

Octakis(*tert*-butoxo)dicerium(IV) [Ce₂(O^tBu)₈]: Synthesis, Characterization, Decomposition, and Reactivity

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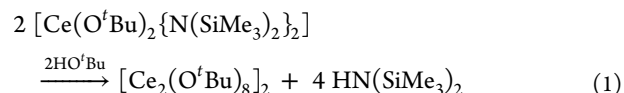
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Supporting Information

ABSTRACT: An advanced synthesis for the homometallic derivative [Ce₂(O^tBu)₈] (**1**) starting from [Ce(O^tBu)₂{N(SiMe₃)₂}]₂ was developed. Structural characterization of a cerium(IV) complex and its decomposition products confirmed the coexistence of both ether elimination and Ce–O bond cleavage processes, which lead to the formation of [Ce₃O(O^tBu)₁₀] and [Ce₃(O^tBu)₁₁] (**2**) derivatives, respectively. Variable-temperature NMR spectroscopy under strict exclusion of moisture enabled insight into the decomposition processes in noncoordinating solvents and at elevated temperature. In addition, structural analysis of the heterovalent **2** and of two new complexes of the general formula [Ce₂(O^tBu)₈(L)] [L = HO^tBu (**3**), OCPH₂ (**4**)] is described.

The *tert*-butoxides of tetravalent main and transition metals are well-studied volatile compounds that have been widely used as precursors for the fabrication of functional ceramic materials and as catalysts.¹ In contrast, structurally described complexes of tetravalent lanthanides and actinides are limited to solvated products such as [Ce(O^tBu)₄(py)₂]² and [Th(O^tBu)₄(py)₂].³ The homoleptic compounds [M^{IV}(O^tBu)₄] (M^{IV} = Ce,⁴ Th⁵) have been reported by Bradley et al.; however, a comprehensive elucidation of the molecular structure was aggravated by their propensity to form an oxo cluster of the M₃O₁₁ class or solvent adducts triggered by their intrinsic coordination unsaturation.^{2,6} Given the importance of cerium oxides as photocatalysts and sensing materials, there is a rapidly growing interest in the chemistry of cerium(IV) *tert*-butoxide, not only from a structural point of view but also more so toward a better chemical understanding of the solution behavior and stability of the starting materials. This is evident in the large number of tetravalent cerium complexes that have been synthesized starting from cerium(IV) alkoxo derivatives.⁷

Bradley et al. obtained [Ce₂(O^tBu)₈] (**1**) by refluxing [Ce₂(O^tPr)₈(HO^tPr)₂] in a mixture of HO^tBu and benzene followed by repeated fractional distillation of the volatiles.⁴ Alternatively, sublimation of [Ce(O^tBu)₄(THF)₂] yielded the *tert*-butoxide compound in a low amount.⁸ In order to develop a more convenient synthesis, the heteroleptic cerium(IV) amide [Ce(O^tBu)₂{N(SiMe₃)₂}]₂ seems to be a good starting material that is easily accessible by the salt metathesis reaction of [Ce(O^tBu)₂(NO₃)₂(THF)₂] and LiN(SiMe₃)₂.⁹ Adding 2 equiv of *tert*-butanol to cerium(IV) amide resulted in the formation of homoleptic tetrakis(*tert*-butoxo)cerium(IV) exclusively (eq 1).



Crystals of **1** were grown by vacuum sublimation, and the crystal structure was solved in the monoclinic space group *P*2₁/*c*. The cerium centers exhibit in the dimeric arrangement a distorted trigonal-bipyramidal coordination sphere ($\tau = 0.70$),¹⁴ whereas the polyhedra share one apical edge (Figure 1). This

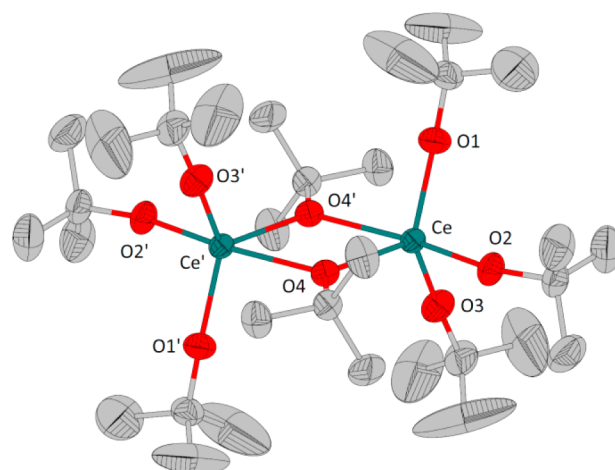


Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ce–O1 2.058(3), Ce–O2 2.059(4), Ce–O3 2.065(3), Ce–O4 2.286(3), Ce–O4' 2.434(3).

results in an asymmetrical bridging motif with one elongated [2.434(3) Å] and one shortened [2.286(3) Å] Ce–O distance. The average Ce–O distance of the terminal alkoxo groups (2.061 Å) is similar to those of literature-known complexes^{2,6} and shows no significant difference between the apical and equatorial positions.

The thermal stability of **1** is controversially discussed in the literature. For instance, Bradley et al. reported good volatility and stability of the complex;⁴ however, the poor yield of the solvent-free compound obtained upon sublimation of [Ce(O^tBu)₄(THF)₂] contradicts this assumption.⁸ In order to clarify these competing observations, a fresh sample of **1** was sealed under vacuum in a 4 mm NMR tube and heated up to 150 °C at a slow rate. The complex started to melt at 141–143 °C,

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and in the course of sublimation, it gradually decomposed with only a small portion of the complex observed as the sublimate. The sample was maintained at this temperature for 3 days followed by NMR spectroscopic analysis. Besides the resonance corresponding to **1**, additional signals for the oxo cluster $[\text{Ce}_3\text{O}(\text{O}^t\text{Bu})_{10}]$ and the heterovalent complex $[\text{Ce}_3(\text{O}^t\text{Bu})_{11}]$ (**2**) were found to appear. Apparently, the melting process associated with a higher degree of freedom and molecular agitation triggers intermolecular reactions under formation of the trinuclear species, which seem to be the thermodynamically stable products. Whereas the structure in the melt is not clear, mass spectrometric measurements indicated the existence of the monomeric complex $[\text{Ce}(\text{O}^t\text{Bu})_4]$ in the gas phase, manifested by the observation of fragments only up to m/z 432 ($[\text{M}]^+$).

The structure in solution was first investigated by Bradley et al. with ebullioscopic measurements of solutions in benzene and toluene, which revealed a molecular complexity of 2.4.⁴ However, the degree of oligomerization is strongly temperature- and solvent-dependent, and often dynamic equilibrium is present in solution.¹⁰ In our hands, the ^1H NMR spectrum of **1** at room temperature showed only one resonance for the *tert*-butoxo groups at 1.58 ppm. Upon lowering of the temperature to -70°C , there were no signs of decoalescence of the signal, which suggested either a fluxional behavior of the ligands or the presence of monomeric species in solution. In order to estimate the solution radius of the complex, the self-diffusion constant of **1** in CDCl_3 was determined by performing a DOSY ^1H NMR experiment. Using the Stokes–Einstein equation, a radius of 18 Å could be calculated, which is consistent with a dimeric structure (see the Supporting Information, SI).

The propensity of homoleptic $[\text{Ce}(\text{O}^t\text{Bu})_4(\text{THF})_2]$ to form the oxo alkoxide $[\text{Ce}_3\text{O}(\text{O}^t\text{Bu})_{10}]$ in noncoordinating solvents is a well-known phenomenon commonly observed in other metal alkoxides of large tri- and tetravalent ions, although comprehensive elucidation of the specific reaction pathway is unequivocally not established so far.^{2,6,11} Because of a rigid exclusion of water, the elimination of $^t\text{Bu}_2\text{O}$ is assumed to be the most likely formation mechanism for $-\text{M}-\text{O}-\text{M}-$ bridges in oxo alkoxide derivatives, which has already been proven for some secondary metal alkoxides.¹¹ The observation that this instability is caused by an intrinsic coordination unsaturation was further manifested by isolation of the mixed-valence *tert*-butoxide **2** from the attempted synthesis of $[\text{Ce}(\text{O}^t\text{Bu})_4(\text{THF})_2]$ starting from cerium ammonium nitrate and NaO^tBu .

In this work, the stability of **1** in noncoordinating solvents was investigated by dissolving **1** in freshly dried benzene- d_6 and sealing the sample under vacuum in a 4 mm NMR tube in order to stringently prevent any influence of atmospheric moisture or residual water in glasswares. After 1 week at room temperature, evolution of the decomposition products could be observed even if the reaction was found to proceed at a very slow rate. When the reaction time was prolonged and the temperature was gradually raised up to 130°C , the degradation was augmented and eventually finished by heating the sample further up to 180°C , resulting in the formation of **2** and $[\text{Ce}_3\text{O}(\text{O}^t\text{Bu})_{10}]$ as products, which were verified by NMR to be present in equal amounts. Further, the resonances corresponding to an equivalent of isobutene and $^t\text{Bu}_2\text{O}$ (integrative ratio) could be detected. Additionally, a broad signal at 1.2 ppm aroused, which showed no coupling to any carbon nuclei, proven by various C–H correlation experiments. Taking these findings into account, we suggest two competing and independent mechanisms involved in the decomposition of **1**. With an increase in the

metal coordination number, *tert*-butoxide can, on the one hand, undergo an ether elimination to form the oxo alkoxide $[\text{Ce}_3\text{O}(\text{O}^t\text{Bu})_{10}]$. On the other hand, homolytic cleavage of the Ce–O bond can be assumed, which results in the formation of **2** and the *tert*-butoxy radical $^t\text{O}t\text{Bu}$. The highly reactive alkoxy radical reacts further to isobutylene and an unidentified byproduct.

Crystals of **2** could be obtained from a concentrated solution of the decomposed **1**. The heterovalent cerium(III)–cerium(IV) complex crystallized, contrary to earlier reports,⁸ in the monoclinic space group $P2_1/a$ with two independent molecules present in the asymmetric unit. The compound adopts the well-known trinuclear M_3O_{11} structural unit with a doubly capped M_3 triangle and six terminal *tert*-butoxo groups (Figure 2). The

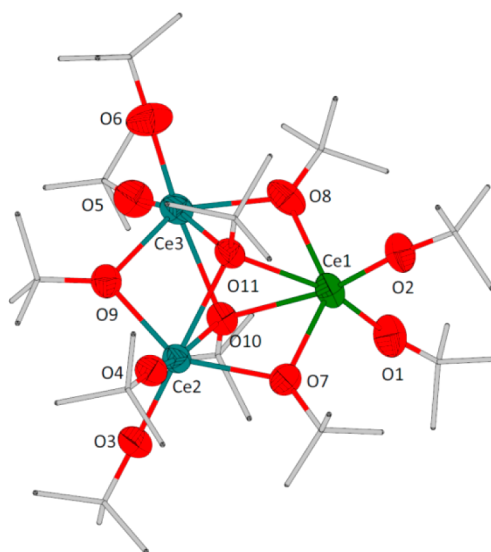
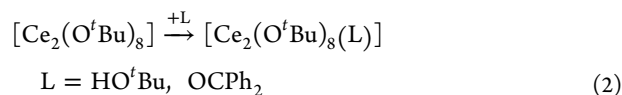


Figure 2. Molecular structure of **2**. Thermal ellipsoids (Ce and O) are shown at 50% probability. For clarity, carbon atoms are depicted as a wireframe and hydrogen atoms have been omitted. Selected bond lengths [Å]: Ce1–O1 2.126(8), Ce1–O2 2.137(7), Ce1–O7 2.438(6), Ce1–O8 2.428(8), Ce1–O10 2.557(6), Ce1–O11 2.580(6), Ce2–O3 2.090(6), Ce2–O4 2.085(6), Ce2–O7 2.338(6), Ce2–O9 2.367(7), Ce2–O10 2.499(6), Ce2–O11 2.495(6), Ce3–O5 2.097(8), Ce3–O6 2.104(9), Ce3–O8 2.353(8), Ce3–O9 2.379(6), Ce3–O10 2.521(7), Ce3–O11 2.509(6).

metal–oxygen bonds show the expected elongation with increasing bridging mode of the alkoxo ligands. Further, the trivalent cerium atom could be identified by significantly longer mean metal–oxygen distances compared to cerium(IV). Because of its paramagnetic nature, the complex exhibited three broad resonances in the ^1H NMR spectra with an integrative ratio of 6:3:2 according to the distinctive bridging motifs.

The pronounced tendency of **1** to oligomerize in order to expand the coordination number of the cerium centers makes it an interesting synthon for the synthesis of advanced heteroleptic or heterometallic compounds. By the addition of a neutral donor ligand to a solution of **1**, the dimeric complex of the general formula $[\text{Ce}_2(\text{O}^t\text{Bu})_8(\text{L})]$ [$\text{L} = \text{HO}^t\text{Bu}$ (**3**), OCPh_2 (**4**)] is formed according to eq 2.



The derivative **3** crystallizes in the orthorhombic space group $Pbcm$, with both cerium ions present in a distorted octahedral coordination environment (see the SI), whereby the neutral alcohol ligand could not be distinguished from the alkoxy ligands on the basis of the bonding parameters. The average Ce–O distances for the terminal alkoxy groups are in the expected range (2.093 Å),^{2,6} and the Ce–O bond lengths of the μ_2 -bridging groups (2.452 Å) are in good agreement with similar complexes exhibiting an octahedral face-sharing motif.² Although analogous complexes $[M_2(O^tBu)_8(HO^tBu)]$ ($M = U, Th$) are reported, **3** represents the first structurally described example.¹² The heteroleptic derivative **4** crystallizes in the monoclinic space group $P2_1/n$. Both cerium centers display an octahedral coordination sphere and are linked over a face-sharing motif of the octahedral (Figure 3). The benzophenone ligand binds in

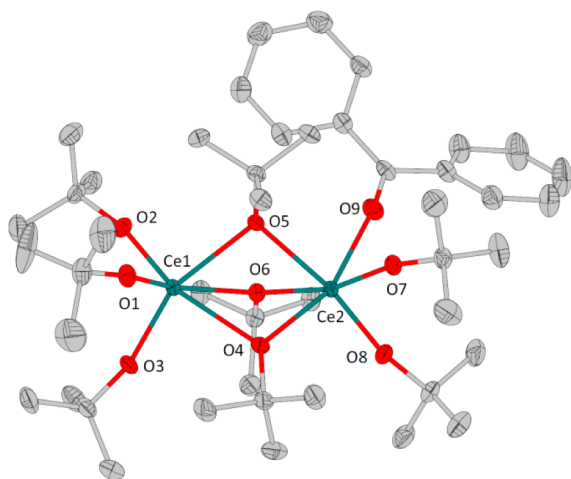


Figure 3. Molecular structure of **4**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Ce1–O1 2.099(2), Ce1–O2 2.085(2), Ce1–O3 2.097(2), Ce1–O4 2.535(2), Ce1–O5 2.422(2), Ce1–O6 2.4811(19), Ce2–O4 2.246(2), Ce2–O5 2.325(2), Ce2–O6 2.302(2), Ce2–O7 2.105(2), Ce2–O8 2.081(2), Ce2–O9 2.473(2).

contrast to the similar complex $[Zr_2(O^tBu)_8(N\equiv CMe)]$ ¹³ in the terminal position, which can be attributed to steric demand. Further, there is a remarkable asymmetry of the Ce–O distances concerning the bridging alkoxy groups, which could also be caused by a strong electronic effect of the benzophenone ligand. The mean μ_2 -Ce–O bond length of Ce2 (2.291 Å), which binds to the ketone group, is drastically shorter than its counterpart Ce1 (2.479 Å), and this effect is even more distinctive for the trans-standing *tert*-butoxy ligand O4. Both **3** and **4** exhibit, despite their dimeric structure, only a single resonance in the ¹H NMR spectra, highlighting their fluxional behavior in solution.

In conclusion, we have presented a new and efficient synthesis for the homoleptic *tert*-butoxide **1** and have performed carefully designed experiments to illustrate its limited stability in solution and at elevated temperatures. These results provide fresh insight into the sensitivity of pristine molecular structures toward storage and synthesis conditions and the fact that different mechanisms compete to transform the coordinatively less saturated homoleptic cerium(IV) alkoxides into more stable oxo and mixed-valence clusters. A deeper mechanistic understanding about bond cleavage and formation phenomena is of ubiquitous interest because of the widespread use of cerium(IV)

alkoxides in the synthesis of tetravalent cerium coordination compounds.⁷

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed experimental description and single-crystal structure refinement data for **1–3** and X-ray crystallographic data files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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