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Clear Evidence Showing the Robustness of a Highly Active Oxygen-evolving Mononuclear Ruthenium Complex with an Aqua Ligand

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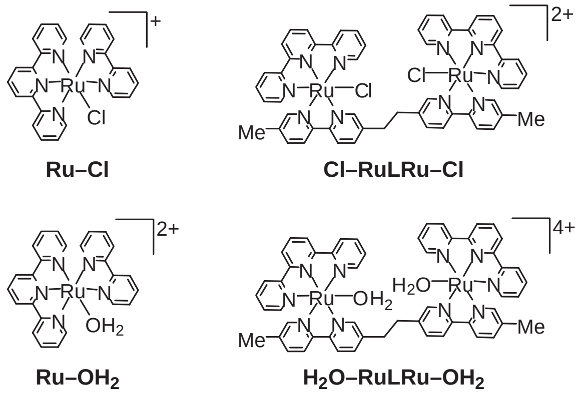
Experiments show that $[Ru(terpy)(bpy)(OH_2)]^{2+}$ is highly active as a catalyst toward oxidation of water into molecular oxygen in spite of the mononuclear character of the complex, while $[Ru(terpy)(bpy)Cl]^{+}$ shows no activity at all. It is also confirmed that $[Ru(terpy)(bpy)(OH_2)]^{2+}$ is fairly stable under strongly oxidizing conditions in the presence of cerium(IV) ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$, which was evidenced by spectrophotometric, mass spectrometric, and gas chromatographic analysis.

Oxidation of water into molecular oxygen ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is one of the most important chemical processes in nature, in which tetramanganese clusters serve as molecular catalysts.[1] However, development of artificial O_2-evolving molecular catalysts remains a challenging target. Such catalysts will play a significant role in artificial solar energy-conversion systems based on visible light-driven water-splitting reactions ($2H_2O + 4h\nu \rightarrow 2H_2 + O_2$). Up to now, dimanganese[2] and diruthenium[3,4] catalysts have been reported to exhibit such activities, even though stability problems must be solved toward future practical applications. The well-known oxo-bridged diruthenium complex developed by Meyer et al., $[\{Ru(bpy)_2(H_2O)\}_2(\mu\text{-}O)](ClO_4)_4$ (H_2O–Ru–O–Ru–OH_2), had been for a long time a rare example of molecular catalyst exhibiting O_2-evolving activity until the discovery of the more highly active diruthenium catalyst developed by Tanaka et al.[4a] Following this, several other active diruthenium catalysts were reported.[4b,4c] Very recently, some mononuclear ruthenium complexes were also reported to be active.[5] Nevertheless, the mechanism of O_2 formation as well as the decomposition pathways of catalysts has not been well rationalized.

In order to develop more highly active and robust O_2-evolving catalysts and also to set down a rational strategy to control the activity of catalysts, various other diruthenium cores with different interaction modes of two metal centers must be explored. In the present study, the O_2-evolving activities of new diruthenium catalysts (Cl–RuLRu–Cl and H_2O–RuLRu–OH_2; see Scheme 1) have been evaluated using cerium(IV) ammonium nitrate as an oxidizing reagent. During the detailed studies on these systems, it was also realized that the mononuclear systems (Ru–Cl and Ru–OH_2), which were first examined in control experiments, are much higher in activity than the diruthenium ones, raising a question about the importance of a dinuclear character in the O_2-evolving catalysis. Although Thummel et al. quite recently, i.e., a week ago, published their work on the O_2-evolving activity of the chloro-coordinated complex Ru–Cl (their work involves various analogues of Ru–Cl with the bpy of Ru–Cl replaced with other bpy derivatives),[5a] we wish to communicate our recent results on the O_2-evolving activities of Ru–OH_2, Cl–RuLRu–Cl, and H_2O–RuLRu–OH_2. Important new findings in this study are as follows: (i) Ru–OH_2 is highly active but Ru–Cl exhibits no activity at all; (ii) Ru–OH_2 is substantially robust during the catalysis. These were not well rationalized in the report of Thummel et al., in which Ru–OH_2 was not examined at all.[5a]



Scheme 1.

The O_2 evolution from water accelerated by these four molecular catalysts is shown in Figure 1, together with their turnover numbers after 12 h. Unexpected observations are that the catalytic activities of the diruthenium catalysts are relatively low in comparison with those of the mononuclear ones. We now assume that this is due to the presence of three possible geometric isomers for each dimer (see Figure S2).[6] It must be also noted that the activities of Cl–RuLRu–Cl and H_2O–RuLRu–OH_2 are much higher than that of H_2O–Ru–O–Ru–OH_2 (Figure S3).[6] In the case of Ru–OH_2, the conversion efficiency based on the oxidant consumed is calculated as ca. 90% at 12 h. Importantly, remarkable induction periods (2–3 h) are

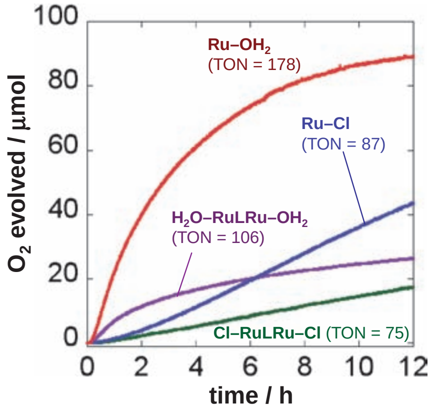


Figure 1. Oxygen evolution from a 20:1 water/acetonitrile mixture (2.1 mL) containing $Ce(NH_4)_2(NO_3)_6$ (190 mM) in the presence of either Ru–Cl (0.238 mM), Ru–OH_2 (0.238 mM), Cl–RuLRu–Cl (0.119 mM), or H_2O–RuLRu–OH_2 (0.119 mM) as a catalyst. Each measurement was initiated by adding a solution of a catalyst in acetonitrile (100 µL) to a solution of the oxidant (0.200 M) dissolved in water (2 mL, pH 0.40) at 20 °C under Ar atmosphere.

observed for the chloro systems (Ru–Cl and Cl–RuLRu–Cl), implying that the aqua instead of the chloro species are active species during the catalysis. On the other hand, the initial rate of O_2 formation for either Ru–OH_2 or H_2O–RuLRu–OH_2 gives a maximum right at the beginning of the reaction without showing any induction period. The ineffectiveness of Ru–Cl as a catalyst towards the O_2 formation is strongly supported by the fact that no O_2 evolves when Ru–Cl is employed as a catalyst in the presence of NaCl (0.5 M) (Figure S4).[6] Under such experimental conditions, the substitution equilibrium shown below must be largely shifted to the left.

$$[\mathrm{Ru(terpy)(bpy)Cl}]^+ + \mathrm{Solv} \rightleftharpoons [\mathrm{Ru(terpy)(bpy)(Solv)}]^{2+} + \mathrm{Cl}^- \quad (\mathrm{Solv} = \mathrm{H_2O} \text{ and } \mathrm{CH_3CN}) \tag{1}$$

These results clearly indicate that the chloro species are inactive and that the solvolysis products, presumably the aqua species, are responsible for the catalysis of O_2 evolution from water. This is a very important conclusion which was not given in the report of Thummel et al.[5a]

On the other hand, a reaction between Ru–OH_2 and 40 equiv of $Ce(NH_4)_2(NO_3)_6$ was monitored spectrophotometrically to better understand the catalytic cycles and to ascertain the stability of the catalyst (Figure S5).[6] The metal-to-ligand charge-transfer (MLCT) band at 476 nm corresponding to the original Ru^{II} species[7] (Figure S5a) was not regenerated even after the cease of O_2 formation when the oxidant is completely consumed, indicating that the Ru^{II} species added as a catalyst does not take part in the actual catalytic cycles (see Figures S5b–S5d).[6] Importantly, an excess of ascorbic acid (23 equiv with regard the catalyst) was added to the final solution after the cease of O_2 evolution to cause quantitative regeneration of the MLCT band which is fully consistent with the spectrum of Ru–OH_2 in water free of the oxidant (Figures S5a and S5e),[6] demonstrating the substantial robustness of Ru–OH_2 during the catalysis. This outstanding feature could not be realized in the studies on Ru–Cl because of the complication arising from the coexistence of the aqua and chloro species.

In order to further ascertain the robustness of Ru–OH_2, the catalysis solutions before and after the O_2 evolution experiment were examined by ESI-TOF mass spectrometry (Figure S6).[6] In these experiments, attempts have also been made to carry out the quantitative analysis of the catalyst, in which a known amount of an internal standard, i.e., $[Ru(bpy)_3](NO_3)_2$, was added to each sample solution just before the mass spectroscopic measurement. Although the quantitative analysis was not successful owing to the relatively low accuracy in integrated intensities, the spectral features of the samples before and after the O_2 evolution experiment are fundamentally consistent with each other, where no new peaks attributable to decomposition products appear after 10 cycles of catalysis. In other words, the results clearly indicate that the major chemical species in solution remain unchanged during the catalysis and that the amount of decomposition products must be negligibly low, if any. It must be also noted here that evolution of carbon dioxide, derived from decomposition of the ligands, is negligible during the catalysis, which was confirmed by gas chromatography (see Supporting Information for details).[6]

Figure 2 shows the dependence of O_2 evolution on the Ru–OH_2 concentration, revealing that the rate is linear to the catalyst concentration. Moreover, the O_2 evolution profile in Figure 2a, which correlates to the decrease in the Ce^{4+} concentration, can be well fitted to a single-exponential curve (Figure S10).[6] These indicate that the rate of O_2 formation is linear to both the catalyst and Ce^{4+} concentrations, and thereby the rate law can be described as $d[O_2]/dt = k[\mathrm{Ru{-}OH_2}][Ce^{4+}]$. It was reported that Ru–OH_2 displays redox couples at 0.81 V (Ru^{II}–OH_2/Ru^{III}–OH_2) and 1.12 V vs. SCE (Ru^{III}–OH_2/Ru^{IV}=O) at pH < 1.[7] Moreover, a large catalytic current corresponding to O_2 evolution is observed for Ru–OH_2 at potentials more positive than 1.3 V vs. SCE (Figure S9).[6] These indicate that the Ru^{IV}=O species must be further oxidized by Ce^{4+} into a higher valence species, such as a Ru^{V}=O species, prior to the actual O_2 evolution. Implications provided with these results are (i) that oxidation of either Ru^{III}–OH_2 or Ru^{IV}=O by Ce^{4+} may be the rate-determining step and (ii) that a coupling of two Ru monomers, e.g., the Ru^{V}=O species, cannot be the rate-determining step. Extended studies are still in progress in our laboratory.

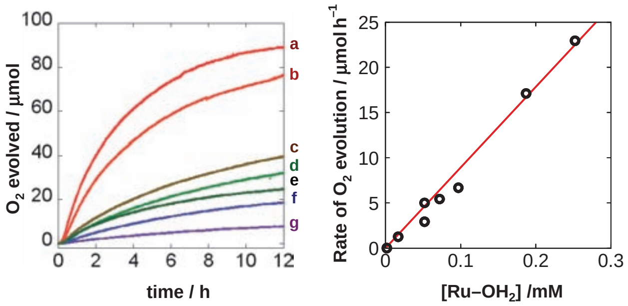


Figure 2. Oxygen evolution from water with $Ce(NH_4)_2(NO_3)_6$ catalyzed by Ru–OH_2 at various catalyst concentrations: (a) 0.238, (b) 0.174, (c) 0.0900, (d) 0.0686, (e) 0.0505, (f) 0.0491, and (g) 0.0149 mM (left). The initial slopes of O_2 formation curves (left, a–g) are plotted as a function of the Ru–OH_2 concentration. All the remaining experimental conditions are same to those given in the caption to Figure 1.

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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