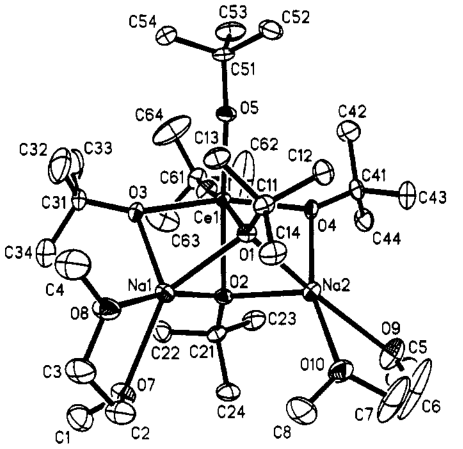

Figure 2. ORTEP plot of $Ce(OCMe_3)_2(\mu\text{-}OCMe_3)_2(\mu_3\text{-}OCMe_3)_2Na_2(DME)_2$ (**5′**) with probability ellipsoids at 30%.

Table II. Selected Bond Distances (Å) and Angles (deg) for $Ce(OCMe_3)_2(\mu\text{-}OCMe_3)_2(\mu_3\text{-}OCMe_3)_2Na_2(DME)_2$ (**5′**)

Ce(1)–O(1)	2.380 (4)	Ce(1)–O(2)	2.367 (4)
Ce(1)–O(3)	2.229 (4)	Ce(1)–O(4)	2.231 (4)
Ce(1)–O(5)	2.136 (4)	Ce(1)–O(6)	2.146 (4)
Na(1)–O(2)	2.410 (5)	Na(1)–O(1)	2.357 (5)
Na(1)–O(7)	2.500 (6)	Na(1)–O(3)	2.371 (5)
Na(2)–O(1)	2.422 (5)	Na(1)–O(8)	2.577 (6)
Na(2)–O(4)	2.338 (5)	Na(2)–O(2)	2.347 (5)
Na(2)–O(10)	2.380 (6)	Na(2)–O(9)	2.657 (7)
Na(1)–Ce(1)–Na(2)	68.3 (1)	O(1)–Ce(1)–O(2)	70.8 (1)
O(1)–Ce(1)–O(3)	83.6 (1)	O(2)–Ce(1)–O(3)	82.4 (1)
O(1)–Ce(1)–O(4)	82.1 (1)	O(2)–Ce(1)–O(4)	83.1 (1)
O(3)–Ce(1)–O(4)	162.2 (1)	O(1)–Ce(1)–O(5)	96.0 (1)
O(2)–Ce(1)–O(5)	166.8 (1)	O(3)–Ce(1)–O(5)	95.5 (2)
O(4)–Ce(1)–O(5)	96.3 (2)	O(1)–Ce(1)–O(6)	166.7 (1)
O(2)–Ce(1)–O(6)	96.2 (2)	O(3)–Ce(1)–O(6)	97.6 (2)
O(4)–Ce(1)–O(6)	94.1 (2)	O(5)–Ce(1)–O(6)	97.0 (2)
Ce(1)–Na(1)–Na(2)	55.7 (1)	O(1)–Na(1)–O(2)	70.5 (1)
O(1)–Na(1)–O(3)	81.1 (2)	O(2)–Na(1)–O(3)	78.6 (2)
O(1)–Na(1)–O(7)	145.3 (2)	O(2)–Na(1)–O(7)	106.0 (2)
O(3)–Na(1)–O(7)	133.1 (2)	O(1)–Na(1)–O(8)	109.9 (2)
O(2)–Na(1)–O(8)	168.0 (2)	O(3)–Na(1)–O(8)	113.4 (2)
O(7)–Na(1)–O(8)	66.5 (2)	Ce(1)–Na(2)–Na(1)	56.0 (1)
Na(1)–O(1)–C(11)	123.7 (3)	Na(1)–Na(2)–O(10)	93.6 (2)
Na(1)–O(2)–C(21)	124.1 (4)	Ce(1)–O(1)–C(11)	133.2 (3)
Na(1)–O(3)–C(31)	119.3 (4)	Ce(1)–O(2)–C(21)	135.0 (4)
Ce(1)–O(4)–C(41)	147.1 (4)	Ce(1)–O(3)–C(31)	151.5 (4)
Ce(1)–O(5)–C(51)	172.5 (4)	Ce(1)–O(6)–C(61)	172.8 (4)

The two nitrate ligands occupy trans positions in the distorted octahedron. The bonding parameters of the NO_3 groups are typical[34] in that they are planar, the N–O bonds involving the oxygen atoms not attached to the metal are shorter than the other N–O bonds, and the O–N–O angles in which both oxygen atoms are attached to cerium are smaller than the other O–N–O angles. The dihedral angle between the planes of the trans nitrate groups is 86.7°. The average Ce–O(nitrate) distance of 2.56 (3) Å is in the range of average Ce^{IV}–O(nitrate) distances in the Ce(IV) nitrates $(NH_4)_2Ce(NO_3)_6$ (2.508 (7) Å)[37] and $Ce(NO_3)_4(OPPh_3)_2$ (2.48 (2) Å),[36] both of which are also six-coordinate, assuming NO_3 occupies one coordination site.

The *tert*-butyl alcohol ligands can be distinguished from the *tert*-butoxide ligands by their Ce–O distances and the Ce–O–C angles. The groups containing O(3) and O(4) have short Ce–O distances (2.026 (5) and 2.023 (5) Å) and large Ce–O–C angles (168.9 (6) and 170.2 (7)°). The groups containing O(1) and O(2)

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Table III. ^1H and ^{13}C NMR Data (ppm) for **1**–**7** in C_6D_6

	^1H NMR			^{13}C NMR		
	OC*Me*$_3$	*H*OCMe$_3$	THF	OC*Me*$_3$	O*C*Me$_3$	THF
$Ce(NO_3)_4(THF)_2$			1.34, 3.65			24.30, 70.05
$Ce(OCMe_3)(NO_3)_3(THF)_2$ (**1**)	1.28 s		1.34, 3.93	31.63	89.20	24.36, 69.57
$Ce(OCMe_3)(NO_3)_3(HOCMe_3)_2$ (**1′**)	1.32 br s	3.89 br s		31.39	86.68	
$Ce(OCMe_3)_2(NO_3)_2(THF)_2$ (**2**)	1.26 s		1.35, 3.90	31.64	89.32	24.33, 71.02
$Ce(OCMe_3)_2(NO_3)_2(HOCMe_3)_2$ (**2′**)	1.27 br s	3.89 br s		30.18	86.20	
$Ce(OCMe_3)_3(NO_3)(THF)_2$ (**3**)	1.31 s		1.44, 3.67	32.45	82.54	24.70, 67.73
$Ce(OCMe_3)_4(THF)_2$ (**4**)	1.58 s		1.62, 4.62	33.24	79.32	24.93, 71.65
$[(THF)_2Na]_2Ce(OCMe_3)_6$ (**5**)	1.63 s		1.28, 3.45	34.69	73.24	24.40, 67.23

	^1H NMR			^{13}C NMR	
	OC*Me*$_3$	μ-OC*Me*$_3$	μ_3-OC*Me*$_3$	OC*Me*$_3$	O*C*Me$_3$
$NaCe_2(OCMe_3)_9$ (**6**)	1.60	1.87	1.75	33.67, 33.71	74.25, 75.49
		1.37		34.57, 35.05	76.53, 81.96
$Ce_3(OCMe_3)_{10}O$ (**7**)	1.44	1.92	1.95	32.86, 33.03	74.10, 77.35
	1.45			33.75, 34.13	82.47, 82.90

have longer Ce–O bonds (2.521 (5) and 2.529 (5) Å) and smaller Ce–O–C angles (138.5 (5) and 138.0 (5)°). The groups containing O(3) and O(4) are assigned to the alkoxide groups since the anionic ligand should form a shorter bond to cerium than the neutral species and large M–O–C angles are common for early-transition-metal and f-element alkoxides.[29,30,38,39] It is interesting to note that, within the limits of the distorted octahedron, the alkoxide ligands are oriented cis to each other rather than trans.

The structure of $Ce(OCMe_3)_2(\mu\text{-}OCMe_3)_2(\mu_3\text{-}OCMe_3)_2Na_2(DME)_2$ (**5′**) is shown in Figure 2, and selected bond distances and angles are given in Table II. Complex **5′** is unambiguously six-coordinate around the cerium atom. Like **2′**, complex **5′** has a distorted-octahedral geometry. The cerium atom is coplanar to within 0.08 Å with each of the three sets of four oxygen atoms that define the three mutually perpendicular planes of the octahedron. The three planes make dihedral angles of 90.1, 89.5, and 97.1° with each other.

The distortions in the octahedral geometry arise despite the fact that the six ligands are all *tert*-butoxides because two of the ligands are terminal, two are doubly bridging, and two are triply bridging. Each set has a different Ce–O bond length average, 2.141 (4), 2.230 (4), and 2.374 (4) Å, respectively. An increase in bond length with increased bridging is common for metal alkoxides.[14,15,40] A comparison of the average Ce^{IV}–O(terminal *tert*-butoxide) distances in **2′** and **5′**, i.e., 2.025 (5) and 2.141 (4) Å, shows that it is reasonable to consider **2′** as six-coordinate. If **2′** were considered as eight-coordinate, then the higher coordinate complex would have much shorter $Ce–O(OCMe_3)$ bonds, which is contrary to the usual correlations between bond lengths and coordination number.[27]

Each sodium atom in **5′** is five-coordinate. The geometry of the five oxygen donor atoms is not close to either square pyramidal or trigonal bipyramidal. The average $Na–O(\mu\text{-}OCMe_3)$ and $Na–O(\mu_3\text{-}OCMe_3)$ distances, 2.35 (2) and 2.38 (3) Å, respectively, follow the order expected for increased bridging, but there is considerable overlap in the ranges, 2.338 (5)–2.371 (5) Å for μ-OCMe$_3$ and 2.347 (5)–2.422 (5) Å for μ_3-OCMe$_3$. These distances are in the range observed for $Na–O(\mu_3\text{-}OCMe_3)$ distances in $(NaOCMe_3)_9$, 2.191 (18)–2.501 (16) Å, and $(NaOCMe_3)_6$, 2.176 (17)–2.335 (16) Å.[41]

The structure of $Ce_2(OCMe_3)_4(\mu\text{-}OCMe_3)_3(\mu_3\text{-}OCMe_3)_2Na$ (**6**) is shown in Figure 3. This complex is analogous to $U_2(OCMe_3)_9K$.[30] The cell constants of **6** are very similar to those of the uranium complex, although it is not isostructural.[42] Some disorder in the alkali-metal part of the structure has prevented a satisfactory refinement of the model, and consequently bond distance and angle data are not included in this discussion. The structural data do unambiguously establish the connectivity of the atoms in **6**, and, as in **2′** and **5′**, the cerium atoms are six-coordinate.

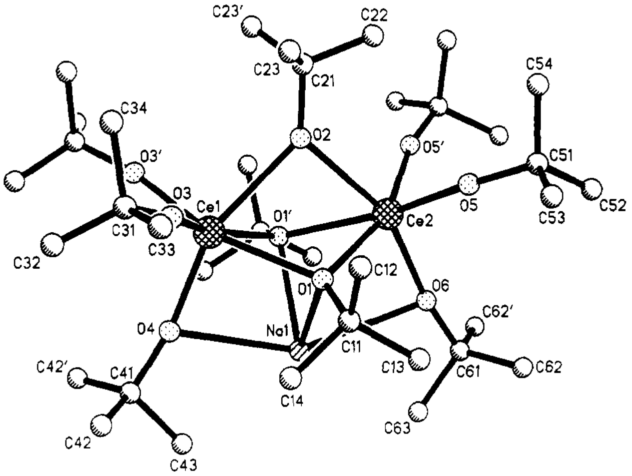

Figure 3. Ball and stick diagram of the structure of $Ce_2(OCMe_3)_4(\mu\text{-}OCMe_3)_3(\mu_3\text{-}OCMe_3)_2Na$ (**6**). The bridging *tert*-butoxide group defined by O(2), C(21), C(22), and C(23) is disordered and was refined with an idealized tetrahedral geometry.

NMR Studies. ^1H and ^{13}C NMR data on **1**–**7** are given in Table III. The spectra of **1**, **1′**, **2**, **2′**, **3**, **4**, and **5** all contain just one alkoxide resonance. This is expected for the monoalkoxides **1** and **1′** and for **2** and **2′**, since the structure of **2′** has the *tert*-butoxide ligands in equivalent positions. The NMR spectra of **4** suggest a symmetrical structure in solution. Although the X-ray crystal structure of **5′** contains terminal and μ- and μ_3-alkoxide ligands, the NMR data indicate that this structure is not maintained in solution. No evidence for free NaOCMe$_3$ is observed in the NMR spectra, however. The single ^1H NMR resonance observed for $Ce(OCMe_3)_3(NO_3)(THF)_2$ (**3**) suggests that the structure is nonrigid in solution. We have found that samples of **3** that have less than 2 equiv of THF per cerium have much more complicated ^1H NMR spectra. THF-free samples of **3** have five alkoxide resonances in their ^1H and ^{13}C NMR spectra, which suggests a more highly associated structure. Addition of THF to these samples restores the single-resonance ^1H NMR spectrum of fully solvated **3**. Both $Ce_2(OCMe_3)_9Na$ (**6**) and $Ce_3(OCMe_3)_{10}O$ (**7**) display several resonances that suggest they maintain their polymetallic nature in solution. The ^1H NMR spectrum of **7** is consistent with the trend found for yttrium and lanthanum alkoxides[14,15] that μ_3-OCMe$_3$ groups resonate at lower field than μ-OCMe$_3$ groups which are at lower field than terminal OCMe$_3$ ligands. The ^1H NMR spectrum of **6** does not follow this trend for the alkoxide ligands attached to sodium. The 1.87 ppm resonance attributed to the μ-OCMe$_3$ group attached only

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(42) Complex **6** crystallizes in space group *Pbcm* with *a* = 14.080 (2) Å, *b* = 19.966 (3) Å, *c* = 16.707 (3) Å, *V* = 4696.6 (14) Å^3, and *Z* = 4 for D_{calcd} = 1.36 g cm^{-3}.

to cerium atoms is at lower field than the 1.60 ppm resonance for the terminal Ce–$OCMe_3$ units, as expected. However, the μ-$OCMe_3$ groups, which connect sodium and cerium, resonate at 1.37 ppm and the μ_3-$OCMe_3$ group, which bridges all three metals, resonates at 1.75 ppm. These data suggest that alkoxide groups attached to sodium as well as a lanthanide will be found at higher field than those attached only to lanthanide ions.

Discussion

Synthesis. The synthetic chemistry observed in this CAN/$NaOCMe_3$ system is consistent with established lanthanide reaction chemistry in that sequential replacement of one anionic ligand by another can be controlled by varying the stoichiometry. For example, lanthanide trichlorides, $LnCl_3$, can be converted to $(C_5H_5)LnCl_2(THF)_3$ (**8**),[43] $(C_5H_5)_2LnCl(THF)$ (**9**),[44] and $(C_5H_5)_3Ln(THF)$ (**10**)[45] by reaction with 1, 2 and 3 equiv, respectively, of $C_5H_5^-$ and **8** and **9** can be converted to **10** by adding more $C_5H_5^-$. An anionic cyclopentadienyl complex, $(C_5H_5)_4Ln^-$, has also been reported to form in the presence of excess $C_5H_5^-$.[11] Homoleptic anionic complexes such as **5** are well-known for the trivalent lanthanides with unidentate ligands, e.g. $Ln(t\text{-}C_4H_9)_4^-$ [46,47] and $LnMe_6^{3-}$.[48,49]

In contrast to the above $LnCl_3/C_5H_5^-$ system in which a polydentate ligand is displacing a monodentate ligand, the CAN/$NaOCMe_3$ reaction involves replacement of the chelating bidentate NO_3 ligand by the monodentate $OCMe_3$. Initially, it seemed to us that this could lead to a more complicated reaction system. However, the insolubility of $NaNO_3$ versus $NaOCMe_3$ in THF probably leads to the clean reaction chemistry observed. The fact that lower yields and other products form in the reactions done in *tert*-butyl alcohol supports this idea.

The formation of $Ce_3(OCMe_3)_{10}O$ (**7**) from $Ce(OCMe_3)_4(THF)_2$ and $Ce_2(OCMe_3)_9Na$ is also quite reasonable. The uranium analogue of **7** is readily formed in the uranium *tert*-butoxide systems.[28-30] Hence, this trimetallic oxide appears to be a common, stable end product with these tetravalent metals.

Structure. Coordination Number. If one assumes that the small-bite NO_3 ligand occupies one coordination site, the structures of **2′**, **5′**, and **6** uniformly contain six-coordinate cerium ions. As discussed earlier, the NO_3 assumption has many precedents[31-36] and is consistent with the relative Ce–O bond lengths in **2′** and **5′**. The six-coordination observed in these Ce(IV) *tert*-butoxide complexes is also consistent with that observed in other structurally characterized La(III) and Y(III) *tert*-butoxide complexes.[14,15] Six-coordination is found for the metal in all of these structures and, therefore, appears to be optimal with $OCMe_3$ ligands and these metals.

Monometallic vs Trimetallic. Superficially, there is less similarity between Ce(IV) and La(III) or Y(III) in terms of the metal nuclearity of their *tert*-butoxide complexes. The Ce(IV) complexes **2′** and **5′** are monocerium species, and the NMR data on **1–5** are consistent with monometallic complexes. In contrast, fully characterized neutral La(III) and Y(III) *tert*-butoxide complexes are all at least trimetallic.[14,15] One might expect this difference since the larger charge on Ce(IV) would allow it to be surrounded by more ligands, leading to less bridging and lower nuclearity. However, this is not the explanation, since six-coordination is found in both the Ce(IV) and La(III) and Y(III) complexes. In the case of the nitrate-containing complexes, it is possible that the nitrate ligand favors the monometallic species. Hence, there may be monometallic mixed-ligand alkoxide nitrate analogues for yttrium and the trivalent lanthanides. Nitrate and related ligands may provide an effective means to destabilize the polymetallic nature of alkoxide complexes of these metals. The fact that THF-free **3** gives NMR spectra consistent with a polymetallic species suggests that subtle factors may influence the degree of association in this class of complexes.

It is interesting to note that if the sodium ions are included in the metal count in the nitrate-free structures **5′** and **6**, then trimetallic units are present as in the yttrium and lanthanum *tert*-butoxide complexes. Hence, the $CeNa_2$ and Ce_2Na triangles in **5′** and **6**, respectively, can be compared to the La_3 and Y_3 triangles in $La_3(\mu_3\text{-}OCMe_3)_2(\mu\text{-}OCMe_3)_3(OCMe_3)_4(THF)_2$ (**11**) and $Y_3(\mu_3\text{-}OCMe_3)(\mu_3\text{-}Cl)(\mu\text{-}OCMe_3)_3(OCMe_3)_4(THF)_2$ (**12**).[14] All four structures have triply bridging ligands above and below the triangle of metals. **6**, **11**, and **12** each have three doubly bridging alkoxides linking the three metals together in the plane. **5′** has only two of these μ-$OCMe_3$ groups because the lower coordination number requirement of sodium means a $Na(\mu\text{-}OCMe_3)Na$ bridge is unnecessary. **5′**, **10**, and **11** each have two terminal ligands on each metal. **6** has no terminal ligands on sodium, again due to its lower coordination number requirements. Hence, **5′** and **6** show yet another variation of the basic $M_3(\mu_3\text{-}OR)(\mu_3\text{-}X)(\mu\text{-}OR)_3$ building-block unit common in yttrium and lanthanum chemistry.[14]

These structures along with the existence of the polymetallic $(NaOCMe_3)_9$ and $(NaOCMe_3)_6$[41] suggest there may be a continuum of polymetallic $Ce_xNa_y(OCMe_3)_z$ complexes. Note that the total charge of the metals in complex **6**, i.e., +9, matches that in **11** and **12**. This suggests that Ce(IV) species may be useful in the formation of polymetallic mixed-metal complexes involving metals with oxidation states lower than +3.

Ce(IV) vs U(IV). The isolation of the Ce(IV) analogues of $U_2(OCMe_3)_9K$ and $U_3(OCMe_3)_{10}O$,[28,29] i.e., **6** and **7**, shows obvious connections between these metals. Another common feature is the preference for six-coordination. The higher oxidation state chemistry available to uranium will obviously lead to differences.[30] The more extensive monometallic chemistry of Ce(IV) *tert*-butoxides, i.e., **1–5**, may arise from the availability of the CAN starting material. In other words, U(IV) analogues to **1–5** may be available by starting from $U(NO_3)_6^{2-}$.[50]

Summary

An extensive series of Ce(IV) *tert*-butoxide complexes has been identified, which shows that the $OCMe_3$ group is a viable ligand to stabilize and solubilize Ce(IV). The reactivity of these Ce(IV) complexes and the opportunity to control their reactivity by use of steric factors will be the subject of another study. The present study shows that the coordination chemistry of Ce(IV) is similar to that of La(III) and Y(III), yet its difference in charge offers possibilities to vary the metallic components of a polymetallic species without changing the overall charge of the complex. This research also shows that comparison of Ce(IV) and U(IV) *tert*-butoxide chemistry may suggest new approaches in both areas.

Experimental Section

The synthesis and subsequent manipulations of the complexes described below were conducted with the rigorous exclusion of air and water by using Schlenk-line and glovebox (Vacuum Atmospheres HE-553 Dri-Lab) techniques. The mixed alkoxide nitrate complexes are more oxygen sensitive than the pure alkoxides. The NMR spectra of **4**, **5**, **6**, and **7** remained unchanged when solutions of these complexes in NMR tubes were exposed to dry oxygen.

Materials. Toluene, hexane, and THF were distilled from sodium benzophenone ketyl, and *tert*-butyl alcohol was distilled from CaH_2. Dimethoxyethane (DME) and C_6D_6 were vacuum-transferred from sodium benzophenone ketyl. Anhydrous ceric ammonium nitrate was obtained from Rhone-Poulenc and was stored under nitrogen until used. Sodium *tert*-butoxide was prepared from the reaction of sodium hydride with *tert*-butyl alcohol and was dried at 10^{-5} Torr before use.

Physical Measurements. Infrared spectra were obtained as previously described.[51] ^1H NMR spectra were recorded by using a Bruker WM

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250-MHz instrument and were referenced by assigning the residual protons in C_6D_6 to 7.15 ppm. ^{13}C spectra were recorded on a General Electric QE 300-MHz spectrometer and were referenced by assigning benzene to 127 ppm. Complexometric titrations were obtained as previously described,[52] except that an excess of ascorbic acid was added to the solution before the titration to reduce all Ce(IV) to Ce(III) (3 mol ascorbic acid/mol of cerium). Complete elemental analyses were obtained from Analytische Laboratorien, Engelskirchen, West Germany. Complexes **1**–**5** lose some coordinated solvent by rotary evaporation during the preparation of analytical samples. As a result, the observed metal analyses are higher than those calculated for the fully solvated species. ^1H and ^{13}C NMR data are given in Table III.

Synthesis. The initial syntheses were carried out in *tert*-butyl alcohol. It was found that much of the reaction product was not soluble in alkanes and arenes. When the toluene-insoluble product was dissolved in THF, $NaNO_3$ precipitation occurred and additional amounts of alkane-soluble products were formed. Subsequent syntheses were carried out in THF with improved yields and shorter reaction times and without the formation of toluene-insoluble byproducts.

$Ce(OCMe_3)(NO_3)_3(THF)_2$ (1). Under nitrogen, $NaOCMe_3$ (1.05 g, 10.9 mmol) dissolved in 100 mL of THF in a Schlenk flask was added by cannula to a suspension of CAN (2.00 g, 3.65 mmol) in 50 mL of THF in a Schlenk flask. Gas evolution was observed. After it was stirred for 2 h, the mixture was filtered to give a white precipitate (0.916 g, 99% of expected $NaNO_3$). Removal of solvent from the filtrate by rotary evaporation gave an oily red solid. Extraction with toluene (100 mL) and removal of the solvent by rotary evaporation left **1** as a red oil (1.12 g, 56%). Anal. Calcd for the disolvate $C_{12}H_{25}CeN_3O_{12}$: Ce, 25.7. Calcd for the monosolvate: Ce, 29.7. Found: Ce, 28.0. IR (KBr): 2970 s, 1510 s br, 1460 m, 1360 s, 1260 m, 1170 s, 1100 w, 1020 s, 930 s br cm^{-1}.

$Ce(OCMe_3)(NO_3)_3(HOCMe_3)_2$ (1′). Under nitrogen, $NaOCMe_3$ (262 mg, 2.73 mmol) dissolved in 50 mL of *tert*-butyl alcohol in a Schlenk flask was added by cannula to a stirred suspension of CAN (500 mg, 0.913 mmol) in 25 mL of *tert*-butyl alcohol in a Schlenk flask. Both flasks were maintained at 30–35 °C during the transfer by using warm-water baths. Gas evolution was observed upon addition of $NaOCMe_3$. After the addition of $NaOCMe_3$ was complete, the reaction was allowed to stir for 20 h in a warm-water bath at 30–35 °C. The mixture was filtered to remove a yellow precipitate (146 mg, 63% of expected $NaNO_3$). Removal of solvent from the filtrate by rotary evaporation gave a red oily solid, which was brought into the glovebox and extracted with toluene (60 mL). Removal of the solvent by rotary evaporation left **1′** as a red microcrystalline powder (90 mg, 18%). Anal. Calcd for the disolvate $CeC_{12}H_{29}N_3O_{12}$: Ce, 25.6; C, 26.3; H, 5.2; N, 7.7. Calcd for $Ce(OCMe_3)(NO_3)_3{\cdot}1.25HOCMe_3$: Ce, 28.49; C, 21.96; H, 4.42; N, 8.54. Found: Ce, 28.2; C, 21.7; H, 4.3; N, 8.5. IR (KBr): 2970 s, 1510 s br, 1460 m, 1360 s, 1260 m, 1170 s, 1100 w, 1020 s, 930 s br cm^{-1}. THF was added to the toluene-insoluble part of the reaction mixture. When the mixture stood for 30 min, white precipitates formed (89 mg). Removal of solvent and extraction with toluene gave **1** (78 mg, 15%).

Conversion of 1′ to 1. **1′** (50 mg, 0.09 mmol) was dissolved in 5 mL of THF. After the solution was stirred for 5 min, the solvent was removed by rotary evaporation to give **1** (identified by ^1H NMR spectroscopy) in quantitative yield.

$Ce(OCMe_3)_2(NO_3)_2(THF)_2$ (2). CAN (2.00 g, 3.65 mmol) in 50 mL of THF was reacted with $NaOCMe_3$ (1.402 g, 14.59 mmol) in 75 mL of THF by following the procedure for **1**. A white precipitate (1.017 g, 82% if $NaNO_3$) was separated by filtration, and removal of solvent from the filtrate gave an oily orange solid. Extraction of this solid with 75 mL of toluene and removal of the solvent by rotary evaporation left an oily orange-red solid. Extraction of this solid with THF and removal of the solvent gave **2** as an orange microcrystalline powder (1.603 g, 80%). Anal. Calcd for $CeC_{16}H_{34}N_2O_{10}$: Ce, 25.3. Calcd for the monosolvate: Ce, 29.0. Found: Ce, 27.3. IR (KBr): 2920 s, 1490 s br, 1350 m, 1260 s, 1170 s, 1100 m, 1020 s, 950 s br, 800 m cm^{-1}.

$Ce(OCMe_3)_2(NO_3)_2(HOCMe_3)_2$ (2′). CAN (750 mg, 1.37 mmol) in 50 mL of *tert*-butyl alcohol was reacted with $NaOCMe_3$ (526 mg, 5.47 mmol) in 150 mL of *tert*-butyl alcohol by following the procedure used to make **1′**. Filtration of the reaction mixture gave a white precipitate (0.410 g, 88% if $NaNO_3$), and removal of solvent from the filtrate gave an orange powder. Extraction of the orange powder with 300 mL of hexane and removal of solvent by rotary evaporation gave **2** (139 mg, 18%). Yellow-orange crystals suitable for X-ray diffraction were grown from a concentrated toluene solution at −37 °C. Anal. Calcd for $CeC_{16}H_{38}N_2O_{10}$: Ce, 25.1. Found: Ce, 26.9. IR (KBr): 2920 s, 1490 s br, 1350 m, 1260 s, 1170 s, 1100 m, 1020 s, 950 s br, 800 m cm^{-1}.

Table IV. Crystallographic Data for $Ce(OCMe_3)_2(NO_3)_2$-$(HOCMe_3)_2$ (**2′**) and $Ce(OCMe_3)_6Na_2(DME)_2$ (**5′**)

	2′	**5′**
formula	$CeC_{16}H_{38}N_2O_{10}$	$CeC_{32}H_{74}Na_2O_{10}$
mol wt	558.7	805.0
space group	$P\bar{1}$ (No. 2, C_i^1)	$Pna2_1$
cell const		
a, Å	10.7548 (56)	20.5337 (36)
b, Å	11.0853 (49)	10.9557 (23)
c, Å	12.4403 (56)	19.4128 (38)
α, deg	72.760 (34)	
β, deg	88.190 (39)	
γ, deg	69.050 (35)	
V, $Å^3$	1318.0 (11)	4367.1 (15)
Z	2	4
D_{calcd}, g cm^{-3}	1.41	1.22
temp, K	295	213
μ_{calcd}, cm^{-1}	18.0	10.42
radiation	MoKα (λ = 0.710 730 Å)	Mo Kα

X-ray Data Collection, Structure Determination, and Refinement for 2′. A bright yellow crystal of approximate dimensions 0.23 × 0.27 × 0.50 mm was mounted in a thin-walled glass capillary under nitrogen and was accurately aligned on a Nicolet P3 automated four-circle diffractometer. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of room-temperature (22 °C) intensity data were carried out by using standard techniques similar to those of Churchill.[53] Details are given in Table IV and in the supplementary material.

A careful survey of a preliminary data set revealed no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The crystal, therefore, belongs to the triclinic system. Possible space groups are the noncentrosymmetric $P1$ (C_1^1 No. 1) or the centrosymmetric $P\bar{1}$ (C_i^1, No. 2). With $Z = 2$ and no expectation of a resolved chiral molecule, the latter centrosymmetric space group is far more probable[54] and was later confirmed as the correct choice by successful solution of the structure.

All 4935 data were corrected for the effects of absorption (μ = 18.0 cm^{-1}) and for Lorentz and polarization factors and reduced to unscaled $|F_o|$ values. A Wilson plot was used to place the data on an approximate absolute scale. No datum was rejected.

The structure was solved by direct methods with the SHELXTL PLUS program set;[55] the position of the cerium atom was located from an E map. The positions of all remaining non-hydrogen atoms were determined from a series of difference-Fourier syntheses. All subsequent crystallographic calculations were performed by using our locally modified version of the UCLA Crystallographic Computing Package.[56] The structure was refined by using full-matrix least-squares methods. The weighting scheme with ρ = 0.05 has been previously described.[57] Hydrogen atom contributions were not included in the refinement. The model converged with R_F = 7.7%, R_{wF} = 7.7%, and GOF = 1.85 for 262 variables refined against all 4935 data (R_F = 6.5%, R_{wF} = 7.6% for those 4301 reflections with $F^2 > 1.5\sigma(F^2)$ and R_F = 6.0%, R_{wF} = 7.4% for those 3913 reflections with $F^2 > 3.0\sigma(F^2)$). A final difference-Fourier map showed no significant features. The final values of the atomic coordinates are given in Table V.

The analytical scattering factors[58a] for the neutral atoms (C, N, O, Ce) were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[58b] were included.

$Ce(OCMe_3)_3(NO_3)(THF)_2$ (3). CAN (1.000 g, 1.82 mmol) in 50 mL of THF was reacted with $NaOCMe_3$ (0.876 g, 9.12 mmol) in 75 mL of THF by following the procedure for **1**. A white precipitate (0.705 g, 92% if $NaNO_3$) was separated by filtration, and removal of solvent from the filtrate gave an orange-yellow powder. Extraction of this solid with 50 mL of toluene and removal of the solvent by rotary evaporation left **3** as a bright yellow powder (1.032 g, 82%). Anal. Calcd for $CeC_{20}H_{35}NO_8$: Ce, 24.8. Found: Ce, 25.5. IR (KBr): 2950 s, 1540 m, 1460 m, 1360

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Table V. Atomic Coordinates for $Ce(OCMe_3)_2(NO_3)_2(HOCMe_3)_2$ (**2′**)

atom	*x*	*y*	*z*
Ce(1)	0.20654 (4)	0.46954 (4)	0.75160 (4)
O(1)	0.0377 (5)	0.3634 (5)	0.8293 (4)
O(2)	−0.0235 (5)	0.6394 (5)	0.6697 (4)
O(3)	0.2983 (6)	0.6007 (6)	0.7507 (5)
O(4)	0.3645 (5)	0.2998 (6)	0.7555 (5)
O(5)	0.1290 (5)	0.4139 (5)	0.5829 (4)
O(6)	0.2381 (6)	0.5493 (6)	0.5448 (5)
O(7)	0.1833 (6)	0.4810 (7)	0.4136 (5)
O(8)	0.1002 (6)	0.5510 (6)	0.9188 (4)
O(9)	0.2789 (6)	0.3720 (6)	0.9606 (5)
O(10)	0.1857 (6)	0.4527 (8)	1.0934 (5)
N(1)	0.1826 (7)	0.4815 (7)	0.5105 (5)
N(2)	0.1878 (7)	0.4587 (7)	0.9927 (6)
C(1)	0.0276 (10)	0.2269 (8)	0.8638 (7)
C(2)	0.1015 (22)	0.1561 (13)	0.9774 (12)
C(3)	−0.1150 (16)	0.2457 (17)	0.8699 (23)
C(4)	0.0858 (24)	0.1637 (15)	0.7781 (15)
C(5)	−0.0936 (9)	0.7885 (8)	0.6325 (8)
C(6)	−0.0442 (16)	0.8363 (11)	0.7167 (11)
C(7)	−0.0528 (18)	0.8402 (12)	0.5175 (10)
C(8)	−0.2415 (13)	0.8156 (13)	0.6315 (18)
C(9)	0.3840 (10)	0.6696 (11)	0.7605 (8)
C(10)	0.3619 (29)	0.7879 (17)	0.6533 (15)
C(11)	0.3466 (22)	0.7241 (23)	0.8580 (16)
C(12)	0.5237 (17)	0.5702 (19)	0.7811 (29)
C(13)	0.4848 (11)	0.1979 (12)	0.7496 (12)
C(14)	0.5583 (20)	0.1369 (24)	0.8604 (18)
C(15)	0.4525 (19)	0.1058 (28)	0.7134 (40)
C(16)	0.5671 (17)	0.2643 (21)	0.6654 (18)

Table VI. Atomic Coordinates for $Ce(OCMe_3)_6Na_2(DME)_2$ (**5′**)

atom	*x*	*y*	*z*
Ce(1)	0.36392 (1)	1.29554 (2)	1.0000
Na(1)	0.3368 (1)	1.3124 (2)	1.1632 (1)
Na(2)	0.4236 (1)	1.5408 (2)	1.0653 (1)
O(1)	0.3166 (2)	1.4482 (3)	1.0715 (2)
O(2)	0.4339 (2)	1.3339 (4)	1.0945 (2)
O(3)	0.3175 (2)	1.1677 (4)	1.0747 (2)
O(4)	0.4145 (2)	1.4570 (3)	0.9549 (2)
O(5)	0.2864 (2)	1.2899 (4)	0.9267 (2)
O(6)	0.4261 (2)	1.1656 (4)	0.9499 (2)
O(7)	0.3745 (3)	1.2937 (5)	1.2852 (3)
O(8)	0.2437 (3)	1.3252 (6)	1.2519 (3)
O(9)	0.5268 (3)	1.6870 (6)	1.0648 (4)
O(10)	0.4262 (3)	1.6821 (5)	1.1584 (3)
C(1)	0.4009 (5)	1.1921 (8)	1.3182 (5)
C(2)	0.3310 (4)	1.3629 (9)	1.3274 (4)
C(3)	0.2632 (4)	1.3171 (9)	1.3230 (4)
C(4)	0.1767 (5)	1.2945 (11)	1.2457 (6)
C(5)	0.5905 (6)	1.6751 (12)	1.0523 (8)
C(6)	0.5142 (9)	1.7800 (11)	1.1110 (12)
C(7)	0.4716 (10)	1.7801 (12)	1.1530 (8)
C(8)	0.4155 (5)	1.6489 (11)	1.2253 (4)
C(11)	0.2600 (3)	1.5198 (6)	1.0659 (3)
C(12)	0.2655 (3)	1.6038 (5)	1.0025 (5)
C(13)	0.1990 (3)	1.4400 (7)	1.0575 (4)
C(14)	0.2527 (3)	1.5983 (7)	1.1301 (4)
C(21)	0.4957 (3)	1.2920 (6)	1.1147 (3)
C(22)	0.4938 (4)	1.1595 (7)	1.1322 (4)
C(23)	0.5448 (3)	1.3104 (7)	1.0558 (4)
C(24)	0.5171 (3)	1.3646 (7)	1.1788 (4)
C(31)	0.2902 (3)	1.0535 (6)	1.0916 (3)
C(32)	0.2173 (5)	1.0711 (11)	1.0969 (7)
C(33)	0.3059 (8)	0.9629 (10)	1.0367 (6)
C(34)	0.3160 (7)	1.0116 (11)	1.1601 (6)
C(41)	0.4387 (3)	1.5144 (6)	0.8949 (3)
C(42)	0.4036 (4)	1.4621 (9)	0.8316 (3)
C(43)	0.4249 (4)	1.6498 (7)	0.8991 (5)
C(44)	0.5112 (3)	1.4940 (8)	0.8891 (4)
C(51)	0.2385 (3)	1.2709 (6)	0.8764 (3)
C(52)	0.2070 (4)	1.3923 (7)	0.8556 (4)
C(53)	0.2692 (4)	1.2139 (8)	0.8127 (4)
C(54)	0.1856 (4)	1.1869 (6)	0.9050 (4)
C(61)	0.4605 (3)	1.0794 (6)	0.9110 (4)
C(62)	0.5051 (9)	1.1384 (12)	0.8658 (9)
C(63)	0.4994 (6)	0.9954 (11)	0.9595 (6)
C(64)	0.4158 (5)	1.0003 (12)	0.8708 (7)

s, 1230 m, 1170 s, 1100 m, 950 s br, 770 s br cm^{-1}. The THF in **3** can be removed by extended rotary evaporation to give a THF-free complex. ^{1}H NMR (C_6D_6): δ 2.09 (s, μ_3-OCMe$_3$, 9 H), 1.57 (s, μ-OCMe$_3$, 27 H), 1.39 (s, OCMe$_3$, 18 H), 1.37 (s, OCMe$_3$, 9 H), 1.24 (s, OCMe$_3$, 18 H). ^{13}C NMR (C_6D_6): δ 90.50, 87.54, 85.23, 79.89, 79.38 (OCMe$_3$), 33.00, 32.79, 32.28, 31.54, 31.16 (OC*Me*$_3$).

$Ce(OCMe_3)_4(THF)_2$ (4). CAN (1.536 g, 2.80 mmol) in 50 mL of THF was reacted with $NaOCMe_3$ (1.616 g, 16.82 mmol) in 75 mL of THF by following the procedure for **1**. A white precipitate (1.369 g, 96% if $NaNO_3$) was separated by filtration, and removal of solvent from the filtrate gave a yellow solid. Extraction of this solid with 15 mL of hexane and removal of the solvent by rotary evaporation left **4** as a yellow powder (1.05 g, 65%). Anal. Calcd for $CeC_{24}H_{52}O_6$: Ce, 24.3. Calcd for the monosolvate: Ce, 27.8. Found: Ce, 25.5. IR (KBr): 2900 s, 1450 m, 1350 s, 1170 s br, 930 s br, 760 m cm^{-1}.

$Ce(OCMe_3)_6Na_2(THF)_4$ (5). CAN (1.000 g, 1.82 mmol) in 50 mL of THF was reacted with $NaOCMe_3$ (1.402 g, 14.59 mmol) in 75 mL of THF by following the procedure for **1**. A white precipitate (0.857 g, 92% if $NaNO_3$) was separated by filtration, and removal of solvent from the filtrate gave a pale yellow solid. Extraction of this solid with 50 mL of toluene and removal of the solvent by rotary evaporation left **5** as a pale yellow microcrystalline powder (0.909 g, 65%). Anal. Calcd for desolvated $Na_2Ce(OCMe_3)_6$, $CeNa_2C_{24}H_{54}O_6$: Ce, 22.4; C, 46.2; H, 8.7; Na, 7.4. Found: Ce, 20.4; C, 47.9; H, 8.8; Na, 6.4. IR (KBr): 2900 s, 1450 m, 1350 s, 1170 s br, 930 s br, 760 m cm^{-1}. Recrystallization of **5** from a concentrated solution of DME at −37 °C resulted in X-ray-quality crystals of $Ce(OCMe_3)_6Na_2(DME)_2$ (**5′**).

X-ray Data Collection, Structure Determination, and Refinement for 5′. A pale yellow crystal of approximate dimensions 0.26 × 0.37 × 0.40 mm was immersed in Paratone-N (Exxon lube oil additive), mounted on a glass fiber, and transferred to the Syntex $P2_1$ diffractometer, which is equipped with a modified LT-1 apparatus. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature (213 K) intensity data were carried out by using standard techniques similar to those of Churchill.[53] Final cell parameters are based on a least-squares analysis of 26 reflections in well-separated regions of reciprocal space. Experimental details are given in Table IV and in the supplementary material.

All 11 048 data were corrected for the effects of absorption and for Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot. A careful survey of a preliminary data set revealed the systematic extinctions $0kl$ for $k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$; the diffraction symmetry was *mmm*. Possible space groups are *Pnam*, a nonstandard setting of *Pnma* (D_{2h}^{16}, No. 62), or $Pna2_1$ (C_{2v}^{9}, No. 33). Structure solution and refinement in the noncentrosymmetric space group proved it to be the correct choice. The Rogers η parameter was refined to establish the absolute structure.[59] The quantity minimized during least-squares analysis was $\sum w(F_0 - F_c)^2$, where $w^{-1} = \sigma^2(F) + 0.003(F)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atom contributions were included by using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and anisotropic thermal parameters led to convergence with R_F = 4.9%, R_{wF} = 6.6%, and GOF = 1.00 for 407 variables refined against those 9092 data with $|F_o| > 1.0[\sigma(|F_o|)]$ (R_F = 3.7%, R_{wF} = 5.6% for those 7510 data with $|F_o| > 6.0[\sigma(|F_o|)]$). A final difference-Fourier synthesis showed no significant features; ρ(max) = 1.83 e Å^{-3}. The final values of the atomic coordinates are given in Table VI.

$Ce_2(OCMe_3)_9Na$ (6). CAN (1.000 g, 1.82 mmol) in 50 mL of THF was reacted with $NaOCMe_3$ (1.139 g, 11.85 mmol) in 75 mL of THF by following the procedure for **1**. A white precipitate (0.878 g, 94% if $NaNO_3$) was separated by filtration, and removal of solvent from the filtrate gave a yellow solid. Extraction of this solid with 50 mL of hexane and removal of the solvent by rotary evaporation left **6** as a yellow powder (0.840 g, 96%). Anal. Calcd for $Ce_2C_{36}H_{81}NaO_9$: Ce, 29.15; C, 44.94; H, 8.51; Na, 2.39. Found: Ce, 31.10; C, 47.24; H, 8.39; Na, 2.56. IR (KBr): 2900 s, 1450 m, 1350 s, 1170 s br, 930 s br, 760 m cm^{-1}. Single X-ray-quality crystals of **6** were grown from a concentrated toluene solution at −37 °C.[42]

$Ce_3(OCMe_3)_{10}O$ (7). In the glovebox, **4** (0.200 g, 0.347 mmol) was dissolved in 5 mL of toluene and the solution was stirred for 72 h. Removal of the solvent gave a quantitative yield of **7** as a yellow powder.

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Anal. Calcd for $Ce_3C_{40}H_{90}O_{11}$: Ce, 36.0. Found: Ce, 35.7. IR (KBr): 2900 s, 1450 m, 1350 s, 1170 s br, 930 s br, 760 m cm^{-1}. $Ce_2(OCMe_3)_9Na$ similarly transforms to **7**, but the reaction takes over 1 week.

Reactions of 1, 2, and 5 with $NaOCMe_3$. Complex **1** has been treated with 1, 2, 3, 3.5, and 5 equiv of $NaOCMe_3$ in THF to form **2**, **3**, **4**, **6**, and **5**, respectively, in good yield (80–95%). Similarly, **2** reacts with 1 and 2 equiv of $NaOCMe_3$ to form **3** and **4**, respectively, in good yield. Complex **5** has been treated with 0.5 equiv of $NaOCMe_3$ to form **6** in good yield. A typical procedure for these reactions follows.

Preparation of 4 from 1. In the glovebox, $NaOCMe_3$ (26.5 mg, 0.276 mmol) dissolved in 5 mL of THF was added to $Ce(OCMe_3)(NO_3)_3(THF)_2$ (50 mg, 0.072 mmol) in 5 mL of THF and a white precipitate formed. After it was stirred for 20 h, the reaction mixture was centrifuged and a white powder (23 mg, 100% if $NaNO_3$) was isolated. Removal of solvent from the centrifuged solution by rotary evaporation gave **4** as an orange powder (49 mg, 94%) identified by ^1H NMR spectroscopy.

Reaction of 5 with NH_4NO_3. $Ce(OCMe_3)_6Na_2(THF)_2$ (50 mg, 0.065 mmol) in 5 mL of THF was added to a Schlenk flask containing NH_4NO_3 (26 mg, 0.325 mmol) suspended in 5 mL of THF. After the mixture was stirred for 2 h, the solution was filtered to remove a pale yellow precipitate (12 mg, 109% yield if pure $NaNO_3$). Removal of solvent from the orange filtrate gave **1** (34 mg, 96%) identified by ^1H NMR spectroscopy.

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Registry No. **1**, 121314-35-0; **1′**, 122423-56-7; **2**, 121314-34-9; **2′**, 122423-65-8; **3**, 122423-57-8; **4**, 122423-58-9; **5**, 122423-59-0; **5′**, 122423-61-4; **6**, 122423-62-5; **7**, 122423-64-7; $(NH_4)_2Ce(NO_3)_6$, 16774-21-3; $Ce(NO_3)_4(THF)_2$, 122423-63-6.

Supplementary Material Available: Tables of crystal data, bond distances and angles, thermal parameters, and hydrogen atom coordinates (13 pages); tables of structure factor amplitudes (56 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of a Tetrameric Tantalum(III) Compound

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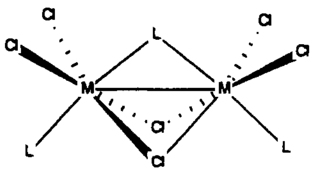
The tetrameric compound $[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}SC_4H_8)]_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2\cdot 2C_7H_8$ has been prepared from the reaction of $Ta_2Cl_4(SC_4H_8)_2(\mu\text{-}Cl)_2(\mu\text{-}SC_4H_8)$ (**1**) with $Ph_2PCH_2CH_2PPh_2$ (dppe). The compound crystallizes in the space group *Bbcm*, which is the *bca* setting of space group No. 64, *Cmca*. The cell parameters are $a = 12.706$ (6) Å, $b = 27.240$ (7) Å, $c = 25.93$ (2) Å, $V = 8976$ (9) Å^3, and $Z = 4$. The structure consists of two confacial bioctahedral units of $Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}SC_4H_8)$ bridged by two $Ph_2PCH_2CH_2PPh_2$ ligands. The Ta=Ta double-bond distance within the bioctahedral units is 2.704 (2) Å with no metal–metal bonding between the separate dimeric units of the tetramer. To our knowledge this compound is the first tetrameric tantalum(III) compound reported in the literature. It is a deviation from the products previously reported for the reactions of analogous niobium or tantalum dimeric compounds with bidentate phosphine ligands, all of which result in the formation of edge-shared dimeric compounds of the type $M_2Cl_6(PP)_2$ (where PP = bidentate phosphine ligand). The fact that the bridging (SC_4H_8) ligand is not substituted in the tantalum tetramer suggests that the ligand is less labile in **1** than in its niobium analogue.

Introduction

Several years ago, we explored the reactions of the dimeric niobium(III) and tantalum(III) compounds $M_2Cl_6L_3$ [L = tetrahydrothiophene (THT) or SMe_2] with a variety of bidentate ligands.[1] The starting compounds $M_2Cl_6L_3$ possess confacial bioctahedral geometry[2,3] (I) and were shown to undergo substitution of the L groups by various neutral ligands. Almost all reactions with neutral bidentate ligands have resulted in dimeric products of the formulation $M_2Cl_6(BB)_2$, where BB = 2,5-dithiahexane, 3,6-dithiaoctane, 2,2′-bipyridine, or ethylenebis(diphenylphosphine). In the case of the ligand $Ph_2PCH_2CH_2PPh_2$ (dppe), only the niobium dimer yielded a complex of the formulation $Nb_2Cl_6(dppe)_2$.[1,4] The structure of this compound has since been reported as an edge-shared bioctahedral dimer with the dppe ligands chelated trans to the bridging chlorines.[5] Repeated attempts to prepare the analogous $Ta_2Cl_6(dppe)_2$ dimer resulted in a compound approaching the stoichiometry $Ta_2Cl_6(dppe)$ rather than the expected $Ta_2Cl_6(dppe)_2$. Since our initial report, many niobium and tantalum dimers have been reported containing bidentate diphosphine ligands, PP (where PP = $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2PPh_2$ (dppm), $Me_2PCH_2CH_2PMe_2$ (dmpe), or $Me_2PCH_2PMe_2$ (dmpm).[5-8,16,17]



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