Tetravalent Chemistry: Inorganic

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Abstract

This chapter gives an overview on the chemistry of tetravalent lanthanide compounds, especially those of tetravalent cerium. Following a brief introduction it covers the tetrahalides, dioxides and other lanthanides(IV) salts. Coordination compounds of cerium in the oxidation state +4 include halogeno complexes and complexes of oxo acids, β-diketonates and related Schiff-base complexes as well as porphyrinates and related complexes.

Introduction

Besides the ubiquitous oxidation state Ln³⁺, the higher oxidation state Ln⁴⁺ is also encountered with some lanthanoids, for example in the case of the ions Ce⁴⁺ (f⁰, orange-yellow), Pr⁴⁺ (f¹, colorless), Nd⁴⁺ (f², blue-violet), Tb⁴⁺ (f⁷, colorless), and Dy⁴⁺ (f⁸, orange-yellow) (Table 1). However, all three states Ln²⁺,³⁺,⁴⁺ are never encountered for the same element. Thus the highly important mechanistic steps of oxidative addition and reductive elimination typical for the d-block metals cannot occur with the f-block metals as they would involve M²⁺ or M⁴⁺ transformations, respectively.¹

Table 1. Possible oxidation states for rare earth metals.

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<th>Ln</th>
<th>Ce</th>
<th>Pr</th>
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Among the tetravalent lanthanide ions, only Ce⁴⁺ is readily available in aqueous solution (E°Ce³⁺/Ce⁴⁺ = +1.44 V in 2M H₂SO₄, 1.61 V in 1M HNO₃, 1.70 V in 1M HClO₄). The different values for the reduction potentials indicate that stable complexes are formed in these acidic media. Thermodynamically, the oxidation of water by the Ce⁴⁺ aqua ion should be possible, but the system is kinetically stable. In contrast, the much more positive normal potentials of the other tetravalent lanthanide ions Pr⁴⁺, Nd⁴⁺, Tb⁴⁺, and Dy⁴⁺ (e.g. Pr: +2.86 V) make them very strong oxidizing agents which readily decompose water under evolution of O₂. The oxidation of Ce³⁺ to Ce⁴⁺ with the use of strong oxidizing agents like MnO₄⁻ or S₂O₈²⁻ (Scheme 1) enables the selective separation of cerium
from lanthanide mixtures. The resulting Ce$^{4+}$ can be precipitated from aqueous nitric acid solution in the form of ceric ammonium nitrate, (NH$_4$)$_2$[Ce(NO$_3$)$_6$].$^1$

$$2 \text{Ce}^{3+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2 \text{Ce}^{4+} + 2 \text{SO}_4^{2-}$$

**Scheme 1**

The readily occurring transition from colorless Ce$^{3+}$ to bright yellow or orange Ce$^{4+}$ forms the basis for the use of cerium(IV) sulfate solutions in redox titrations ("cerimetric" analysis). The ease of access to various tetravalent cerium compounds makes cerium(IV) most valuable in research as well as in various practical applications. Important fields of application for cerium(IV) compounds include organic syntheses, bioinorganic chemistry, materials science, and industrial catalysis (e.g. vehicle emissions control, oxygen storage etc.).$^1$

**Lanthanide(IV)-tetrahalides**

Only the tetrafluorides of Ce, Pr, and Tb exist, the three lanthanides with the most stable +4 oxidation state. Fluorine is most likely to support a high oxidation state, and even though salts of ions like [CeCl$_6$]$^{2-}$ are known, no binary tetrachlorides have ever been isolated as pure materials. Anhydrous LnF$_4$ (Ln = Ce, Pr, Nd, Tb, Dy) can be made by fluorination of the trifluorides or, in the case of Ce, by fluorination of metallic Ce, CeCl$_3$, or CeO$_2$. The method employing cerium dioxide appears to be the most straightforward one. CeF$_4$ can be crystallized from aqueous solution as a monohydrate. In the solid state, all tetrafluorides adopt the MF$_4$ structure with dodecahedral eight-coordination and are thus isomorphous with UF$_4$. Factors that favor formation of the tetrafluorides include a low value of I$_4$ for the metal and a high lattice energy. This is most likely to be found with the smallest halide, i.e. fluoride. The low bond energy of F$_2$ is an additional supporting factor.

Other tetrahalides do not exist. Thus, although both CeCl$_3$ and salts of the [CeCl$_6$]$^{2-}$ ion are quite stable, CeCl$_4$ cannot be made. The reasons for this are those that enable fluorine to support high oxidation states. Similar factors indicate that tetrabromides and tetraiodides are much less likely to be isolated.$^1$

**Lanthanide(IV)-dioxides**

Rare earth metals generally react with dioxygen under formation of the lanthanide(III) oxides, Ln$_2$O$_3$, with the exception of cerium, praseodymium, and terbium. In these cases, CeO$_2$, Pr$_6$O$_{11}$, and Tb$_4$O$_7$ are formed, respectively. Lanthanide dioxides, LnO$_2$ (Ln = Ce, Pr, Tb) crystallize in the fluorite (CaF$_2$) structure. Defects in the oxygen positions lead to various mixed Ln$^{3+}$/Ln$^{4+}$ oxides of the type (for praseodymium) Pr$_{12}$O$_{22}$, Pr$_{11}$O$_{20}$, Pr$_{10}$O$_{18}$, Pr$_9$O$_{16}$, Pr$_8$O$_{14}$, Pr$_7$O$_{12}$, and Pr$_6$O$_{10}$ before the row ends with Pr$_2$O$_3$.$^1$ Under forcing conditions, e.g. heating in pure oxygen under pressure, these will eventually yield Pr$_2$O$_3$ (or TbO$_2$ in the case of terbium).$^1$
Among these materials, cerium dioxide (ceria) is of particular importance. Very pure ceria is a white powder, but more often it appears pale-yellow, and less pure samples can even be brownish. A brownish coloration could be indicative for the presence of impurities such as praseodymium and neodymium. Nevertheless, impure ceria can be used for applications where purity is not critical, e.g. for polishing glass or stones. Ceria can be prepared by calcination of suitable precursors such as cerium nitrate, Ce(NO$_3$)$_3$, cerium oxalate, Ce$_2$(C$_2$O$_4$)$_3$, or cerium hydroxide, Ce(OH)$_3$, in air. At room temperature and under atmospheric pressure it is more stable than the Ce$_2$O$_3$ phase. Cerium dioxide is basic and can be dissolved in acids (although with some difficulty).\(^1\)

Cerium dioxide has found numerous practical applications, e.g. as oxidation catalyst and as catalyst support (e.g. for gold nanoparticles), in ceramics, self-cleaning ovens, and catalytic converters, for sensitizing photosensitive glasses and for polishing glass and stones. Ceria is also being used in infrared filters and as a replacement for radioactive thorium dioxide in incandescent mantles. While cerium dioxide is transparent for visible light, it is a strong ultraviolet light absorber. Thus it has been envisaged as a prospective replacement for ZnO and TiO$_2$ in sunscreens, although its photocatalytic activity is somewhat lower.

Most of the practical uses of cerium dioxide in organic synthesis and catalysis are based on its oxidizing properties. For example, its use in the walls of so-called self-cleaning ovens make use of the fact that it assists oxidation of sticky hydrocarbon deposits during the high-temperature cleaning process. Ceria is also of great current interest as a material for solid oxide fuel cells (SOFC’s) because of its relatively high oxygen ion conductivity.\(^2\) Another very important application of ceria is its use in catalytic converters in automotive applications. Cerium dioxide is able to release or store oxygen in the exhaust stream of an automobile because the material is able to become non-stoichiometric in its oxygen-content. The catalytic activity of ceria has been found to depend directly on the number of oxygen. It is able to effectively reduce the NO$_x$ emissions and also to oxidize toxic carbon monoxide to non-toxic CO$_2$. The use of inexpensive ceria in such catalysts also presents an economic advantage as it reduces the amount of platinum needed for reducing NO$_x$ emissions and achieving complete combustion of harmful exhaust gases. In addition, ceria has been found to be a useful co-catalyst in a variety of industrially important reactions including various oxidation reactions, the Fischer-Tropsch reaction, as well as the water-gas shift reaction and steam-reforming of diesel fuel to give hydrogen gas and carbon dioxide (in combination with various transition metal or metal oxide catalysts).

Furthermore a laboratory demonstration of thermochemical water splitting cycles based on the CeO$_2$/Ce$_2$O$_3$ pair (Scheme 2) has been reported. Thermal reduction of Ce$^{4+}$ to Ce$^{3+}$ (endothermic step) has been performed in a solar reactor featuring a controlled inert atmosphere. The feasibility of this first step has been demonstrated and the operating conditions have been defined (T = 2000 °C, P = 100–200 mbar). The subsequent hydrogen generation step (water-splitting with Ce$_2$O$_3$) carried out in a fixed bed reactor was complete with a fast kinetic in the studied temperature range 400–600 °C. The recovered CeO$_2$ was then recycled in the first step. In this process, water is the only material input and heat is the only energy input. The only outputs are hydrogen and oxygen, and these two
gases are obtained in different steps avoiding a high temperature energy consuming gas-phase separation. Furthermore, pure hydrogen is produced which can be used directly in fuel cells. These results have shown that the cerium oxide two-step thermochemical cycle is a promising process for hydrogen production.\textsuperscript{3}

\[
\begin{align*}
2 \text{CeO}_2 & \rightarrow \text{Ce}_2\text{O}_3 + \frac{1}{2} \text{O}_2 \\
\text{Ce}_2\text{O}_3 + \text{H}_2\text{O} & \rightarrow 2 \text{CeO}_2 + \text{H}_2
\end{align*}
\]

Scheme 2

Finally, a surprising application of cerium dioxide in nanomedicine has been reported. It was discovered that cerium dioxide nanoparticles can scavenge reactive molecules in the eye and prevent degenerative retinal disorders in rats. The results suggested that nanoceria particles could be used to treat a variety of problems that cause blindness.\textsuperscript{4}

**Other lanthanide(IV) salts**

Pale yellow cerium(IV) hydroxide can be prepared by addition of bases, such as aqueous ammonia, to solutions of cerium(IV) salts, e.g. cerium(IV) nitrate or ceric ammonium nitrate. Nanocrystalline cerium(IV) hydroxide (NCs-Ce(OH)\textsubscript{4}) is an intermediate in the production of cerium dioxide, which has been synthesized successfully using a novel and simple wet chemical route at ambient temperature for the preparation of nanocrystalline Ce\textsubscript{2}O\textsubscript{3} powder and films on mass scale for various purposes. The average crystallite size of NCs-Ce(OH)\textsubscript{4} has been estimated by the Scherrer equation to be 3–4 nm. Absorption and luminescence spectroscopic studies have been examined for future application in the development of optical devices.\textsuperscript{5}

**Cerium(IV) nitrate** can be crystallized in the form of its pentahydrate, Ce(NO\textsubscript{3})\textsubscript{4}\cdot5\text{H}_2\text{O}, which presumably contains 11-coordinate Ce(NO\textsubscript{3})\textsubscript{4}(\text{H}_2\text{O})\textsubscript{3} molecules with all four nitrato units acting as chelating ligands as in the corresponding thorium nitrate complex. Cerium(IV) sulfate, also called ceric sulfate, is a yellow to yellow-orange commercially available Ce\textsuperscript{4+} compound. It can be prepared by heating of cerium dioxide with concentrated sulfuric acid (Scheme 3).

\[
\begin{align*}
\text{CeO}_2 + 2 \text{H}_2\text{SO}_4 & \rightarrow \text{Ce(SO}_4)_2 + 2 \text{H}_2\text{O}
\end{align*}
\]

Scheme 3

Cerium(IV) sulfate exists as the anhydrous salt Ce(SO\textsubscript{4})\textsubscript{2}, but a few hydrated forms are also known: Ce(SO\textsubscript{4})\textsubscript{2}\cdot\text{nH}_2\text{O} (n = 4, 8, or 12). It is moderately soluble in water and dilute acids. Its neutral solutions slowly decompose, depositing light yellow CeO\textsubscript{2}. Solutions of ceric sulfate have an intense yellow color. The tetrahydrate will lose the water when heated to 180-200 °C. The Ce\textsuperscript{4+} ion is a strong oxidizer, especially under acidic conditions. If ceric sulfate is added to dilute hydrochloric acid, then
elemental chlorine is formed, albeit slowly. With stronger reducing agents it reacts much faster. For example, with sulfite in acidic solutions it reacts quickly and completely. Ceric sulfate is frequently used in analytical chemistry for redox titrations, often together with a redox indicator. Cerium(IV) sulfate is also one of the reagents in the oscillating Belousov–Zhabotinsky reaction. In this reaction mixture consisting of potassium bromate, cerium(IV) sulfate, malonic acid and citric acid in dilute sulfuric acid, the concentration ratio of the Ce$^{4+}$ and Ce$^{3+}$ ions oscillates, causing the color of the solution to oscillate between yellow and colorless. This is due to the Ce$^{4+}$ ions being reduced by malonic acid to Ce$^{3+}$ ions, which are then oxidized back to Ce$^{4+}$ ions by bromate(V) ions.

*Cerium(IV) acetate*, Ce(OAc)$_4$, has been synthesized by first heating a solution of Ce(OAc)$_3$ and anhydrous Ce(NO$_3$)$_3$ in a mixture of glacial acetic acid and acetic anhydride until NO$_2$ evolution was complete. The resulting solution of Ce(OAc)$_3$ was ozonized at 70 °C to form Ce(OAc)$_4$ in quantitative yield and excellent purity. The presence of nitrate was essential for obtaining such good yield and purity. IR and X-ray diffraction measurements showed that Ce(OAc)$_4$ is isomorphous with Th(OAc)$_4$ and U(OAc)$_4$. Cerium(IV) trifluoromethanesulfonate has been prepared by the reaction of cerium(IV) carbonate with trifluoromethanesulfonic acid. The powerful oxidizing ability of this compound was observed in the oxidation of benzyl alcohols and alkylbenzenes. Further cerium(IV) salts include, among others, the hydrated *cerium(IV) chromates* Ce(CrO$_4$)$_2$·H$_2$O and Ce(CrO$_4$)$_2$·2H$_2$O. *Cerium(IV) perchlorate* is readily formed by the reaction of cerium(IV) hydroxide with HClO$_4$, but this process is complicated by hydrolysis and partial reduction of Ce$^{4+}$.

**Coordination compounds of tetravalent lanthanides**

With only a few exceptions, the coordination chemistry of rare earth elements in the oxidation state is basically the coordination chemistry of tetravalent cerium. Even then well-characterized coordination compounds are limited to only a few classes of compounds. Notable are *e.g.* halogeno complexes and complexes of oxo acids, β-diketonates and related Schiff-base complexes as well as porphyrinates and related complexes. Two other important classes of cerium(IV) compounds, the alkoxydes and amides of Ce$^{4+}$, can be regarded as "pseudo-organometallics" and will be discussed together with the organocerium(IV) complexes in the following Chapter.

**Halogeno complexes**

Several halogeno complexes of tetravalent lanthanides are known. For example, the tetrafluorides form three series of fluoro complexes, [LnF$_6$]$^{2-}$ (*e.g.* in K$_2$[PrF$_6$]), [LnF$_7$]$^{3-}$ (*e.g.* in Cs$_2$[NdF$_7$]), and [LnF$_8$]$^{4+}$ (*e.g.* in (NH$_4$)$_4$[CeF$_8$]). In the case of the fluorocerates(IV), ammonium salts like (NH$_4$)$_4$[CeF$_8$] (square antiprismatic coordination) and (NH$_4$)$_3$[CeF$_7$(H$_2$O)] can be isolated by crystallization from aqueous solution. The synthesis of alkali metal derivatives of the types M$_2$CeF$_6$ and M$_3$CeF$_7$ (M = Na, K, Rb, Cs) requires the use of solid state methods such as the the reaction of CeO$_2$/MCl mixtures with elemental fluorine. The same is true for the fluoro metallates of other lanthanides in the oxidation state +4, for which the alkali metal fluoro complexes M$_2$LnF$_6$ (M = Na, K,
Rb, Cs; Ln = Tb, Pr) and Cs₃LnF₇ (Ln = Pr, Nd, Tb, Dy) are known. All these materials can only be prepared by anhydrous solid-state methods such as the fluorination of Ln₂O₃/MCl mixtures using elemental fluorine or fluorination of Cs₃LnCl₆ with XeF₂.¹

Hexachlorocerates(IV) stabilized by bulky Group 15 cations are easily prepared as shown in Scheme 4 starting with hydrated cerium dioxide.¹ Among these, especially the bright yellow pyridinium salt (pyH)₂[CeCl₆] has frequently been employed as alternative Ce(IV) precursor.⁹

\[
\text{CeO}_2 \cdot x \text{H}_2\text{O} \xrightarrow{\text{HCl (g)}} \text{EtOH} \xrightarrow{[\text{R}_4\text{E}]} [\text{R}_4\text{E}]_2[\text{CeCl}_6] \\
\text{R}_4\text{E} = \text{Et}_4\text{N}, \text{Pyridinium, Ph}_3\text{PH, Ph}_4\text{As}
\]

**Scheme 4**

The corresponding hexachloroceric acid has been isolated in the form of its adduct with diglyme (diglyme = diethylene glycol dimethyl ether) by treatment of hydrated ceria with thionyl chloride in the presence of diglyme according to Scheme 5:

\[
\text{CeO}_2 \cdot x \text{H}_2\text{O} \xrightarrow{\text{SOCl}_2, \text{diglyme}} [\text{H}_2(\text{diglyme})_3][\text{CeCl}_6]
\]

**Scheme 5**

The diglyme-stabilized hexachloroceric acid also served as starting material for a series of stable adducts of cerium(IV) tetrachloride with O-donor ligands (Scheme 6). Like their uranium(IV) congeners, these complexes adopt an octahedral coordination geometry with the O-donor ligands arranged in the *trans*-positions.

\[
\text{H}_2(\text{diglyme})_3[\text{CeCl}_6] \xrightarrow{2 \text{L}} \text{EtOAc} \xrightarrow{\text{CeCl}_4\text{L}_2} [\text{L} = \text{Ph}_3\text{AsO; } \text{tBu}_2\text{SO; } (\text{Me}_2\text{N})_2\text{PO; trans}]
\]

**Scheme 6**

In contrast, the closely related bis(triphenylphosphine oxide) adduct comprises the *cis*-configuration. This compound was prepared according to Scheme 7.

\[
(\text{NH}_4)_2[\text{Ce(NO}_3)_6] \xrightarrow{\text{HCl(g)}} \text{Ph}_3\text{PO} \xrightarrow{\text{CeCl}_4(\text{Ph}_3\text{PO})_2} (\text{cis})
\]

**Scheme 7**
While pure cerium(IV) tetrahalides other than CeF₄ have never been isolated, it has been possible to convert hexachlorocerates (cf. Scheme 4) into the homologous salts containing the [CeBr₆]²⁻ anion. These purple hexabromocerates(IV) can be prepared by treatment of the hexachloro precursors with gaseous HBr. It was not possible to make the corresponding hexaiodocerates(IV), most likely due to internal redox reactions.

**Complexes of oxo acids**

*Ceric ammonium nitrate*, (NH₄)₂[Ce(NO₃)₆] (= CAN), is perhaps the most common Ce⁴⁺ precursor. This bright orange, water-soluble salt is widely used as a standard oxidant in quantitative analysis as well as an oxidizing agent in organic synthesis. The hexanitratocerate anion forms directly upon dissolution of cerium(III) oxide in nitric acid. Thus CAN can be prepared by dissolving Ce₂O₃ in hot concentrated nitric acid, followed by precipitation with ammonia. In the hexanitratocerate(IV) anion, the bite angle of the nitrato ligands is so small that they can all act as bidentate ligands, giving rise of an icosahedral coordination geometry (coordination number 12) around cerium. Starting from CAN, some 10-coordinate neutral nitrato complexes containing additional O-donor ligands have been prepared, such as the bis(triphenylphosphine oxide) derivative shown in Scheme 6.

\[
\text{(NH₄)₂[Ce(NO₃)₆]} \overset{\text{Ph₃PO}}{\text{Ph₃PO}} \text{Me₂CO} \rightarrow \text{Ce(NO₃)₄(Ph₃PO)} (\text{trans})
\]

Scheme 6

CAN also served as a useful precursor for the synthesis of cerium(IV) alkoxydes and mixed-ligand alkoxy/nitrato complexes. Practical applications include its use as a component of chrome etchant, a material that is used in the production of liquid crystal displays and photomasks. The most important and versatile applications of CAN, however, are those in organic synthesis, where it is used as a strong oxidizing agent, as catalyst in the synthesis of heterocycles (e.g. quinolines, quinoxalines) and as a deprotection agent.

*Ceric ammonium sulfate*, (NH₄)₂[Ce(SO₄)₃], is frequently used as a safe and non-toxic oxidizing agent in redox titrations (color change from orange Ce⁴⁺ to colorless Ce³⁺). Monohydrated *cemic ammonium phosphate*, (NH₄)₂[Ce(PO₄)₂].H₂O, was hydrothermally synthesized from the system NH₃/CeO₂/H₃PO₄ and characterized by powder X-ray diffraction and various other analytical techniques. Several interesting complexes containing the bis-µ-peroxo-hexacarbonatocerate(IV) anion, \([\text{(CO}_₃]₃\text{Ce(µ-O}_₂\text{)}₂\text{Ce(CO}_₃]₃\text{)}₈⁻\], have been isolated and structurally characterized. Examples include \(\text{K}_2\text{Na}_6[(\text{CO}_₃]₃\text{Ce(µ-O}_₂\text{)}₂\text{Ce(CO}_₃]₃\text{)}·13\text{H}_2\text{O}\), \(\text{Rb}_8[(\text{CO}_₃]₃\text{Ce(µ-O}_₂\text{)}₂\text{Ce(CO}_₃]₃\text{)}·12\text{H}_2\text{O}\), and \(\text{Cs}_8[(\text{CO}_₃]₃\text{Ce(µ-O}_₂\text{)}₂\text{Ce(CO}_₃]₃\text{)}·10\text{H}_2\text{O}\). A Ce(µ-O₂)₂Ce unit with bridging, doubly bidentate peroxide groups has also been found in the the \(\text{N}_2\text{N}_2\text{N}_2\text{N}_2\text{-ethylenediamine-tetraacetato (= EDTA) derivative Na}_2\text{K}_2[(\text{EDTA})\text{Ce(µ-O}_₂\text{)}₂\text{Ce(EDTA))}\].
Cerium(IV) β-diketonates and related complexes

Homoleptic β-diketonate complexes of tetravalent cerium, Ce[R\(^{1}C(O)CHC(O)R^{2}\)]\(_{4}\), are easily accessible and form a well-investigated class of cerium(IV) complexes.\(^{15,16}\) Scheme 7 lists a small selection of known complexes of this type.

Most remarkably, the corresponding homoleptic β-diketonate complexes of trivalent cerium, Ce[R\(^{1}C(O)CHC(O)R^{2}\)]\(_{3}\), tend to be readily oxidized in the presence of air. Thus a typical synthetic procedure for preparing the more stable Ce\(^{4+}\) derivatives involves the reaction of the Na salt of the diketonate with Ce(NO\(_{3}\))\(_{3}\)\(\cdot\)6H\(_{2}\)O in aqueous EtOH solution. When the reaction is carried out in air, oxidation will easily take place and the cerium(IV) product is formed directly. Alternatively, the cerium(IV) precursor (NH\(_{4}\))\(_{2}\)[Ce(NO\(_{3}\))]\(_{6}\) (= CAN) can be treated with the sodium β-diketonate in ethanol. The homoleptic Ce[R\(^{1}C(O)CHC(O)R^{2}\)]\(_{4}\) complexes form dark red or purple crystalline solids, which are soluble in organic solvents such as toluene or CH\(_{2}\)Cl\(_{2}\). The coordination geometry around cerium is in most cases square antiprismatic, but distorted dodecahedral and distorted bicapped trigonal prismatic geometries have also occasionally been found.\(^{15,16}\)

Mixed-ligand complexes containing chelating β-diketonate ligands are also known. For example, Ce(OPPh\(_{3}\))\(_{2}\)(TTA)\(_{2}\)(NO\(_{3}\))\(_{2}\) (HTTA = thenoyltrifluoroacetone) has been prepared from Ce(OPPh\(_{3}\))\(_{2}\)(NO\(_{3}\))\(_{4}\) (cf. Scheme 6) and HTTA. Due to their relatively high volatility, homoleptic cerium(IV) tetrakis(β-diketonates) have been successfully employed as molecular precursors for the MOCVD (= metal-organic chemical vapor deposition) production of pure CeO\(_{2}\) and yttria-doped CeO\(_{2}\) thin films.\(^{17,18}\)

Recently, the very bulky tripodal Schiff-base ligand N[CH\(_{2}\)CH\(_{2}\)N=CH(C\(_{6}\)H\(_{2}\)Bu\(_{2}\)-3,5-OH-2)]\(_{3}\) (= H\(_{3}\)TRENDSAL) has also been found to form very stable complexes with tetravalent cerium. As with the β-diketonates, it was found that the cerium(III) derivative Ce(TRENDSAL) is quite air-sensitive. Thus a straightforward preparation of the cerium(IV) chloro derivative involves treatment of hydrated cerium trichloride with the \textit{in situ}-prepared ligand in the presence of oxygen as illustrated in Scheme 8.\(^{19}\) Halide abstraction from (TRENDSAL)CeCl upon reaction with Na[BPh\(_{4}\)] in acetonitrile afforded the first cationic complex of tetravalent cerium, [Ce(TRENDSAL)][BPh\(_{4}\)], which was isolated as a black, crystalline solid.\(^{20}\)
The use of ceric ammonium nitrate (= CAN) as precursor allowed the synthesis of the corresponding nitrato complex according to Scheme 9.19

Cerium(IV) sandwich complexes with tetrapyrrrole-type ligands

Formally tetravalent cerium is long known to form stable sandwich complexes with tetrapyrrrole-type macrocyclic ligands such as porphyrines, phthalocyanines, and 2,3- naphthalocyanines (Scheme 10).21-23 For the rare earth sandwich complex series, virtually all the neutral complexes can be formulated as Ln\(^{III}\)(ring-1\(^2\))(ring-2\(^-\)), in which a trivalent rare earth metal center is sandwiched between a dianionic macrocycle and a radical anionic ligand, having different extent of electron delocalization. Among the entire lanthanide series, cerium is the only exception. Having an electronic configuration of [Xe]4f\(^5\)5d\(^1\)6s\(^2\), cerium may also utilize the electron in the extended 4f orbital, leading to predominantly tetravalent neutral sandwich complexes.
Several synthetic methods have been established for the preparation of cerium sandwich complexes. Scheme 11 illustrates some typical preparations. For example, the homoleptic bis(phthalocyaninato) complex Ce[Pc(OC\text{12}H\text{25})\text{8}]_2 was prepared by treatment of Ce(acac)_3\cdot nH_2O with
4,5-bis(dodecyloxy)phthalonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 11a). This represents a general procedure which has been employed previously to prepare the pentyloxy Ce[Pc(OC₅H₁₁)₈]₂ and octyloxy Ce[Pc(OC₈H₁₇)₈]₂ analogues as well as other bis(phthalocyaninato) rare earth complexes. The bis(naphthalocyaninato) analogues Ln[Nc('Bu)₄]₂ (Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Y, Er) have also been synthesized in a similar manner using 6-tert-butynaphthalonitrile as the starting material. The yield of the cerium sandwich complex Ce[Nc('Bu)₄]₂ (71%) was much higher than those of the phthalocyanine counterparts mentioned above (9-49%), following the trend observed for the Ln[Nc('Bu)₄]₂ series, the yield of which decreases gradually with decreasing the size of the metal center. Neutral cerium(IV) sandwich complexes can also be obtained by deliberate oxidation of the anionic cerium(III) precursors. For example, anodic or chemical oxidation with dibenzoylperoxide of solutions of bis(phthalocyaninato)cerate(III) in dichloromethane yielded selectively the sparingly soluble bis(phthalocyaninato)cerium(IV), Ce(Pc)₂ as green, needle-like crystals. Ce(Pc)₂ is a sandwich complex in which the cerium atom is 8-coordinated by the isoindole nitrogens of the two staggered convex Pc-rings.

The mixed ring double-decker Ce(Pc)(TPyP) was prepared by a stepwise procedure as shown in Scheme 11b. Reaction of Ce(acac)₃·nH₂O with Li₂Pc in 1,2,4-trichlorobenzene (TCB) followed by the addition of H₂(TPyP) led to Ce(Pc)(TPyP) in 69% yield together with a substantial amount of the tripledecker Ce₂(Pc)(TPyP)₂ and Ce₂(Pc)₂(TPyP). This procedure is one of the most common
synthetic methods to prepare mixed double-deckers M(Pc)(Por). By using a convenient one-pot procedure, the mixed sandwich complexes Ce(Nc)(TBPP) and Ce(Nc)(OEP) were also synthesized. As shown in Scheme 11c, treatment of Ce(acac)₃·nH₂O with the corresponding metal-free porphyrin and naphthalonitrile in the presence of DBU in n-octanol afforded these complexes in ca. 20% yield. It has been found that the cerium sandwich complexes always show different electronic absorption and electrochemical properties from the whole series of tervalent rare earth analogues. To resolve and clarify this issue, a series of cerium double-deckers using a range of tetrapyrrole ligands with different electronic properties have been synthesized according to Scheme 11 and studied systematically with respect to their electrochemical and spectroscopic properties. The results showed that the oxidation state of the cerium center varies from +3 to +4 depending on the electronic nature of the two tetrapyrrole ligands. As revealed by X-ray absorption near-edge structure (XANES) study, the valence of the cerium center is 3.59 for Ce[Pc(OC₅H₁₁)₈]₂ and 3.68 for Ce(Pc)(TPyP) [TPyP = meso-tetra(4-pyridyl)porphyrinate] and Ce(Nc)(OEP), while that in Ce[Nc(tBu)₄]₂ is virtually 3.²³

References
