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Unprecedented Examples of Heterobimetallic Cerium(IV) Disiloxanediolates

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The first disiloxanediolate complexes of cerium(IV) are reported. Starting from the readily available precursor (^{t}BuO)$_3$Ce^{IV}(NO$_3$)(THF)$_2$ (**1**), we prepared the novel heterobimetallic compounds [{(Ph$_2$SiO)$_2$O}{K(THF)$_2$}]$_2$Ce(O^{t}Bu)$_2$ (**2**) and [{(Ph$_2$SiO)$_2$O}$_2${(DME)-KO^{t}Bu}{(Ph$_2$SiO$_2$)K}Ce]$_2$ (**3**) and structurally characterized them by X-ray diffraction.

Because of their high oxidation potential, cerium(IV) compounds are widely used in various areas of chemistry and technology. Important fields of application include organic synthesis,[1] bioinorganic chemistry,[2] materials science,[3] and industrial catalysis (automotive three-way catalysts, oxygen storage, etc.).[4] Thus there is a constant demand for new, well-defined cerium(IV) species. Cerium(IV) alkoxides form a well-investigated class of compounds which are of interest as precursors for the MOCVD production of thin CeO$_2$ layers.[5] In sharp contrast, information about the homologous cerium(IV) siloxides containing Ce–O–Si bonds is very scarce. To the best of our knowledge, Ce(OSiPh$_3$)$_4$(DME)$_x$ ($0.5 < x < 1$)[6] and a cerium(IV) metallasilsesquioxane complex[7] are the only fully characterized compounds of this type. We report here the preparation and structural characterization of two unprecedented examples of cerium(IV) disiloxanediolates.

As a suitable cerium(IV) precursor, we chose the readily available alkoxide nitrate complex (^{t}BuO)$_3$Ce^{IV}(NO$_3$)(THF)$_2$ (**1**). Mixed-ligand complexes of this type were developed by Evans et al. as soluble and versatile cerium(IV) reagents.[8] Bright yellow (^{t}BuO)$_3$Ce(NO$_3$)(THF)$_2$ (**1**) is easily made by allowing ceric ammonium nitrate, (NH$_4$)$_2$[Ce(NO$_3$)$_6$] (CAN), to react with NaO^{t}Bu in a 1:5 molar ratio. In the first experiment, **1** was treated with (Ph$_2$SiOK)$_2$O (made in situ by deprotonation of 1,1,3,3-tetraphenyl-1,3-disiloxanediol[9,10] with KN(SiMe$_3$)$_2$) in a molar ratio of 1:2 according to Scheme 1. From this reaction, the novel heterobimetallic potassium/cerium(IV) disiloxanediolate complex [{(Ph$_2$SiO)$_2$O}{K(THF)$_2$}]$_2$Ce(O^{t}Bu)$_2$ (**2**) was isolated in the form of yellow, block-shaped crystals in 81% yield (Scheme 1). Its structure was studied by single-crystal X-ray diffraction (Figure 1).

In the molecule of **2**, two potassium disiloxanediolate ligands are coordinated to cerium(IV) in a slightly bent coordination geometry. Two *t*-butoxide ligands remain as functionalizable groups coordinated to Ce. The central cerium is in a distorted octahedral coordination environment. A very similar distorted octahedral coordination of tetravalent cerium was found in Ce(OSiPh$_3$)$_4$(DME)$_x$.[6] One phenyl ring of each disiloxanediolate ligand is engaged in an intramolecular η^1-π-coordination to potassium (K(1)–C(22) 3.395(4) Å). Phenyl-π-coordination to K$^+$ has been observed, for example,

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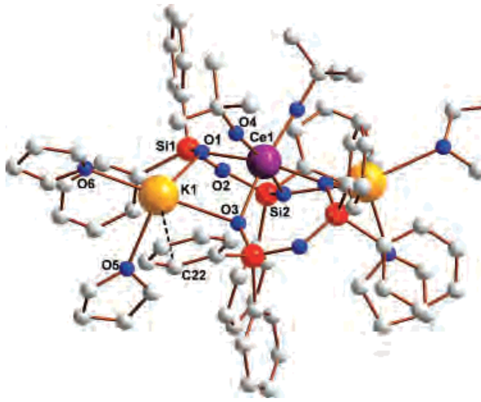
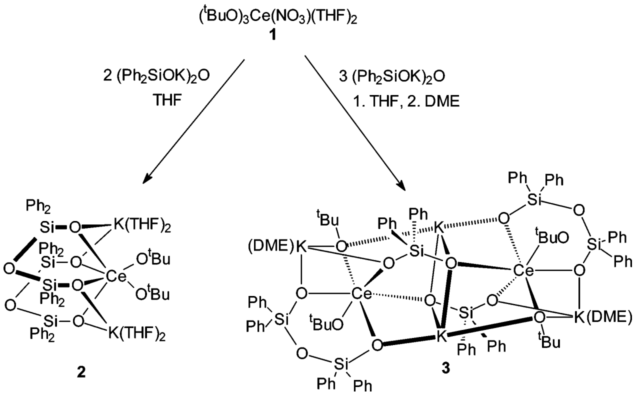


Figure 1. Molecular structure of $[\{(Ph_2SiO)_2O\}\{K(THF)_2\}]_2Ce(O^tBu)_2$ (**2**). Selected bond lengths (Å): Ce−O(1) = 2.279(2), Ce−O(3) = 2.292(2), Ce−O(4) = 2.102(2), K(1)−O(1A) = 2.696(2), K(1)−O(3) = 2.718(2), K(1)−C(22) = 3.395(4).

Scheme 1. Synthesis of Ce(IV) Disiloxanediolates **2** and **3**



in potassium pyrazolylborates, phosphine(phosphinimino)methanides, phenoxides, and thiolates.[11]

The same reaction carried out in a molar ratio of 1:3 took a completely different course. In this case, a light yellow compound could be isolated in high yield (∼70%), which was shown by X-ray crystallography to be the novel heterobinuclear potassium/cerium(IV) disiloxanediolate cluster $[\{(Ph_2SiO)_2O\}_2\{(DME)KO^tBu\}\{(Ph_2SiO_2)K\}Ce]_2$ (**3**, Figure 1). The X-ray study revealed that, in **3**, not only the expected dianions of 1,1,3,3-tetraphenyl-1,3-disiloxanediol act as ligands but also the dianions of diphenyl-1,1-silanediol, which originate from cleavage of the disiloxanediolate. Such transformations are not uncommon in the chemistry of silanediolates, disiloxanediolates, and trisiloxanediolates.[10]

In the unprecedented centrosymmetric cluster molecule **3**, a planar K_2O_2 ring forms the central structural unit. The central cerium atoms are in a distorted octahedral coordination environment. Two disiloxanediolate dianions act as chelating ligands toward each Ce(IV) and simultaneously bridge two potassium ions with the cerium. An unusual μ^3,μ^2-bridging coordination mode was found for the dianionic diphenyl-1,1-silane-diolate ligands. One oxygen from each of the two $Ph_2SiO_2^{2-}$ ligands bridges one Ce and two potassium ions, while the other oxygen forms a μ^2-bridge to Ce and K. The overall coordination geometry around each cerium is slightly distorted octahedral. Four *t*-butoxide groups originating from precursor **1** are also present in the molecular structure of **3**, two of them bridging (K, K) and the other two terminally bonded to cerium. Given the high isolated yield, it is clear that despite its highly unusual structure, compound **3** is the main product of the reaction of **1** with 3 equiv of $(Ph_2SiOK)_2O$. The coordinative unsaturation of the potassium ions (coordination numbers 4 and 5, respectively) is relieved by η^1- and η^2-π-interactions with neighboring phenyl substituents.[11] The respective K⋯C distances are in the range of 3.173−3.527(4) Å. The fact that the nitrate group of the starting material was completely eliminated demonstrates the usefulness of **1** as a precursor for the synthesis of novel cerium(IV) siloxide species. Because of the remaining two ᵗBuO ligands compound **2** also represents a potentially useful synthon for other tetravalent cerium species.

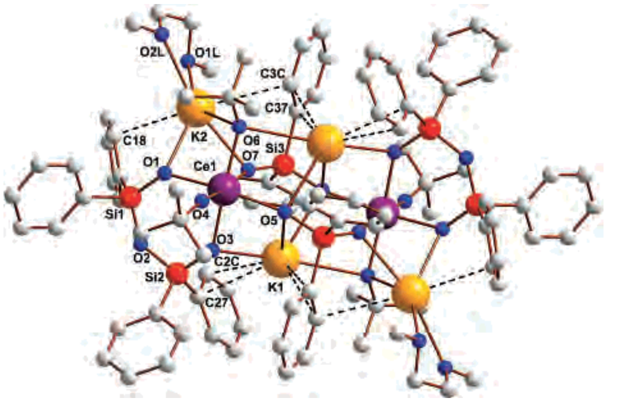


Figure 2. Molecular structure of $[\{(Ph_2SiO)_2O\}_2\{(DME)KO^tBu\}\{(Ph_2SiO_2)K\}Ce]_2$ (**3**). Selected bond lengths (Å): Ce(1)−O(1) = 2.278(3), Ce(1)−O(3) = 2.248(2), Ce(1)−O(4) = 2.105(2), Ce(1)−O(5) = 2.227(2), Ce(1)−O(6) = 2.230(2), Ce(1)−O(7) = 2.318(2), K(1)−O(5) = 2.743(3), K(1)−O(5A) = 3.064(3), K(1)−O(3A) = 2.742(3).

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Supporting Information Available: CIF files giving X-ray structural data for **2** and **3** and experimental details on the preparation and characterization of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org. $(^tBuO)_3Ce^{IV}(NO_3)(THF)_2$ (**1**), the novel heterobimetallic compounds $[\{(Ph_2SiO)_2O\}_2\{(DME)KO^tBu\}\{(Ph_2SiO_2)K\}Ce]_2$ (**2**) and $[\{(Ph_2SiO)_2O\}\{K(THF)_2\}]_2Ce(O^tBu)_2$ (**3**) have been prepared and structurally characterized by X-ray diffraction.

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