

The Presence of Water in the Common CeCl₃/RLi Alkylation System

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Abstract: Dehydration of CeCl₃(H₂O)₇ following standard procedures for making the commonly-used CeCl₃/RLi reagent forms a material containing water and not anhydrous CeCl₃. Heating CeCl₃(H₂O)₇ at 150 °C and 0.03 Torr for 12 h forms a material which has an elemental composition of [CeCl₃(H₂O)]_n, contains water by Karl Fischer analysis, reacts with MeLi to form methane, and crystallizes from THF as [Ce(μ-Cl)₃(THF)(H₂O)]_n in space group *P* $\bar{1}$ with *a* = 6.691(2) Å, *b* = 7.433(2) Å, *c* = 10.092(2) Å, α = 84.46(2)°, β = 76.72(2)°, γ = 74.76(3)°, *V* = 471.0(2) Å³, ρ_{calcd} = 2.37 g/cm³, and *Z* = 2 at *T* = 158 K. [Ce(μ-Cl)₃(THF)(H₂O)]_n crystallizes in a layered structure in which eight-coordinate cerium atoms are ligated to terminal water and THF ligands and six bridging chlorides in a distorted square antiprismatic geometry. The THF ligands extend above and below the layers which contain the water molecules. Reactions of “CeCl₃/RLi” must take into account the presence of 1 equiv of water.

Introduction

An important recent development in organic synthesis has been the extension of metal-based reagents from the main group and transition metals to the lanthanide metals.^{1,2} The three most common lanthanide reagents in organic synthesis are ceric ammonium nitrate (CAN), (NH₄)₂Ce(NO₃)₆, samarium diiodide, SmI₂(THF)_x, and a reagent written as CeCl₃/RLi.

The first two of these reagents are well-defined. Ceric ammonium nitrate has long been used for oxidations and there is little question about its identity and purity. It has been crystallographically characterized³ and is neither oxygen nor moisture sensitive. Recently, samarium diiodide has been fully characterized by X-ray diffraction and shown to be SmI₂(THF)₅ in the crystalline state.⁴ Elemental analyses have established that as a powder this reagent is SmI₂(THF)₂.^{4,5} The preparation of samarium diiodide in pure form is straightforward since it can be made from the elemental metal and diiodoethane.

On the other hand, the identity and purity of the reagent written as CeCl₃/RLi^{6,7} is not well established. The procedure

for making this reagent involves heating commercially-available hydrated CeCl₃(H₂O)₇ under reduced pressure and adding RLi to what is presumed to be anhydrous CeCl₃. Several precise recipes for dehydrating CeCl₃(H₂O)₇ to make CeCl₃/RLi have been given in the literature and range from heating the hydrate at 140 °C at 0.1 Torr for 2 h⁶ to heating it for over 12 h at 150 °C and 0.1 Torr.⁷ The procedures to make this reagent have evolved to include special details like gradual heating to the specified temperatures and intermediate grinding. Excess RLi is typically used in the subsequent reaction, and in some cases, it is recommended to add excess RLi in case the dehydration was not optimum.⁷

Prior studies of the dehydration of lanthanide halides suggest that these dehydration procedures would not make CeCl₃, but instead a material that would contain some oxygen either as water, hydroxide, or oxide.^{8–10} Hence, truly anhydrous samples of LnCl₃ are typically made under more forcing conditions, e.g. heating a mixture of LnCl₃(H₂O)_x and excess NH₄Cl to 150 °C under high vacuum (10^{−3} Torr) for 24 h followed by heating at 260 °C and sublimation of NH₄Cl.⁸ One role of the NH₄Cl is to react with any OH formed to make H₂O and NH₃ (which are removed under vacuum) and leave Cl in the place of OH.¹⁰ Furthermore, a detailed fluorescence study of the several steps in the dehydration of EuCl₃(H₂O)₆ at 10 Torr showed that under these conditions the first three water molecules of hydration were lost at 124 °C, the fourth at 151 °C, and the fifth at 165 °C. Further heating failed to remove the final water of hydration, but instead led to the formation of Eu(OH)Cl₂ at 215 °C and EuOCl at 342 °C.⁹

We report here that “CeCl₃”, prepared following the standard procedures for making CeCl₃/RLi, gives a material which contains water as determined by IR spectroscopy, Karl Fischer

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analysis, elemental analysis, chemical analysis, and X-ray crystallography.

Experimental Section

General. $\text{CeCl}_3(\text{H}_2\text{O})_7$ was obtained from Research Chemicals, Inc. Elemental analysis was obtained from Analytische Laboratorien, Gummertsbach, Germany. Karl Fischer analysis was conducted on a Fisher Scientific Accumet 150. Infrared spectra were obtained on a Mattson Galaxy FTIR 5000.

$[\text{CeCl}_3(\text{H}_2\text{O})]_n$ (1). $\text{CeCl}_3(\text{H}_2\text{O})_7$ (10 g, 26.8 mmol) was placed into a 500-mL Schlenk flask containing a magnetic stir bar. The flask was attached to a vacuum manifold connected to a liquid nitrogen trap and a mechanical pump. Following a literature procedure,⁷ but at a lower pressure, the flask was evacuated to 0.03 Torr, slowly heated to 150 °C over 3 h with an oil bath, and agitated at this temperature for 12 additional hours to give **1** as a colorless solid. The vessel was moved from the vacuum line to a nitrogen-containing glovebox in which samples of **1** were taken for analysis. Anal. Calcd for $[\text{CeCl}_3(\text{H}_2\text{O})]_n$: Ce, 53.00; Cl, 40.21; H, 0.76; O, 6.05. Found: Ce, 53.20; Cl, 40.07; H, 0.72; O (by difference), 6.01. A saturated solution of **1** in THF was prepared and found by Karl Fischer analysis to contain 0.22–0.23 mg of $\text{H}_2\text{O}/\text{mL}$ which corresponds to 90–95% of the water expected from the formula $[\text{CeCl}_3(\text{H}_2\text{O})]_n$ based on a measured solubility of 3.5 mg/mL. Compound **1** (277 mg, 1.05 mmol) was placed in a tube fitted with two greaseless high-vacuum stopcock adapters, one attached to a 24/40 joint and the other to a septum-capped sidearm. Excess MeLi (2.9 mmol) obtained by removing Et_2O from a commercial solution (Aldrich) was added to the tube and the apparatus was attached to a high-vacuum line connected to a Toepler pump. THF was added by syringe through the sidearm and gas evolution was observed when it contacted the solids. The gas was collected by Toepler pump and identified as methane by mass spectrometry (10.5 mL, 0.43 mmol). Recrystallization at 25 °C from a THF solution which had been saturated by stirring **1** in boiling THF followed by removal of excess solid via centrifugation gave crystals of $[\text{Ce}(\mu\text{-Cl})_3(\text{H}_2\text{O})(\text{THF})]_n$.

X-ray Data Collection, Structure Determination, and Refinement for $[\text{Ce}(\mu\text{-Cl})_3(\text{H}_2\text{O})(\text{THF})]_n$. A colorless crystal of approximate dimensions $0.20 \times 0.20 \times 0.21$ mm was mounted on a Siemens P4 diffractometer. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was carried out according to standard procedures.¹¹ Low-temperature (158 K) intensity data were collected via a 2θ -omega scan technique with Mo $K\alpha$ radiation. All 1807 data were corrected for absorption¹² and for Lorentz and polarization effects and placed on an approximately absolute scale. The crystal class is triclinic and the space group is centrosymmetric $P\bar{1}$. Details appear in Table 1.

All crystallographic calculations were carried out using the UCI modified version of the UCLA Crystallographic Computing Package¹³ and the SHELXTL¹⁴ program. The analytical scattering factors¹⁵ for neutral atoms were used throughout the analysis. The structure was solved by direct methods and refined by full-matrix least-squares techniques (SHELXTL). Refinement of the model led to convergence with $wR_2 = 0.0507$ and $\text{GOF} = 1.09$ for 100 parameters refined against all 1650 unique data ($R_1 = 0.021$ for those 1584 data with $F_o > 4.0\sigma(F_o)$).

Results and Discussion

Heating $\text{CeCl}_3(\text{H}_2\text{O})_7$ at 150 °C for 12 h and 0.03 Torr following the extremes of literature procedures for preparing CeCl_3/RLi ^{6,7} produces a colorless powder, **1**, which has an elemental analysis consistent with the formula $[\text{CeCl}_3(\text{H}_2\text{O})]_n$.

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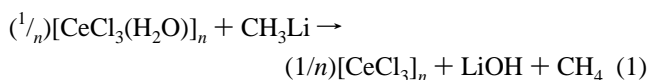
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Table 1. Crystal Data and Structure Refinement Information on $[\text{Ce}(\mu\text{-Cl})_3(\text{THF})(\text{H}_2\text{O})]_n$

empirical formula	$\text{C}_4\text{H}_{10}\text{CeCl}_3\text{O}_2$
formula weight	336.59
temperature	158 K
wavelength	0.710 73 Å
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 6.691(2)$ Å; $\alpha = 84.46(2)^\circ$ $b = 7.433(2)$ Å; $\beta = 76.72(2)^\circ$ $c = 10.092(2)$ Å; $\gamma = 74.76(3)^\circ$
volume, Z	471.0(2) Å ³ , 2
density (calcd)	2.374 g/cm ³
abs coeff	5.627 mm ⁻¹
$F(000)$	318
crystal size	0.21 × 0.20 × 0.20 mm
θ range for data collection	2.07–25.00°
limiting indices	$-2 \leq h \leq 7$, $-8 \leq k \leq 8$, $-12 \leq l \leq 11$
reflens collected	1807
independent reflens	1650 ($R_{\text{int}} = 0.0248$)
abs corr	semiempirical from ψ scans
max and min transmission	0.4904 and 0.3882
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	1650/0/100
goodness-of-fit on F^2	1.085
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0206$, $wR_2 = 0.0499^a$
R indices (all data)	$R_1 = 0.0224$, $wR_2 = 0.0507^a$
largest diff peak and hole	0.859 and -1.306 eÅ ⁻³

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

The infrared spectrum of **1** contained a strong absorption at 3440 cm^{-1} , which is consistent with an OH stretch. The presence of water in **1** was detected by dissolving a sample in THF and analyzing the solution by the Karl Fischer technique. On the basis of the measured solubility of **1**, the analyses detected 90–95% of the amount of water expected for the stoichiometry $[\text{CeCl}_3(\text{H}_2\text{O})]_n$. When THF was added to a mixture of **1** and MeLi in a Toepler pump system, gas was immediately evolved which proved to be methane by mass spectroscopy. The amount of methane obtained accounted for a 40% yield according to the stoichiometry of eq 1.



The low yield may be due to incomplete dissolution of **1** under the reaction conditions.

X-ray Crystal Structure of $[\text{CeCl}_3(\text{H}_2\text{O})(\text{THF})]_n$. Crystallization of **1** from THF gave single crystals which were analyzed by X-ray diffraction as $[\text{Ce}(\mu\text{-Cl})_3(\text{H}_2\text{O})(\text{THF})]_n$ (Figure 1). This experiment unequivocally established the presence of water in this system.

The complex crystallizes in an interesting polymeric layered structure in which all of the chloride ligands are bridging, i.e. the monomeric unit is $\text{Ce}(\mu\text{-Cl})_3(\text{THF})(\text{H}_2\text{O})$. As a result, each cerium is eight coordinate due to ligation by six bridging chlorides and the two oxygen donor groups. The eight donor atoms describe a distorted square antiprism in which the oxygen atoms are adjacent, but reside on different square faces (Figure 2). The two square faces are defined by the atoms O(1), Cl(2), Cl(2A), and Cl(1A), which are coplanar to within 0.1 Å, and the atoms O(2), Cl(1), Cl(3), and Cl(3A), which are coplanar to within 0.08 Å. The dihedral angle between these two squares is 3.2°. The δ angles used to evaluate distortions from idealized structures in 8-coordinate geometries¹⁶ are 7.9, 9.7, 38.5, and 52.2° compared to 29.5° for a perfect dodecahedron and 0.0

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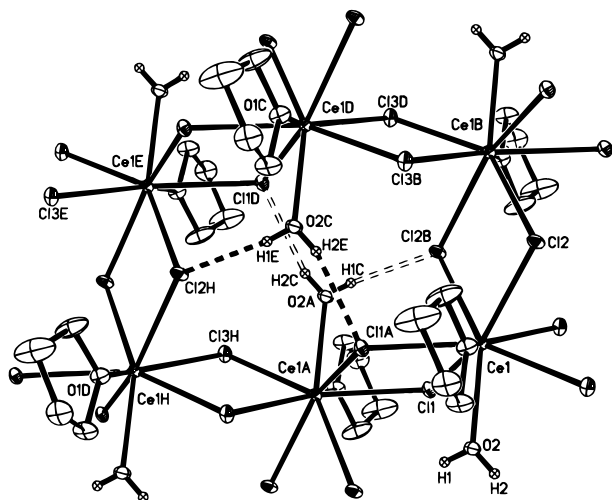


Figure 1. Part of the extended structure of $[Ce(\mu-Cl)_3(THF)(H_2O)]_n$.

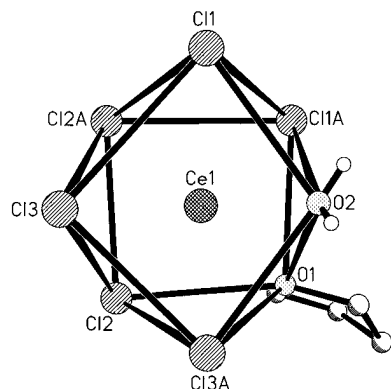


Figure 2. Diagram of the donor atom coordination geometry around cerium in $[Ce(\mu-Cl)_3(THF)(H_2O)]_n$.

and 52.4° for a perfect square antiprism. The ϕ angles are 22.5° and 21.7° compared to 0° for a dodecahedron and 24.5° for an ideal square antiprism.

The structure differs from that obtained by crystallization of truly anhydrous $CeCl_3$, which crystallizes from THF with a seven-coordinate bridged structure of formula $[CeCl(\mu-Cl)_2(THF)_2]_n$.¹⁷ This seven-coordinate extended structure is common for solvated lanthanide halides and has been observed in a number of other solvated lanthanide halide structures.^{17,18}

Each cerium atom in the structure of $[Ce(\mu-Cl)_3(THF)(H_2O)]_n$ forms three bridges to other cerium atoms via chlorine atoms labeled 1, 2, and 3. Each pair of cerium atoms is linked by a $Ce(\mu-Cl)(\mu-Cl')Ce'$ unit, each of which is located about an inversion center such that there are only six independent Ce–Cl distances. As shown in Table 2, the bond distances in $[Ce(\mu-Cl)_3(THF)(H_2O)]_n$ are slightly larger than those in $[CeCl(\mu-Cl)_2(THF)_2]_n$ as would be expected for the higher coordinate structure.¹⁹ The Ce–O(THF) distance is 0.02 \AA larger and the Ce–Cl(bridging) average distance is 0.03 \AA larger (cf. eight-coordinate Ce(III) is 0.073 \AA larger than seven-coordinate Ce(III)¹⁹).

The $2.492(3)\text{-\AA}$ Ce–O(H_2O) distance is quite reasonable compared to other data on Ln–O(H_2O) distances in the literature²⁰ and is longer than would be expected for a lanthanide

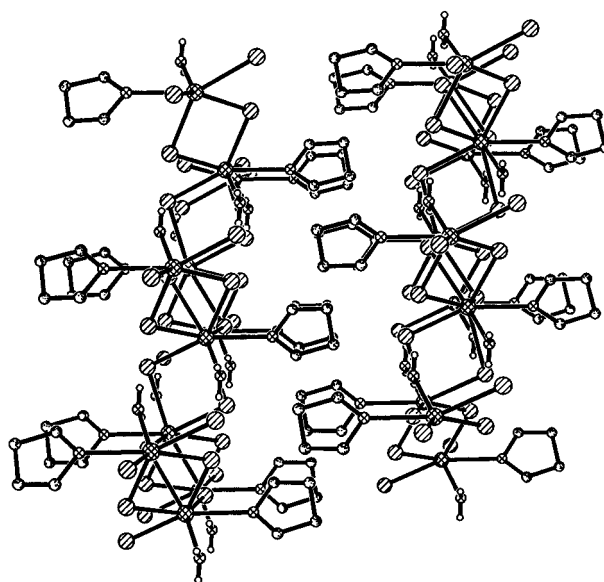


Figure 3. Side view of the layers of $[Ce(\mu-Cl)_3(THF)(H_2O)]_n$ showing the interleaving of THF between layers containing cerium, chloride, and water.

Table 2. Selected Bond Distances (\AA) for $[Ce(\mu-Cl)_3(H_2O)(THF)]_n$ with Comparable Values for $[CeCl(\mu-Cl)_2(THF)_2]_n$ ¹⁷ Listed Side by Side

	$[Ce(\mu-Cl)_3(H_2O)(THF)]_n$	$[CeCl(\mu-Cl)_2(THF)_2]_n$	
Ce(1)–Cl(1)	2.930(1)	Ce(1)–Cl(1)	2.828(1)
Ce(1)–Cl(2)	2.861(1)	Ce(1)–Cl(3)	2.880(1)
Ce(1)–Cl(3)	2.823(1)	Ce(1)–Cl(3A)	2.825(1)
Ce(1)–Cl(1A)	2.888(1)	Ce(1)–Cl(1B)	2.856(1)
Ce(1)–Cl(2B)	2.875(1)		
Ce(1)–Cl(3C)	2.846(1)		
Ce(1)–O(1)	2.528(3)	Ce(1)–O(1)	2.492(3)
		Ce(1)–O(2)	2.508(3)
Ce(1)–O(2)	2.492(3)		

hydroxyl Ln–O(OH) bond.²¹ Nd–O(H_2O) distances are typically $2.46\text{--}2.55 \text{ \AA}$ for 8- to 10-coordinate structures.²² In comparison, the metal hydroxyl Nd–O(OH) distance in 8-coordinate $[(Me_3CC_5H_4)_2Nd(\mu-OH)]_2$ is only $2.329(2) \text{ \AA}$.²³ The Ce–O(H_2O) distance in **1** is identical to the $2.490(4)\text{-\AA}$ Nd–O(H_2O) distance in the structurally similar 8-coordinate $[Nd(\mu-Cl)_2Cl_2(H_2O)_2]^-$ anion in $(MeNH_3)_8(NdCl_6)[NdCl_4(H_2O)_2]_2Cl_3$.²⁴

The overall structure of $[Ce(\mu-Cl)_3(THF)(H_2O)]_n$ consists of layers of cerium and chloride atoms linked as shown in Figure 1 with THF groups extending above and below the plane of the layer. These THF groups interleave between the layers as shown in Figure 3. Hence, the structure has layers of THF and layers of cerium and chloride atoms. It is within the cerium chloride layer that the water molecules are found. Within the cerium chloride sheets, rectangles are formed by every six cerium centers as shown in Figure 1. The water molecules reside inside these rectangles. Next nearest neighbor calculations show that each hydrogen is located between the oxygen to which it is bonded and a chloride ion attached to a different cerium. The shortest hydrogen chloride contacts are the 2.37-\AA

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H(1C)···Cl(2B) and 2.53-Å H(2C)···Cl(1D) distances. Due to the inherent uncertainty in locating hydrogen atoms in the presence of heavy atoms, it is better to specify the associated oxygen chloride distances, which are 3.28 Å for O(2A)···Cl(1D) and 3.13 Å for O(2A)···Cl(2B). These distances are in the range of distances expected for O–H···Cl hydrogen bonding.²⁵ Hence, the water molecules are anchored via the Ce–O bond and hydrogen bonding inside the rectangles in the cerium chloride layers and these in turn are sandwiched between layers of THF.

Conclusion

The usual preparation of the reagent written as “CeCl₃/RLi” does not lead to anhydrous CeCl₃ as a precursor, but rather to the solvated species [CeCl₃(H₂O)]_n. Hence, this reagent is better written as [CeCl₃(H₂O)]_n/RLi. Use of excess RLi may well lead to CeCl₃/RLi, but it should be realized that LiOH or Li₂O may also be present and these may affect the chemistry. Given the tendency of the lanthanide metals to form complexes of high coordination number^{20,26} as well as the tendency of lithium salts to bridge lanthanide structures,²⁷ it is likely that this “CeCl₃/RLi” reagent is better considered as [CeCl_aR_b(OH)_cO_dLi_e]_f. The complex may well be polymetallic (i.e. $f > 1$), since this is typical of lanthanide complexes containing small ligands. The extended bridged structures of [CeCl₃(H₂O)(THF)]_n and [CeCl₃(THF)₂]_n are but two examples. If the complex is polymetallic or if the structure contains lithium, the ligands could be bridging

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instead of terminal and this can affect their reactivity.²⁸ The reagent should not be considered to be RCeCl₂ and any mechanistic interpretations of its chemistry as this discrete species are too simplistic.

None of these discoveries diminishes the observed effectiveness of this reagent. Its use should continue to be explored. However, it is possible that additional exceptional chemistry could be obtained by using a truly anhydrous CeCl₃/RLi or by using stoichiometric combinations of lithium salts with CeCl₃/RLi. Indeed, the variability of results obtained with this reagent may be due to variable amounts of lithium salts present depending on how the drying was done. Precise control of the amount of LiOH or Li₂O present may lead to better reproducibility and specificity in reactivity.

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Note Added in Proof: The composition CeCl₃(H₂O) has also been identified in thermal gravimetric analyses of hydrated cerium trichlorides (Reuter, G.; Fink, H.; Seifert, H. *J. Z. Anorg. Allg. Chem.* **1994**, 620, 665–671).

Supporting Information Available: A view of the hydrogen bonding and tables of crystallographic data (11 pages). Ordering information is given on any current masthead page.

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