

Cerium(IV)-driven oxidation of water catalyzed by mononuclear ruthenium complexes

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Abstract This paper reviews results from study of mononuclear ruthenium complexes capable of catalyzing the oxidation of water to molecular oxygen. These catalysts may be classified into three groups, with different rate laws associated with O₂ evolution. In one class, O₂ evolution proceeds via radical coupling of the oxygen atom of an Ru^V=O species with a hydroxocerium(IV) ion. O₂ evolution catalyzed by the second class occurs via acid–base reaction of the oxygen atom of an Ru^V=O species with a water molecule. In the third group, the dominant mechanism is oxo–oxo radical coupling between two Ru^V=O species. Several significant properties of the oxidant Ce(IV) are also discussed, including the singlet biradical character of the hydroxocerium(IV) ion.

Keywords O₂ evolution · Ruthenium complexes · Cerium

Introduction

Solar energy is used to convert CO₂ and water into sugars and O₂ by a wide variety of photosynthetic organisms, including plants, algae, and cyanobacteria. In this process, the light-driven splitting of water into O₂, protons, and “energy rich” electrons is facilitated by photosystem II (PSII), a large cofactor–protein complex found in the thylakoid membranes of chloroplasts. In PSII, the four-electron

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oxidation of water ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) is effectively catalyzed by a functional unit known as the oxygen-evolving complex (OEC). The OEC consists of an inorganic core composed of four manganese, one calcium, and five oxygen bridges in the form of a Mn_4CaO_5 cluster surrounded by a functionally important protein matrix [1].

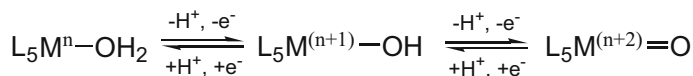
In many ways, natural photosynthesis is the ideal objective when designing direct solar fuel-production systems, because it is driven purely by solar light and uses a catalyst based on inexpensive and abundant metals. The molecular structure of the OEC, in particular, is proof that the reactivity of molecular O_2 -evolving catalysts can be optimized by molecular design involving a wide range of redox-active metal centers and ligands. Although the development of highly efficient molecular catalysts for water oxidation is a key step in the production of chemical fuels from solar energy, this development is a serious challenge, because the oxidation reaction requires removal of four protons and four electrons [2–6]. Much work has been devoted to study of catalysts which may be applicable to this process, and several materials based on Ru [6], Mn [7–11], Ir [12–14], Co [15–17], and other metals [18–22] have been extensively investigated. Reports on the development of Ru-based O_2 -evolving catalyst systems, in which cerium(IV) is typically used as oxidant, are especially numerous.

This review begins with a brief summary of historical results concerning the development of Ru-based molecular catalysts active in the O_2 evolution reaction. Our own mechanistic studies into O_2 -evolving catalysts based on Ru complexes are then described. In addition, on the basis of the fundamental properties of the cerium(IV) ion, the crucial function of cerium(IV) as a radical in catalysis of the oxidation of water by Ru complexes is discussed.

General consideration of the mechanisms of O_2 evolution

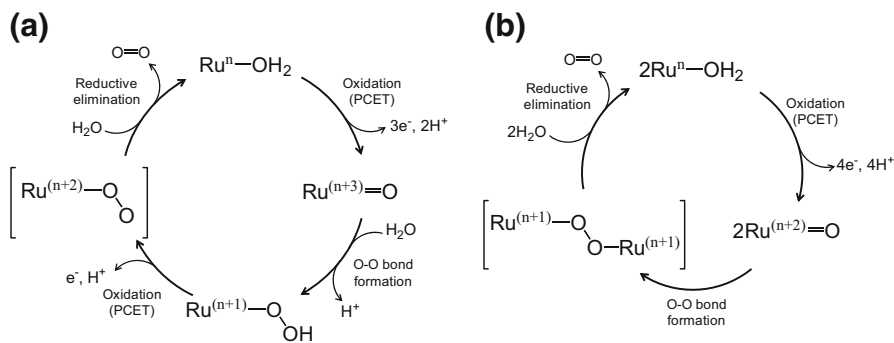
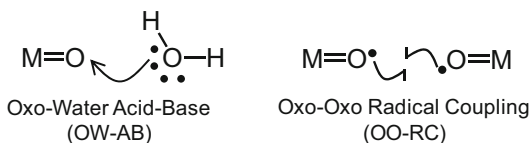
The reaction mechanisms of O_2 evolution by molecular catalysts have been widely investigated, because an understanding of such mechanisms is necessary to enable the development of new, highly-active catalysts. In typical reaction mechanisms, a high-valent metal–oxo species has been identified as the crucial intermediate in O_2 -evolution reactions. The high-valent metal–oxo species ($\text{M}^{(n+2)}=\text{O}$) is typically generated from the corresponding water-coordinated metal ion ($\text{M}^n\text{-OH}_2$) via two-step proton-coupled electron-transfer (PCET) processes, as summarized in Scheme 1 (L = ancillary ligand).

In this reaction sequence, higher oxidation states are readily accessible, primarily because of the σ and π -donating character of the oxo group. In addition, proceeding via the PCET process usually avoids high-energy intermediates and/or electrostatic



Scheme 1 Proton-coupled electron-transfer (PCET) reactions of a water-coordinated metal ion

Scheme 2 Proposed reaction pathways for formation of O₂ catalyzed by metal complexes



Scheme 3 Proposed mechanistic cycles for typical O₂ evolution catalyzed by ruthenium complexes via **a** the OW-AB pathway and **b** the OO-RC pathway

charge buildup during the reactions [23, 24]. The resulting high-valent metal-oxo species is believed to be involved in formation of the O–O bond.

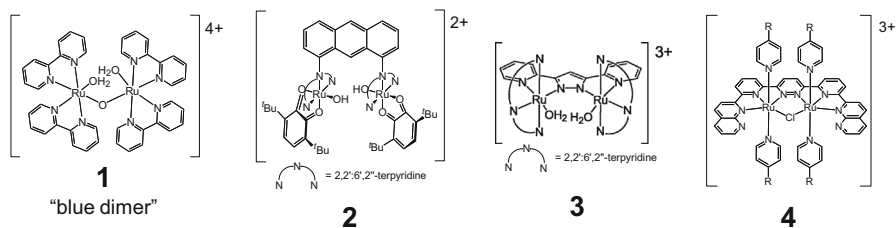
The O–O bond-formation process is the most important step in the reaction mechanism, because it is significantly more difficult than the other reaction steps. Therefore, it is important to have a good understanding of the O–O bond-formation process to enable efficient design of a catalyst suitable for water oxidation. Two possible O–O bond formation pathways have been proposed:

- 1 acid–base coupling between the high-valent metal–oxo species and a water molecule (the OW-AB pathway in Scheme 2); and
- 2 radical coupling between two high-valent metal–oxo species (the OO-RC pathway in Scheme 2).

It is believed the O–O bond-formation process is usually the rate-determining step (RDS) of O₂ evolution, and successive reductive elimination affords O₂, with regeneration of the water-coordinated catalyst (Scheme 3).

Catalysis of evolution of O₂ by ruthenium complexes

Ruthenium (Ru) is one of the most extensively studied transition metal ions in redox chemistry, catalysis, and photoreaction. On the basis of the well-established fundamental redox chemistry and reactivity of Ru complexes, numerous Ru-based catalysts of O₂ evolution have been reported. A typical example of an Ru-based catalyst with applications to water oxidation is *cis,cis*-[{(H₂O)(bpy)₂Ru^{III}}



Scheme 4 Structures of dinuclear Ru-based catalysts of O₂ evolution

(μ -O){Ru^{III}(bpy)₂(OH₂)₂}⁴⁺ (**1** in Scheme 4; bpy = 2,2'-bipyridine), the so called "blue dimer" [25, 26] reported by Meyer in 1982. This compound, the first successful molecular catalyst of O₂ evolution is active in the water-oxidation reaction during either electrochemical or chemical oxidation with Ce⁴⁺ as terminal oxidant, although both its catalytic activity and stability are quite low. After discovery, several analogous oxo or chloro-bridged diruthenium complexes were also reported as catalysts of O₂ evolution [27–33]. These newer derivatives, however, with the original blue dimer, are poorly stable during the catalysis reaction, because of gradual decomposition of the μ -oxo bridged diruthenium core. Several, more robust, multinuclear catalysts with rigid bridging ligands have since been developed by Tanaka [34, 35], Llobet [36], Thummel [37] (**2–4** in Scheme 4), and others [38–41].

Because of the need for multi-electron-transfer processes in the water oxidation reaction mechanism, it has long been assumed that the O₂-evolving activity of multinuclear complexes will be substantially higher than that of mononuclear complexes [6]. Indeed, several mononuclear complexes, e.g. Ru(bpy)₂Cl₂, have been examined as control experiments for **1**, and show almost no catalytic activity toward O₂ evolution [32, 33]. Before 2008, the basic strategy for development of diruthenium catalysts of O₂ evolution was, therefore, to design the structure of the catalyst such that two ruthenium-oxo groups were situated in close proximity, to facilitate oxo–oxo radical coupling, as in the OO-RC pathway in Scheme 2 [6]. Both ¹⁸O-isotopic-labeling studies and DFT calculations have in fact revealed that O₂-evolution reactions catalyzed by some diruthenium systems, including catalysts **2** and **3**, proceed via the intramolecular oxo–oxo radical-coupling pathway [42–45]. It has, however, been suggested that O₂ evolution reactions catalyzed by blue dimer and its analogues proceed via the oxo-water acid–base pathway in which O–O bond formation occurs between the oxygen atom bound to the ruthenium center and the oxygen atom of a water molecule in the bulk solution (as shown in the OW-AB pathway in Scheme 2) [46–48]. Because this result contradicts the basic strategy for development of catalysts of O₂ evolution, it seems it should be possible to use similar O₂ evolution pathways by using monoruthenium complexes as catalysts of O₂ evolution.

Recently, several different groups, including our own, have discovered that mononuclear ruthenium complexes with a single labile site have surprisingly high catalytic activity toward evolution of O₂ from water in the presence of Ce⁴⁺ as

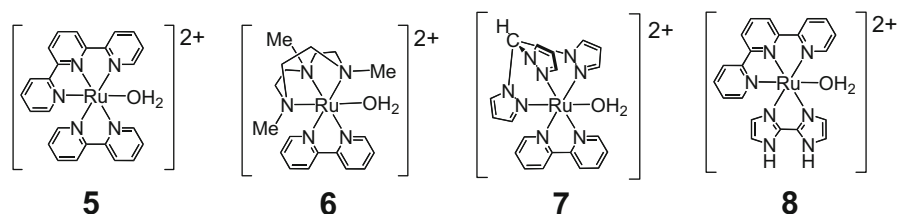
Table 1 Turnover number (TON) values and associated oxidants for several mononuclear Ru-based catalysts of O₂ evolution

Complex	Oxidant	TON	[Ce ⁴⁺]/[Cat.]
5	Ce ⁴⁺ , electrode	310	1,600
6	Ce ⁴⁺	148	1,600
7	Ce ⁴⁺	123	1,600
8	Electrode	Not reported	Not reported
9	Ce ⁴⁺	390	5,000
10	Ce ⁴⁺ , electrode	7.68	30
11	Ce ⁴⁺	690	50,000
12	Ce ⁴⁺ , electrode	ca. 8	30
13	Ce ⁴⁺ , electrode	ca. 8	30
14	Ce ⁴⁺	Not reported	30
15	Ce ⁴⁺ , electrode, [Ru(bpy) ₃] ³⁺	120	13,750
16	Ce ⁴⁺ , electrode	8,360	2,222–35,867

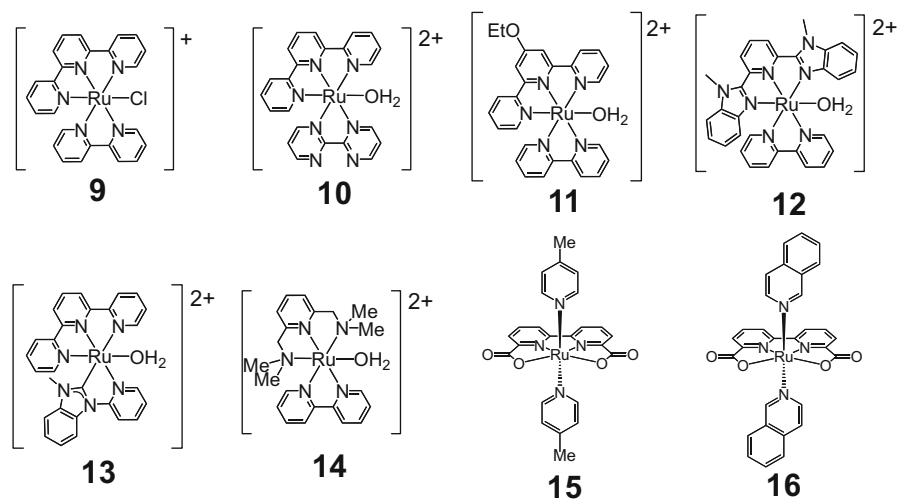
oxidant (Table 1) This is a surprising development, because it has been the long-held belief that the mononuclear complexes have almost no activity as catalysts of O₂ evolution [33, 49]. Specifically, in 2008, the authors reported that the mononuclear aquaruthenium complex [Ru^{II}(terpy)(bpy)(OH₂)²⁺ (**5** in Scheme 5; terpy = 2,2':6',2''-terpyridine) has significant activity on the catalytic evolution of O₂ and, in addition, seems robust throughout the course of the reaction [50, 51]. We also reported that other analogous mononuclear aquaruthenium complexes have such O₂-evolving activity (**6–8** in Scheme 5) [53–56]. Several other researchers have also shown that specific monoruthenium systems (for example **9–16** in Scheme 6) have similarly high catalytic activity towards O₂ evolution when Ce⁴⁺ is used as the oxidant [57–77]. These findings were a significant breakthrough in this field and led to subsequent reports of a variety of highly efficient catalysts. For example, although turnover frequencies (TOFs) of the most active diruthenium catalysts were ca. 10⁻² s⁻¹ [31, 36] they improved dramatically after the discovery of monoruthenium catalysts (TOF = 0.11 s⁻¹ for **11** [65], 3.6 s⁻¹ for **13** [63], and 300 s⁻¹ for **16** [72]).

Reaction kinetics of O₂ evolution catalysis

To further elucidate the O–O bond-formation pathways involved in the catalytic action of mononuclear ruthenium complexes, several researchers, including the authors, attempted to identify the intermediate species involved in the reaction and to confirm the rate-determining step (RDS). The authors initially tried to characterize the active species and other intermediates in O₂ evolution catalyzed by **5**, by studying mixtures of **5** with 10 equiv. Ce⁴⁺ in 0.1 M HClO₄ by use of stopped-flow apparatus. In these trials, the intense absorption band of **5** at 475 nm decayed rapidly after mixing, after which new absorption bands at 500 and 700 nm



Scheme 5 Structures of mononuclear Ru-based catalysts of O₂ evolution discovered by the authors

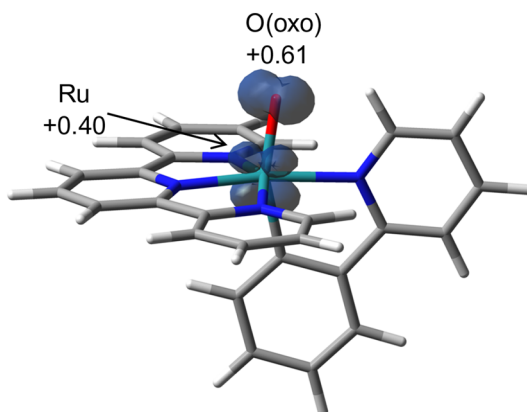


Scheme 6 Structures of mononuclear Ru-based catalysts of O₂ evolution discovered by other researchers

gradually appeared as the reaction proceeded. These spectral changes were analyzed by use of the singular value decomposition (SVD) method in the SPECFIT software package [78]; the results suggested the presence of five detectable Ru-based chemical species during the overall reaction process. These spectral components were successfully identified on the basis of TD-DFT calculations ((U)B3LYP/LanL2DZ) and, on the basis of the results, the Ru^V=O species was determined to be the primary final product and, as such, is believed to be the dominant higher-valent species during the catalytic O₂ evolution reaction [55].

The authors also calculated the electronic structure of the Ru^V=O species by use of the DFT method (UB3LYP/LanL2DZ) and determined that the O(oxo) atom of the species has substantial radical character (Fig. 1), which can also be understood as Mulliken spin density located at the O(oxo) atom [55]. This clearly indicates that the Ru^V=O species has the characteristics of a highly reactive oxo radical which can be reasonably represented by the two resonance structures Ru^V=O ↔ Ru^{IV}-O·. The oxygen atom bound to the Ru ion thus simultaneously exhibits characteristics of not only a Lewis acid but also a radical.

Fig. 1 Spin density distributions of $[\text{Ru}^{\text{V}}(\text{terpy})(\text{bpy})(\text{O})]^{3+}$. The values of the spin density of the oxygen atom and ruthenium atoms are depicted with α spins having positive signs



Several of groups, including the authors' group, also attempted to determine the RDS of O_2 evolution as catalyzed by mononuclear Ru complexes. The rate of O_2 formation catalyzed by **6**, as estimated from the initial slope, is described by a quadratic equation based on catalyst concentration and which is independent of Ce^{4+} concentration (i.e., is zero order) [54]. The rate law for this reaction can therefore be described as follows:

$$v_{\text{O}_2} = d[\text{O}_2]/dt = k[\text{Catalyst}]^2$$

Because the rate-determining step for catalysis by **6** is second-order with regard to catalyst concentration and zero order with regard to Ce^{4+} concentration, the OO-RC pathway (Scheme 2) is likely to be the predominant mechanism of O_2 evolution as catalyzed by **6**. The kinetics of $\text{Ce}(\text{IV})$ -driven catalytic oxidation of water in aqueous solution was also determined to be second-order, depending on the concentration of **15** [68], which suggests that the O_2 evolution reaction catalyzed by **15** also proceeds via the OO-RC path [70].

In contrast, electrochemical studies performed by our group using an ITO electrode modified with a derivative of **5** revealed that O–O bond formation can also occur by direct attack of a water molecule, as in the OW-AB pathway [53]. The Ru–Ru distance in this system, 35 Å, does not allow two or more ruthenium centers to engage in the same O_2 evolution event, hence the electrocatalytic evolution of O_2 from water which occurs in this process is due solely to events at a single aquaruthenium site. This same pathway has also been described by Thummel [57–59], Meyer [60–63], van Voorhis [79], and Llobet [73, 74]. In Meyer's work, the rate of evolution of O_2 catalyzed by **10** in aqueous 0.1 M HNO_3 was first-order with regard to catalyst concentration and zero-order with regard to Ce^{4+} concentration, so the reaction catalyzed by **10** must proceed via the OW-AB pathway, in accordance with the rate law:

$$v_{\text{O}_2} = d[\text{O}_2]/dt = k[\text{Catalyst}]$$

Meyer explains these results by theorizing that the nucleophilic attack of water on $\text{Ru}^{\text{V}}=\text{O}$ is the RDS of the O_2 evolution reaction as it proceeds via the OW-AB

pathway, which progresses via the putative intermediate species $\text{Ru}^{\text{III}}\text{-OOH}$. This species is subsequently oxidized to $\text{Ru}^{\text{IV}}(\text{OO})$, followed by reductive elimination of O_2 .

In contrast, the rate of evolution of O_2 during catalysis by **5** is linearly dependent on both catalyst concentration and Ce^{4+} concentration [51, 54]; the rate law for this reaction can therefore be summarized as:

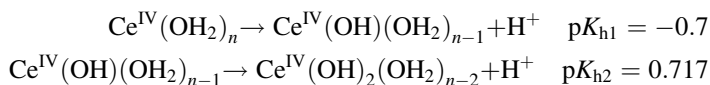
$$v_{\text{O}_2} = d[\text{O}_2]/dt = k[\text{Catalyst}][\text{Ce}^{4+}]$$

This rate law suggests that the $\text{Ru}^{\text{V}}=\text{O}$ species and cerium(IV) form an encounter complex during the transition state in the RDS. This is problematic, however, because cerium(IV) has long been regarded as a simple, one-electron oxidant and, if this is the case, the observed rate law cannot be explained. In addition, several researchers have reported that the nitrate ion attached to cerium(IV) is also involved in the catalytic cycle of O_2 evolution as a minor pathway [76, 80]. These results indicate the anomalous function of cerium(IV) in O_2 evolution. Consequently, to better describe the reactivity it is necessary to obtain a better understanding of the evidently complicated properties of cerium(IV) as a metal ion.

Fundamental properties of cerium(IV)

Over the last three decades, cerium(IV) ammonium nitrate (CAN) has been most commonly used as a so-called simple, one-electron oxidant, and numerous catalysts of O_2 evolution based on metal complexes have been developed in conjunction with use of cerium(IV) as an oxidant. Despite this significant body of research, however, several anomalies have been observed in the function of cerium(IV) in the catalysis of O_2 evolution.

To further clarify the Ce(IV)-based evolution of O_2 from water, it is vital to understand the complicated properties of cerium(IV). Cerium(IV) is well known not only as a strong oxidant, but also as a strong Lewis acid [81–83]. The first and second hydrolysis equilibrium constants ($\text{p}K_{\text{h1}}$, $\text{p}K_{\text{h2}}$) for cerium(IV) were determined by Yu and O'Keefe as follows [84, 85]:



Owing to this hydrolysis equilibrium, the formal potential of the Ce(IV)/Ce(III) system changes on varying the acid concentration; for example, $E_0 = +1.26$ V versus NHE in 0.1 M HNO_3 yet +1.37 V versus NHE in 1.0 M HNO_3 [86]. In addition, compared with $\text{Ce}^{\text{IV}}(\text{OH})$, $\text{Ce}^{\text{IV}}(\text{OH})_2$ readily forms less-reactive [87–90] μ -oxo cerium(IV) dimers (for example $\text{Ce}^{\text{IV}}(\mu\text{-O})\text{Ce}^{\text{IV}}$) [91, 92] or oligomers [93], which leads to additional complications. At $\text{pH} > 2\text{--}3$, cerium(IV) also forms stable precipitates, for example CeO_2 [84, 85]. Notwithstanding these complexities, $\text{Ce}^{\text{IV}}(\text{OH})$ is the dominant chemical species under the standard reaction conditions used during O_2 evolution ($\text{pH} \approx 0$).

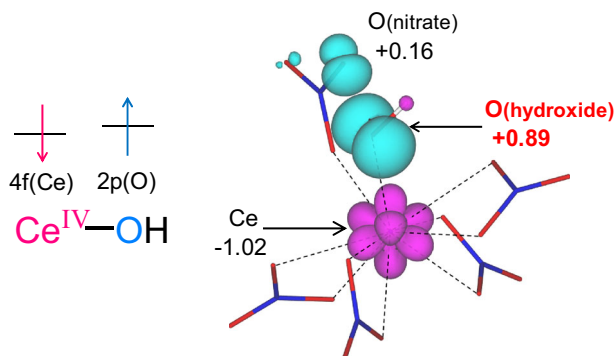
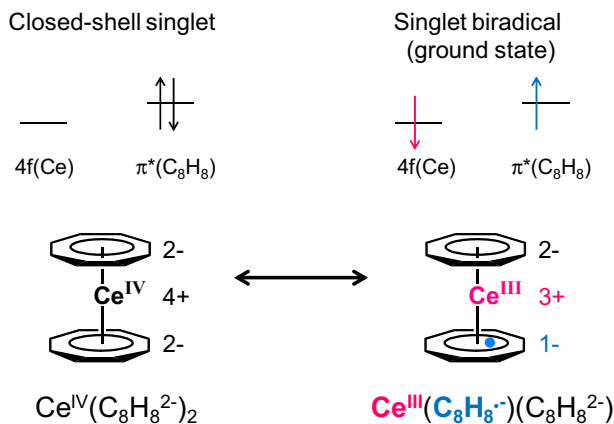


Fig. 2 Spin density distributions of $[\text{Ce}^{\text{IV}}(\text{OH})(\text{NO}_3)_5]^{2-}$ in the open-shell singlet state. The values of the spin density of the oxygen atom and cerium atoms are depicted with α and β spins having positive and negative signs, respectively

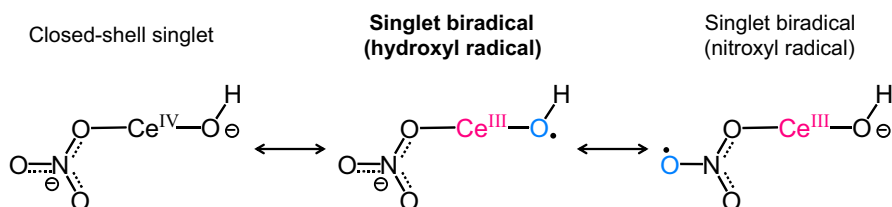
Importantly, it has been suggested the $\text{Ce}^{\text{IV}}(\text{OH})$ species exists in an unusual electronic state. The authors computed the electronic structure of one of the possible hydroxocerium(IV) ions, $[\text{Ce}^{\text{IV}}(\text{OH})(\text{NO}_3)_5]^{2-}$, by use of the DFT method (UM05-2X/CEP-4G) [54] and found that Mulliken atomic spin densities of +0.89 and -1.02 are present on the O(hydroxide) and Ce atoms, respectively (Fig. 2). These spin density distributions show that one spin occupies the 4f orbital of the cerium ion whereas the other is primarily located on the O(hydroxide) atom, indicating that this ion can be described more accurately as $[\text{Ce}^{\text{III}}(\cdot\text{OH})(\text{NO}_3)_5]^{2-}$, and so the spins localized on the Ce^{III} and O(hydroxide) atoms are antiferromagnetically coupled. The spin density is also somewhat localized on the O(nitrate) atom. These results reveal the singlet biradical character of the hydroxocerium(IV) ion [54].

Although it has been widely assumed that compounds of Ce^{4+} have a $4f^0$ configuration (e.g., $[\text{Xe}](6s)^0(4f)^0$ for Ce(IV)) and simple diamagnetism, some cerium(IV) complexes also have singlet biradical character [94–96]. Neumann and Fulde first investigated the detailed electronic structure of $\text{Ce}(\text{C}_8\text{H}_8)_2$ (cerocene, in which $\text{C}_8\text{H}_8^{2-}$ is the cyclooctatetraene dianion), and revealed that the compound is better described as $\text{Ce}^{\text{III}}(\text{C}_8\text{H}_8^{2-})(\text{C}_8\text{H}_8^-)$, in which one spin is localized on the cerium ion ($4f^1$) and the other on one of the ligands (Scheme 7) [94]. This is now understood as an open-shell singlet state in which two spins within the molecule are antiferromagnetically coupled. In other words, cerocene also has a singlet biradical ground state.

The singlet biradical character of the hydroxocerium(IV) ion indicates that a highly reactive hydroxyl radical ($\text{HO}\cdot$) is, formally, localized throughout the ion (Scheme 8). If this is so, cerium(IV) functions not only as an oxidant but also as a radical. Indeed, cerium(IV) oxidizes aldehydes, ketones, and alcohols at the α -carbon atom via a radical-like H-atom abstraction mechanism, suggesting radical-like reactivity of the hydroxocerium(IV) species [97–99]. This is further supported by the fact that cerium(IV) readily generates free radicals in response to photo-excitation [100–102]. Cerium(IV) complexes with an O-donor ligand also have a broad absorption band in the near-UV to visible region, corresponding to the charge



Scheme 7 Singlet biradical character of cerocene

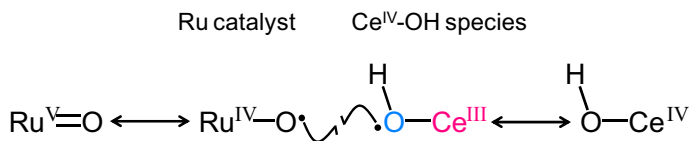


Scheme 8 Possible resonance structures of the $\text{Ce}^{\text{IV}}(\text{OH})(\text{NO}_3)$ species

transfer band from the O atom to the metal [103]. Evans and Uri have reported that photo-excitation of this absorption band induces generation of a free hydroxyl radical, leading to O_2 evolution [100].

Mechanism of cerium(IV)-driven water oxidation

The radical-like character of cerium(IV) clearly explains the mechanism of O_2 evolution during catalysis with **5**. As noted above, the rate of evolution of O_2 catalyzed by **5** is first-order with regard to both catalyst and Ce^{4+} concentrations. In addition, the O(oxo) atoms of both the $\text{Ru}^{\text{V}}=\text{O}$ species and the $\text{Ce}^{\text{IV}}(\text{OH})$ species have substantial radical characteristics. On the basis of these findings, we proposed that the pathway of O_2 evolution during catalysis by **5** proceeds primarily via the oxo-hydroxocerium(IV) radical-coupling pathway (the OH-RC pathway). In this process, cerium(IV) functions both as an oxidant and as a radical and provides an efficient pathway enabling radical–radical coupling between the catalyst and the cerium(IV) [54, 55]. Because the spin density is also partially located on the O(nitrate) atom of the $\text{Ce}^{\text{IV}}(\text{OH})(\text{NO}_3)$ species, the NO_3 ligand might also have radical-like reactivity. Our interpretation of the reaction mechanisms seems to take



Scheme 9 O–O bond formation step in the oxidation of water promoted by the radical-like character of the hydroxocerium(IV) species

into account the specific characteristics of cerium(IV). It is also noteworthy that most Ru-based catalysts of O₂ evolution reported to date have used CAN as oxidant [25–80], which implies that use of CAN is crucial.

In summary, it is reasonable to conclude that O₂-evolving reactions catalyzed by **5** proceed preferentially via the oxo-hydroxocerium(IV) radical coupling path (the OH-RC pathway; Scheme 9), even though this reaction may also proceed via coupling with oxygen in the water bulk (the OW-AB pathway) in the absence of the hydroxocerium(IV) species. A possible interpretation of these findings is that O–O bond formation occurs as the RDS via coupling of the Ru^V=O (\leftrightarrow Ru^{IV}-O·) and hydroxocerium(IV) species, leading to formation of either the Ru^{IV}-O-O(H)-Ce^{III} or the Ru^{IV}-O-O-Ce^{III} species, followed by elimination of Ce³⁺ to give Ru^{III}-(OO·) [55]. The Ru^{III}-OH₂ species is then regenerated by reductive elimination of O₂ from Ru^{III}-(OO·).

The nitrate ion attached to cerium(IV) is also involved in the catalytic cycle of O₂ evolution, as follows:

- 1 As reported by Berlinguette and co-workers, a small number of oxygen atoms derived from [Ce(NO₃)₆]²⁻ are incorporated into the final dioxygen product during reactions catalyzed by **5** [76].
- 2 Stull et al. identified new intermediate species by analysis of distinct features in EPR, optical, and resonance Raman (RR) spectra when the cerium(IV)-nitrate complex was used as an oxidant [80].

The radical-like character of cerium(IV) also clearly explains the specific reactivity of the nitrate ion attached to cerium(IV), because the spin density is also partially located on the O(nitrate) atom of the Ce^{IV}(OH)(NO₃) species.

Concluding remarks

In this review we have summarized recent notable developments in investigations of the mechanisms of O₂-evolving reactions catalyzed by ruthenium complexes with cerium(IV) as an oxidant. Although mononuclear complexes are believed to have almost no activity compared with multinuclear complexes, in recent years several mononuclear ruthenium complexes with a single labile site have been developed as efficient catalysts for oxidation of water, and have been described herein. These findings led to dramatic improvement of O₂-evolving activity, (e.g., the rate of O₂ evolution). Three distinct O–O bond-formation pathways, the OO-RC, OW-AB, and

OH-RC pathways, involved in evolution of O₂ catalyzed by mononuclear ruthenium complexes were considered. This review also affirmed the crucial function of cerium(IV) in the water-oxidation process. The discovery of the utility of this species was so important that most Ru-based catalysts of O₂ evolution reported to date have incorporated use of cerium(IV) as oxidant. These novel concepts of catalysis will provide new ideas with regard to the design of more highly active catalysts of O₂ evolution.

References

1. Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature* **473**, 55 (2011)
2. G.W. Brudvig, R.H. Crabtree, *Prog. Inorg. Chem.* **37**, 99 (1989)
3. T.J. Meyer, *Acc. Chem. Res.* **22**, 163 (1989)
4. W. Rüttinger, G.C. Dismukes, *Chem. Rev.* **97**, 1 (1997)
5. M. Yagi, M. Kaneko, *Chem. Rev.* **101**, 21 (2001)
6. Romero, M. Rodríguez, C. Sens, J. Mola, M. R. Kollipara, L. Francàs, E. Mas-Marza, L. Escriche, A. Llobet, *Inorg. Chem.* **47**, 1824 (2008)
7. J. Limburg, J.S. Vrettos, L.M. Liable-Sands, A.L. Rheingold, R.H. Crabtree, G.W. Brudvig, *Science* **283**, 1524 (1999)
8. Y. Shimazaki, T. Nagano, H. Takesue, B.-H. Ye, F. Tani, Y. Naruta, *Angew. Chem. Int. Ed.* **43**, 98 (2004)
9. M. Yagi, K. Narita, *J. Am. Chem. Soc.* **126**, 8084 (2004)
10. K. Poulsen, A. Rompel, C.J. McKenzie, *Angew. Chem. Int. Ed.* **44**, 6916 (2005)
11. R. Brimblecombe, G.F. Swiegers, G.C. Dismukes, L. Spiccia, *Angew. Chem. Int. Ed.* **47**, 7335 (2008)
12. N.D. McDaniel, F.J. Coughlin, L.L. Tinker, S. Bernhard, *J. Am. Chem. Soc.* **130**, 210 (2008)
13. J.F. Hull, D. Balcells, J.D. Blakemore, C.D. Incarvito, O. Eisenstein, G.W. Brudvig, R.H. Crabtree, *J. Am. Chem. Soc.* **131**, 8730 (2009)
14. A.R. Parent, T.P. Brewster, W. De Wolf, R.H. Crabtree, G.W. Brudvig, *Inorg. Chem.* **51**, 6147 (2012)
15. Q. Yin, J.M. Tan, C. Besson, Y.V. Geletii, D.G. Musaev, A.E. Kuznetsov, Z. Luo, K.I. Hardcastle, C.L. Hill, *Science* **328**, 342 (2010)
16. D.J. Wasylenko, C. Ganesamoorthy, J. Borau-Garcia, C.P. Berlinguette, *Chem. Commun.* **47**, 4249 (2011)
17. S. Tanaka, M. Annaka, K. Sakai, *Chem. Commun.* **48**, 1653 (2012)
18. W.C. Ellis, N.D. McDaniel, S. Bernhard, T.J. Collins, *J. Am. Chem. Soc.* **132**, 10990 (2010)
19. J.L. Fillol, Z. Codolà, I. Garcia-Bosch, L. Gómez, J.J. Pla, M. Costas, *Nat. Chem.* **3**, 807 (2011)
20. G. Zhu, E.N. Glass, C. Zhao, H. Lv, J.W. Vickers, Y.V. Geletii, D.G. Musaev, J. Song, C.L. Hill, *Dalton Trans.* **41**, 13043 (2012)
21. S.M. Barnett, K.I. Goldberg, J.M. Mayer, *Nat. Chem.* **4**, 498 (2012)
22. Z. Chen, T.J. Meyer, *Angew. Chem. Int. Ed.* **52**, 700 (2013)
23. M.H. Huynh, T.J. Meyer, *Chem. Rev.* **107**, 5004 (2007)
24. J.J. Warren, T.A. Tronic, J.M. Mayer, *Chem. Rev.* **110**, 6961 (2010)
25. S.W. Gersten, G.J. Samuels, T.J. Meyer, *J. Am. Chem. Soc.* **104**, 4029 (1982)
26. J.A. Gilbert, D.S. Eggleston, W.R. Murphy Jr, D.A. Geselowitz, S.W. Gersten, D.J. Hodgson, T.J. Meyer, *J. Am. Chem. Soc.* **107**, 4029 (1985)
27. R. Ramaraj, A. Kira, M. Kaneko, *Angew. Chem. Int. Ed.* **25**, 1009 (1986)
28. F.P. Rotzinger, S. Munavalli, P. Comte, J.K. Hurst, M. Grätzel, F. Pern, A.J. Frank, *J. Am. Chem. Soc.* **109**, 6619 (1987)
29. F.P. Rotzinger, S. Munavalli, P. Comte, J.K. Hurst, M. Grätzel, F. Pern, A.J. Frank, *J. Am. Chem. Soc.* **109**, 6619 (1987)
30. H.H. Petach, M. Elliott, *J. Electrochem. Soc.* **139**, 2217 (1992)
31. M. Yagi, Y. Osawa, N. Sukegawa, M. Kaneko, *Langmuir* **15**, 7406 (1999)

32. K. Nagoshi, S. Yamashita, M. Yagi, M. Kaneko, *J. Mol. Catal. A: Chem.* **144**, 71 (1999)
33. J.P. Collin, J.P. Sauvage, *Inorg. Chem.* **25**, 135 (1986)
34. T. Wada, K. Tsuge, K. Tanaka, *Angew. Chem. Int. Ed.* **39**, 1479 (2000)
35. T. Wada, K. Tsuge, K. Tanaka, *Inorg. Chem.* **40**, 329 (2001)
36. C. Sens, I. Romero, M. Rodríguez, A. Llobet, T. Parella, J. Benet-Buchholz, *J. Am. Chem. Soc.* **126**, 7798 (2004)
37. R. Zong, R.P. Thummel, *J. Am. Chem. Soc.* **127**, 12802 (2005)
38. Y.V. Geletti, B. Botar, P. Kögerler, D.A. Hillesheim, D.G. Musaev, C.L. Hill, *Angew. Chem. Int. Ed.* **47**, 3896 (2008)
39. Sartorel, M. Carraro, G. Scorrano, R. De Zorzi, S. Geremia, N. D. McDaniel, S. Bernhard, M. Bonchio, *J. Am. Chem. Soc.* **130**, 5006 (2008)
40. Y. Xu, A. Fischer, L. Duan, L. Tong, E. Gabrielsson, B. Åkermark, L. Sun, *Angew. Chem. Int. Ed.* **49**, 8934 (2010)
41. M.D. Kärkäs, E.V. Johnston, E.A. Karlsson, B.-L. Lee, T. Åkermark, M. Shariatgorji, L. Ilag, Ö. Hansson, J.-E. Bäckvall, B. Åkermark, *Chem. Eur. J.* **17**, 7953 (2011)
42. S. Romain, F. Bozoglian, X. Sala, A. Llobet, *J. Am. Chem. Soc.* **131**, 2768 (2009)
43. F. Bozoglian, S. Romain, M.Z. Ertem, T.K. Todorova, C. Sens, J. Mola, M. Rodríguez, I. Romero, J. Benet-Buchholz, X. Fontrodona, C.J. Cramer, L. Gagliardi, A. Llobet, *J. Am. Chem. Soc.* **131**, 15176 (2009)
44. J.T. Muckerman, D.E. Polyansky, T. Wada, K. Tanaka, E. Fujita, *Inorg. Chem.* **47**, 1787 (2008)
45. K. Tanaka, H. Isobe, S. Yamanaka, K. Yamaguchi, *Proc. Natl. Acad. Sci. U.S.A.* **109**, 15600 (2012)
46. X. Yang, M.-H. Baik, *J. Am. Chem. Soc.* **128**, 7476 (2006)
47. J.K. Hurst, J.L. Cape, A.E. Clark, S. Das, C. Qin, *Inorg. Chem.* **47**, 1753 (2008)
48. J.L. Cape, W.F. Siems, J.K. Hurst, *Inorg. Chem.* **48**, 8729 (2009)
49. T.A. Betley, Q. Wu, T.V. Voorhis, D.G. Nocera, *Inorg. Chem.* **47**, 1849 (2008)
50. S. Masaoka, K. Sakai, The 88th Annual Meeting of Chemical Society of Japan, Tokyo, Paper No. 1E6-39 (2008)
51. S. Masaoka, K. Sakai, *Chem. Lett.* **38**, 182 (2009)
52. M. Yoshida, S. Masaoka, K. Sakai, *Chem. Lett.* **38**, 702 (2009)
53. J. Kiyota, J. Yokoyama, M. Yoshida, S. Masaoka, K. Sakai, *Chem. Lett.* **39**, 1146 (2010)
54. M. Yoshida, S. Masaoka, J. Abe, K. Sakai, *Chem. Asian J.* **5**, 2369 (2010)
55. K. Kimoto, M. Yamauchi, S. Yoshida, K. Masaoka, Sakai, *Chem. Commun.* **48**, 239 (2012)
56. M. Okamura, M. Yoshida, R. Kuga, K. Sakai, M. Kondo, S. Masaoka, *Dalton Trans.* **41**, 13081 (2012)
57. H.-W. Tseng, R. Zong, J.T. Muckerman, R. Thummel, *Inorg. Chem.* **47**, 11763 (2008)
58. D.E. Polyansky, J.T. Muckerman, J. Rochford, R. Zong, R.P. Thummel, E. Fujita, *J. Am. Chem. Soc.* **133**, 14649 (2011)
59. J.L. Boyer, D.E. Polyansky, D.J. Szalda, R. Zong, R.P. Thummel, E. Fujita, *Angew. Chem. Int. Ed.* **50**, 12600 (2011)
60. J.J. Concepcion, J.W. Jurss, J.L. Templeton, T.J. Meyer, *J. Am. Chem. Soc.* **130**, 16462 (2008)
61. J.J. Concepcion, M.-K. Tsai, J.T. Muckerman, T.J. Meyer, *J. Am. Chem. Soc.* **132**, 1545 (2010)
62. J.J. Concepcion, J.W. Jurss, M.R. Norris, Z. Chen, J.L. Templeton, T.J. Meyer, *Inorg. Chem.* **49**, 1277 (2010)
63. Z. Chen, J.J. Concepcion, T.J. Meyer, *Dalton Trans.* **40**, 3789 (2011)
64. S. Tajima, M. Komi, K. Sone, M. Yagi, The 88th Annual Meeting of Chemical Society of Japan, Tokyo, Paper No. 1E6-36 (2008)
65. M. Yagi, A. Syouji, S. Yamada, M. Komi, H. Yamazaki, S. Tajima, *Photochem. Photobiol. Sci.* **8**, 139 (2009)
66. M. Yagi, S. Tajima, M. Komi, H. Yamazaki, *Dalton Trans.* **40**, 3802 (2011)
67. H. Yamazaki, T. Hakamata, M. Komi, M. Yagi, *J. Am. Chem. Soc.* **133**, 8846 (2011)
68. L. Duan, A. Fischer, Y. Xu, L. Sun, *J. Am. Chem. Soc.* **131**, 10397 (2009)
69. L. Duan, Y. Xu, P. Zhang, M. Wang, L. Sun, *Inorg. Chem.* **49**, 209 (2010)
70. J. Nyhlén, L. Duan, B. Åkermark, L. Sun, T. Privalov, *Angew. Chem. Int. Ed.* **49**, 1773 (2010)
71. L. Tong, L. Duan, Y. Xu, T. Privalov, L. Sun, *Angew. Chem. Int. Ed.* **50**, 445 (2011)
72. L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun, *Nat. Chem.* **4**, 418 (2012)
73. S. Romain, L. Vigara, A. Llobet, *Acc. Chem. Res.* **42**, 2009 (1944)

74. X. Sala, M.Z. Ertem, L. Vigara, T.K. Todorova, W. Chen, R.C. Rocha, F. Aquilante, C.J. Cramer, L. Gagliardi, A. Llobet, *Angew. Chem. Int. Ed.* **49**, 7745 (2010)
75. D.J. Wasylenko, C. Ganesamoorthy, B.D. Koivisto, M.A. Henderson, C.P. Berlinguette, *Inorg. Chem.* **49**, 2202 (2009)
76. D.J. Wasylenko, C. Ganesamoorthy, M.A. Henderson, B.D. Koivisto, H.D. Osthoff, C.P. Berlinguette, *J. Am. Chem. Soc.* **132**, 16094 (2010)
77. D.J. Wasylenko, C. Ganesamoorthy, M.A. Henderson, C.P. Berlinguette, *Inorg. Chem.* **50**, 3662 (2011)
78. SPECFIT; Spectrum Research Associate: Chapel Hill, NC
79. L.-P. Wang, Q. Wu, T.V. Voorhis, *Inorg. Chem.* **49**, 4543 (2010)
80. J.A. Stull, R.D. Britt, J.L. McHale, F.J. Knorr, S.V. Lymar, J.K. Hurst, *J. Am. Chem. Soc.* **134**, 19973 (2012)
81. H.G. Offner, D.A. Skoog, *Anal. Chem.* **38**, 1520 (1966)
82. M. Komiyama, N. Takeda, Y. Takahashi, H. Uchida, T. Shiiba, T. Kodama, M. Yashiro, *J. Chem. Soc. Perkin Trans.* **2**, 269 (1995)
83. P.M. Cullis, E. Snip, *J. Am. Chem. Soc.* **121**, 6125 (1999)
84. P. Yu, S.A. Hayes, T.J. O'Keefe, M.J. O'Keefe, J.O. Stoffer, *J. Electrochem. Soc.* **153**, C74 (2006)
85. P. Yu, T.J. O'Keefe, *J. Electrochem. Soc.* **153**, C80 (2006)
86. F. Liu, J.J. Concepcion, J.W. Jurss, T. Cardolaccia, J.L. Templeton, T.J. Meyer, *Inorg. Chem.* **47**, 1727 (2008)
87. M. Ardon, G. Stein, *J. Chem. Soc.* 104 (1956)
88. M. Ardon, *J. Chem. Soc.* 1811 (1957)
89. D.L. Mathur, G.V. Bakore, *J. Indian Chem. Soc.* **411**, 363 (1971)
90. M.D. Fernandez, G.Z. Guzman, *Eur. Polym. J.* **25**, 1165 (1989)
91. T.J. Hardwick, E. Robertson, *Can. J. Chem.* **29**, 818 (1951)
92. D.J. Savage, T.W. Kyffin, *Polyhedron* **5**, 743 (1986)
93. E.L. King, M.L. Pandow, *J. Am. Chem. Soc.* **74**, 1966 (1952)
94. C.-S. Neumann, P. Fulde, *Z. Phys.* **B74**, 277 (1989)
95. M. Dolg, P. Fulde, W. Kuchle, C.-S. Neumann, H. Stoll, *J. Chem. Phys.* **94**, 3011 (1991)
96. C.H. Booth, M.D. Walter, M. Daniel, W.W. Lukens, R.A. Andersen, *Phys. Rev. Lett.* **95**, 267202 (2005)
97. J. Shorter, *J. Chem. Soc.* 1868 (1962)
98. D.L. Mathur, G.V. Bakore, *Bull. Chem. Soc. Jpn* **44**, 2600 (1971)
99. G.G. Rao, B.M. Rao, *Anal. Chim. Acta* **59**, 461 (1972)
100. M.G. Evans, N. Uri, *Nature* **166**, 602 (1950)
101. L. Dogliotti, E. Hayon, *J. Phys. Chem.* **71**, 3802 (1967)
102. E. Baciocchi, T. Del Giacco, S.M. Murgia, G.V. Sebastiani, *Tetrahedron* **44**, 6651 (1988)
103. B. Yusov, V. P. Shilov, *Russ. Chem. Bull., Int. Ed.* **49**, 1925 (2000)