Lanthanide Oxo Complexes **Hot Paper**

DOI: 10.1002/anie.201309764

A Tetravalent Cerium Complex Containing a Ce=O Bond**

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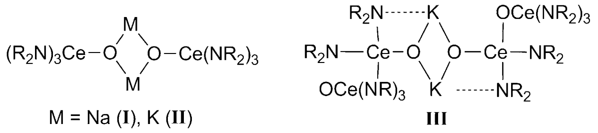
Dedicated to Professor Michael F. Lappert F.R.S. on the occasion of his 85th birthday

Abstract: *Whereas terminal oxo complexes of transition and actinide elements are well documented, analogous lanthanide complexes have not been reported to date. Herein, we report the synthesis and structure of a cerium(IV) oxo complex, $[Ce{=}O(L_{OEt})_2(H_2O)]\cdot MeC(O)NH_2$ (**1**; $L_{OEt}^- = [Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$), featuring a short Ce=O bond (1.857(3) Å). DFT calculations indicate that the hydrogen bond to cocrystallized acetamide plays a key role in stabilizing the Ce=O moiety of **1** in the solid state. Complex **1** exhibits oxidizing and nucleophilic reactivity.*

Metal complexes with multiply bonded ligands, such as oxo, nitrido, and imido, are of importance owing to their applications in organic synthesis and their involvement in bioinorganic catalysis.[1] Although metal–ligand multiple bonds are common features for transition and actinide elements, lanthanide terminal oxo complexes remain elusive.[2] To date, Sc^{III} arylimido complexes are the only rare-earth-metal complexes containing terminal multiply bonded ligands that have been characterized by X-ray diffraction.[3] On the other hand, lanthanide compounds supported by chelating carbene ligands, notably bis(iminophosphorano)methanediide, have been more extensively studied.[4,5]

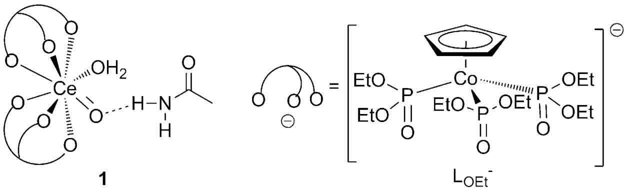
One might expect that an increase in metal oxidation state can lower the metal orbital energy, thus enhancing the covalency of lanthanide–ligand interactions.[6] Therefore, cerium, the only lanthanide element for which the tetravalent state is accessible in solution, is a good candidate for the study of lanthanide–ligand multiple bonding.

In sharp contrast with the group 4[7] and actinide (e.g. U[8]) analogues, Ce^{IV} terminal oxo complexes are unknown; only a few dinuclear and polynuclear Ce^{IV} μ-oxo species have been previously synthesized.[9] An EXAFS study revealed that in perchloric acid the Ce^{IV} ion exists predominately as an oxo-bridged dimer.[10] Of note is the synthesis of heterometallic Ce^{IV}-O-M (M = Na or K) complexes **I–III** (Scheme 1) from $[Ce(NR_2)_3]$ (R = $SiMe_3$) and dioxygen in the presence of $[M(NR_2)]$, which were reported by Lappert and co-workers.[9a] These bimetallic Ce^{IV} oxo complexes are very air and thermally sensitive, and their reactivity has not been reported. A theoretical study suggests that $[Cp_2Ce^{IV}{=}X]$ (Cp = η^5-C_5H_5; X = oxo, imido, carbene) complexes are feasible synthetic targets.[6] This prompted us to explore the possibility of synthesizing Ce^{IV} terminal oxo complexes.



Scheme 1. Lappert's bimetallic Ce^{IV} oxo complexes.[11]

In previous work, we synthesized a dinuclear Ce^{IV} μ-oxo complex by reaction of $[Ce\{N(iPr_2PO)_2\}_2Cl_2]$ with Ag_2O.[9b] In an effort to prevent μ-oxo formation, we sought to synthesize Ce^{IV} oxo species supported by the bulky Kläui oxygen tripodal ligand $[CoCp\{P(O)(OEt)_2\}_3]^-$ (L_{OEt}^-; Scheme 2), which can stabilize tetravalent metal ions in aqueous media.[11] Herein, we report the isolation of the first Ce^{IV} complex containing a terminal oxo ligand, $[Ce{=}O(L_{OEt})_2(H_2O)]\cdot MeC(O)NH_2$ (**1**; Scheme 2), and its reactivity toward CO_2 and CO.



Scheme 2. Ce^{IV} oxo complex **1**.

The treatment of $[Ce(L_{OEt})_2Cl_2]$, which was prepared from $(Et_4N)_2[CeCl_6]$ and NaL_{OEt} and characterized by X-ray diffraction, with 1 equivalent of Ag_2O in acetonitrile gave ca. two equivalents of AgCl and a yellow solid in low yield (< 5 %). Recrystallization of this from hexanes afforded yellow crystals, which were identified by X-ray diffraction as the oxo aqua complex $[Ce{=}O(L_{OEt})(H_2O)]\cdot MeC(O)NH_2$ (**1**). The ^{1}H NMR spectrum in CD_3CN displayed sharp signals from L_{OEt}^- and the cocrystallized acetamide. The observed ^{31}P resonance at $\delta = 112.8$ ppm is typical for diamagnetic Ce^{IV}–

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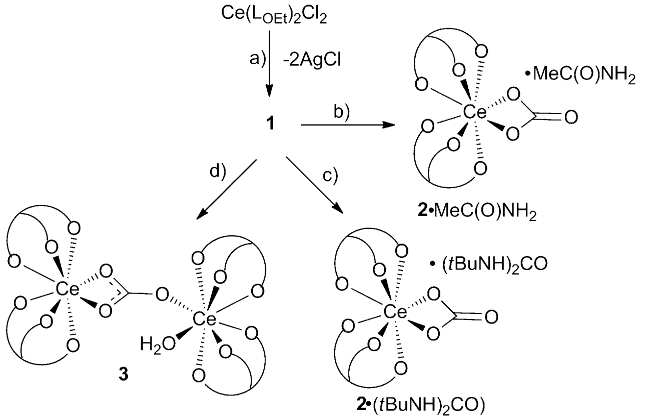
[**] This work was supported by the Hong Kong Research Grants Council (602310) and the Hong Kong University of Science and Technology.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201309764.

L_{OEt} complexes.[12] The acetamide in **1** was apparently derived from oxidative hydrolysis of acetonitrile, presumably assisted by Ce^{IV}. The IR spectrum (KBr) of **1** showed a shoulder at ca. 684 cm^{-1} that is assignable to ν(Ce-O), which is absent for $[Ce(L_{OEt})_2Cl_2]$ and shifted to ca. 674 cm^{-1} after ^{18}O-labelling of **1** (by reacting $[Ce(L_{OEt})_2Cl_2]$ with $Ag_2{}^{18}O$). The small observed isotopic shift (10 cm^{-1} cf. theoretical value of ca. 32 cm^{-1}) can be attributed to the H-bonding between the oxo and acetamide (see below). The ν(Ce-O) of 684 cm^{-1} is close to our DFT-calculated value (699.7 cm^{-1}, unscaled; see the Supporting Information). The Ce–O stretching frequency for **1** is rather low compared with those of the heavier U analogues (e.g. 765 cm^{-1} for $[U^{IV}(O)Cp'_2(dmpy)]$; $Cp' = \eta^5$-1,3,5-tBu$_3$C$_5$H$_2$, dmpy = 2,6-dimethylpyridine),[13] presumably owing to the H-bonding and/or the contribution of the Ce^+-O^- resonance form (see below).

The low yield of isolated **1** was deemed to be possibly due to a lack of acetamide (and perhaps water) in the reaction mixture. Indeed, the subsequent reaction of $[Ce(L_{OEt})_2Cl_2]$ with 1 equivalent of Ag_2O in acetonitrile (5 mL) in the presence of 2 equivalents of acetamide and excess water (ca. 0.1 mL) afforded **1** as a yellow solid in much better yield (over 50%) (Scheme 3). Single crystals of **1** could be obtained by recrystallization of the yellow solid from hexanes.



Scheme 3. Synthesis and reactivity of **1**. Reagents and conditions: a) Ag_2O (1 equiv), $MeC(O)NH_2$ (2 equiv), $MeCN/H_2O$, RT; b) CO_2, MeCN, RT; c) excess tBuNCO, H_2O, MeCN, RT; d) CO, MeCN, RT.

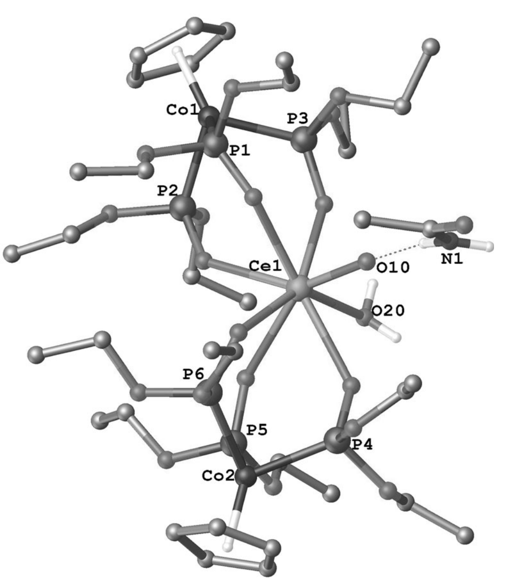


Figure 1. Molecular structure of **1**. Thermal ellipsoids drawn at a 30% probability level. Hydrogen atoms, except those of the aqua ligand and acetamide amido group, are omitted for clarity. Only the hydrogen bond between the oxo group and the acetamide is shown. Selected bond lengths [Å]: Ce–O(10) 1.857(3), Ce–O(20) 2.572(3), O(10)···N(1) 2.786(5).

Figure 1 shows the solid-state structure of **1**. The asymmetric unit consists of a $[Ce{=}O(L_{OEt})_2(OH_2)]$ molecule H-bonded to an acetamide [N1···O10 distance = 2.786(5) Å]. In the crystal packing, two acetamides mutually bridge two Ce–oxo complexes by H-bonding (see the Supporting Information). The geometry around Ce is distorted square antiprismatic. The Ce-O(oxo) distance (1.857(3) Å) is the shortest known, and significantly shorter than those in reported dinuclear and polynuclear Ce^{IV} oxo complexes (Supporting Information, Table S6), which is consistent with a multiple bond. The metal–oxo distance in **1** compares well with those of U^{4+} (which has a similar ionic radius to Ce^{4+}) analogues, such as $[U^{IV}(O)Cp'_2(dmap)]$ (dmap = N,N-dimethylaminopyridine; 1.860(3) Å)[13] and $[U^{IV}(O)Tp^*_2]$ (Tp^{*-} = hydrotris(3,5-dimethylpyrazolyl)borate; 1.863(4) Å).[14] The Ce–OH_2 distance in **1** (2.572(3) Å) is long, and there is no indication that mixed hydroxy species are present in the solid state. Electron density peaks corresponding to the hydrogen atoms of the aqua ligand and those of the acetamide NH_2 group were located in difference maps from the X-ray structure. To our knowledge, **1** is the first example of a lanthanide complex with a terminal oxo ligand that has been characterized by X-ray diffraction. It should be noted that the Ce-O(M) distances in Lappert's bimetallic oxo complexes shown in Scheme 1 are also quite short (**I**: 1.948(4), **II**: 1.908(3), **III**:1.862(2) Å).[9a] These bimetallic complexes are probably best represented by the forms $Ce{=}O{:}{\rightarrow}M \leftrightarrow Ce^+{-}O^-{-}M$.

The isolation of complex **1** raises the issue of the relative stability of the Ce^{IV} oxo aqua compound compared with its dihydroxy tautomer. Therefore, DFT calculations of model complexes containing $[CoCp\{P(O)(OMe)_2\}_3]^-$ ($L_{OMe}{}^-$) ligands were performed in order to understand the stability and electronic structures of the Ce^{IV} oxo aqua and dihydroxy compounds. Geometry optimizations have been performed at the Becke3LYP (B3LYP) level of theory. First, we calculated the stability of the two compounds in the absence of the acetamide, that is, $[Ce(L_{OMe})_2(O)(H_2O)]$ (**A**) and $[Ce(L_{OMe})_2(OH)_2]$ (**B**; Figure S4). The calculations show that **B** is more stable than **A** by only 0.9 kcal mol^{-1} in the gas phase (0.1 kcal mol^{-1} when the solvation effect is considered), which suggests that **A** and **B** are energetically similar tautomer forms that might be expected to rapidly interconvert in solution.

We next calculated the stability of the two compounds in the presence of a H-bonded acetamide (**C** and **D**). The calculated bond lengths in **C** are in good agreement with the experimental values of **1**, which is indicative of the reliability of the calculation. In the presence of the H-bonded acetamide, the oxo-aqua compound **C** is now calculated to be more stable than the dihydroxy analogue **D** by 3.1 kcal mol^{-1} in the gas-phase (3.6 kcal mol^{-1} when the solvation effect is considered). These results indicate that the hydrogen bonds between the Ce^{IV} oxo compound and acetamide contribute significantly to the stability the Ce=O moiety in the solid state.

Figure 2 shows the most important occupied molecular orbitals that are relevant to the Ce–oxo π- and σ-bonding interactions based on the optimized geometry of **A**. The π-bonding molecular orbital featuring the overlap between Ce 5d/4f orbitals (5.4% 5d and 7.6% 4f) and an O 2p orbital (51%) is mostly localized on oxygen, suggesting that the Ce–oxo bond should be quite ionic, and that the oxo ligand possesses nucleophilic character, which is consistent with the experimental observation (see below). The Ce–O σ-bonding molecular orbital is also polarized (8.6% Ce 5d, 16.0% Ce 4f and 55.0% O 2s/2p). In addition to the above two bonding molecular orbitals, there is another occupied orbital (see the Supporting Information) that is predominantly localized on the oxo (less than 5.0% Ce 5d/4f and 62.0% O 2p), which can be described as a nonbonding orbital associated with the O 2p orbital. The natural bond orbital (NBO) analysis shows that the natural atomic charges of the Ce and O atoms (1.547 and −0.766, respectively) and the breakdown of the Ce−O bond (see the Supporting Information) are consistent with the formulation of a polarized multiple bond. In summary, the Ce–oxo bond in **1** is best described as a polarized Ce=O double bond. Similar polarized Ce^{IV}–C σ- and π-multiple-bond interactions have also recently been found for a Ce^{IV} bis(iminophosphorano) carbene complex.[5]

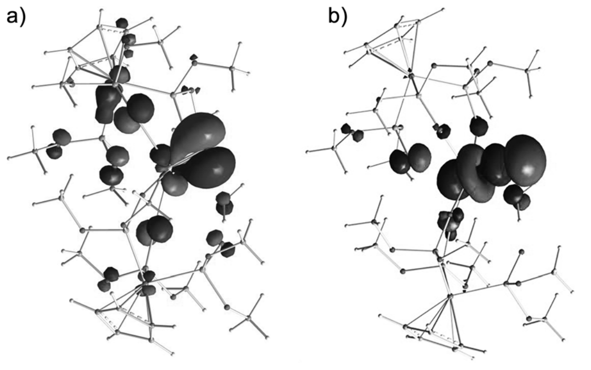


Figure 2. Plots of the molecular orbitals showing the Ce–O π-bonding (a) and σ-bonding (b) in [Ce(L$_{OMe}$)$_2$(O)(H$_2$O)], based on the optimized geometry of **A**. An isosurface value of 0.05 *e*Å^{-1} was chosen in the orbital plot.

Complex **1** is reasonably stable in solution at room temperature under nitrogen (for < 4 h), but air sensitive in both the solid state and solution. Upon exposure to air, a yellow solution of **1** in CD$_3$CN readily turned orange. ^{31}P{^{1}H} NMR spectroscopy indicates that the orange solution contained a Ce^{IV} species ($\delta = 116.3$ ppm) identified as the Ce^{IV} carbonate complex [Ce(L$_{OEt}$)$_2$(CO$_3$)] (**2**), which was isolated as the acetamide cocrystal **2**·MeC(O)NH$_2$. **2** can be readily obtained from the reaction of **1** with CO$_2$, even in the solid state, thus indicating that the Ce=O moiety in **1** is strongly nucleophilic. The ^{13}C NMR spectrum of a ^{13}C-enriched sample of **2** (obtained from the reaction of **1** with ^{13}CO$_2$) showed a resonance at $\delta = 165.7$ ppm, which is typical for metal carbonate complexes.[15]

Similarly, the reaction of **1** with *t*BuNCO in acetonitrile gave the cocrystal **2**·2(*t*BuNH)$_2$CO·Et$_2$O. An X-ray diffraction study confirmed that the carbonate ligand in **2** binds to the Ce center by a κ$_2$-*O*,*O′* mode (see the Supporting Information). It seems likely that the di-*tert*-butylurea was formed by hydrolysis of *t*BuNCO, and the CO$_2$ that was also generated then reacted with **1** to give the carbonate complex.

In addition to the nucleophilic reactivity, **1** can function as an oxidizing agent. The treatment of **1** in acetonitrile with CO at room temperature yielded the dinuclear Ce^{III} carbonate complex [(L$_{OEt}$)$_2$Ce(μ-CO$_3$)Ce(H$_2$O)(L$_{OEt}$)$_2$] (**3**). No reaction was found between CO and other Ce^{IV}–L$_{OEt}$ complexes such as [Ce(L$_{OEt}$)$_2$Cl$_2$] and [Ce(L$_{OEt}$)$_2$(NO$_3$)$_2$] under the same experimental conditions, thus indicating that the Ce=O moiety is involved in the CO oxidation. The mechanism of the CO oxidation by **1** is under investigation.

In conclusion, we have synthesized and structurally characterized the first Ce^{IV} complex containing a terminal oxo ligand, **1**, which was isolated as an acetamide cocrystal. DFT calculations show that the hydrogen bond between the oxo and acetamide plays an important role in stabilizing the Ce=O moiety in **1** and hence the unexpected oxo-aqua tautomer form. The Ce–oxo bond is best described as a polarized Ce=O double bond. The Ce^{IV} oxo complex reacts with CO$_2$ and CO to give Ce^{IV} and Ce^{III} carbonate complexes, respectively. The exploration of the reactivity of nucleophilic, oxidizing Ce^{IV} terminal oxo complexes such as **1** is underway.

Received: November 9, 2013
Published online: January 8, 2014

Keywords: cerium · crystal structure · density functional calculations · multiple bonds

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[12] ^{31}P NMR signals for Ce^{IV}–L_{OEt} complexes such as $[Ce(L_{OEt})_2Cl_2]$ are usually observed at $\delta = 115$–125 ppm, whereas those for the Ce^{III} analogues such as $[Ce(L_{OEt})_2(H_2O)_2Cl]$ occur at $\delta = 160$–170 ppm. In addition, ^{1}H NMR spectra of Ce^{III}–L_{OEt} complexes exhibit paramagnetically shifted broad signals.

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