Oxygen Evolution from Water Catalyzed by Mononuclear Ruthenium Complexes with a Triazamacrocyclic Ligand in a Facial Fashion

Masaki Yoshida, Shigeyuki Masaoka, and Ken Sakai*
Department of Chemistry, Faculty of Science, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

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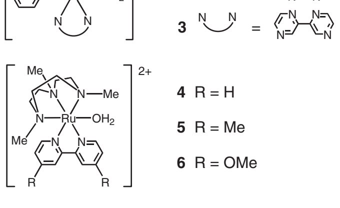
$[Ru(tmtacn)(R_2bpy)(OH_2)]^{2+}$ (tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane; R_2bpy = 4,4′-disubstituted-2,2′-bipyridines, R = H, Me, and OMe) with tmtacn ligated in a facial fashion is found to be active as O_2-evolving catalysts. It is also found that the stronger electron-donating character of R_2bpy gives rise to the higher O_2-evolving activity.

Visible light-driven water splitting reaction ($2H_2O + 4h\nu \rightarrow 2H_2 + O_2$) has attracted much attention due to its potential application toward artificial solar energy conversion and storage. Development of molecular catalysts toward water oxidation ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is considered as a more serious challenge than the reduction side because it requires the removal of four protons and four electrons.[1] Due to the necessity of multi-electron-transfer processes, it has long been believed that the O_2-evolving activities of multinuclear complexes are considerably higher than those of mononuclear complexes.[1e] Up to now, dimanganese[2] and diruthenium[3,4] catalysts have been reported to exhibit such activities. However, very recent works,[5,6] including that of the authors,[6] demonstrated that some mononuclear ruthenium complexes with tri- or tetradentate polypyridines such as 2,2′:6′,2″-terpyridine (terpy) (**1**–**3** in Scheme 1) exhibit surprisingly high activity toward the oxidation of water into molecular oxygen. Two questions arise from these observations as follows. (i) Is the meridional ligation essential for the enhancement of O_2-evolving activity of the catalyst? (ii) What is the change in O_2-evolving activity if the redox potentials at the metal centers are lowered, for example, by adopting polyamine ligands instead of polypyridyl ones.[7]

In the above context, we have selected tmtacn derivatives to examine both the effect of adopting a facial ligation at the Ru coordination sphere and the effect of lowering the redox potential at the metal center. Here we report, for the first time, on the O_2-evolving activities of mononuclear ruthenium complexes with a macrocyclic polyamine ligand in a facial fashion, **4**–**6** (Scheme 1), where the substituent R is varied so as to control the electron-donating ability of R_2bpy. Complex **4** was first prepared by Che et al.,[8] in which the $Ru^{IV}{=}O$ species given from **4** reacted with an olefin to give a stoichiometric amount of the corresponding epoxide.



Scheme 1.

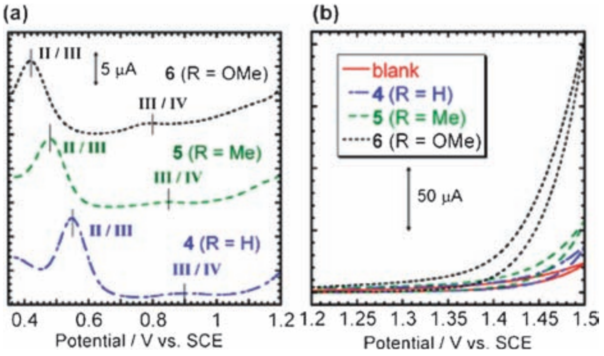


Figure 1. (a) Square wave voltammograms of **4**, **5**, and **6** (0.5 mM) in an aqueous 0.5 M sulfuric acid sotution under Ar atmosphere, recorded at a scan rate of $50\,mV\,s^{-1}$. (b) Cyclic voltammograms of **4**, **5**, and **6** (0.5 mM) in an aqueous 0.5 M sulfuric acid solution under Ar atmosphere, recorded at a scan rate of $10\,mV\,s^{-1}$ (working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, saturated calomel electrode).

Complexes **5** and **6** were obtained by reacting $Ru(tmtacn)Cl_3$[9] and the corresponding 4,4′-disubstituted-2,2′-bipyridine derivatives in the presence of zinc powder in aqueous media, where the yields were 49 and 63%, respectively (see Supporting Information for details).[10] These compounds were characterized by ^1H NMR, ESI-TOF MS, and elemental analysis.

In order to investigate the O_2 evolution from water catalyzed by complexes **4**–**6**, cyclic and square wave voltammograms of them in an aqueous 0.5 M H_2SO_4 solution (pH 0.4) under Ar atmosphere were measured (Figure 1). It was reported that complex **4** displays two redox couples at $E_{1/2} = 0.55\,V$ (Ru^{II}–OH_2/Ru^{III}–OH) and 0.90 V (Ru^{III}–OH/$Ru^{IV}{=}O$), where potentials are given in volts vs. SCE.[8] Complexes **5** and **6** exhibit voltammograms similar to that of **4**, but the potentials corresponding to the Ru^{II}–OH_2/Ru^{III}–OH and Ru^{III}–OH/$Ru^{IV}{=}O$ couples are shifted to the lower potential ($E_{1/2} = 0.48$ and 0.85 V for **5**, and $E_{1/2} = 0.42$ and 0.80 V for **6**, respectively). Compared with the active mononuclear ruthenium catalyst **1**, the potentials of the Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV} couples of **4**–**6** are largely shifted to the lower potential ($E_{1/2} = 0.81$ and 1.12 V for **1** under the same conditions),[6,11] due to the stronger σ-donating character and the lack of π-acceptor ability of tmtacn in comparison with terpy. In addition to these two redox couples, cyclic voltammograms of **4**–**6** exhibit strong irreversible anodic currents at positive potentials, which are obviously attributed to the electrocatalytic oxidation of water into molecular oxygen. These results suggest that the $Ru^{V}{=}O$ or further oxidized species of **4**–**6** participate in the electrocatalytic water oxidation cycle, as was the case for **1**–**3**.[5,6] It is also found that the potential at which the cat-

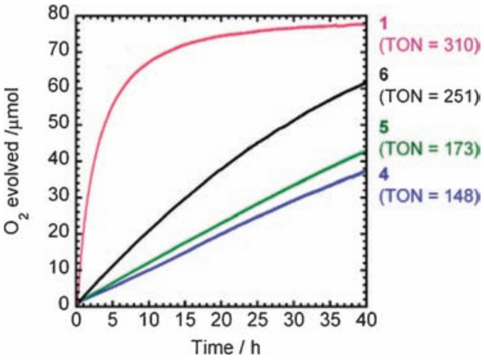


Figure 2. Oxygen evolution from an aqueous 0.2 M $Ce(NH_4)_2(NO_3)_6$ solution (2 mL, pH 0.40) in the presence of complexes **1** and **4**–**6** (0.125 mM). Each measurement was initiated by adding a solution of a catalyst in water (2.52 mM catalyst, 0.1 mL) to a solution of $Ce(NH_4)_2(NO_3)_6$ in water (0.210 M Ce^{4+}, 1.9 mL) at 20 °C under Ar atmosphere.

alytic current for water oxidation starts to flow (hereafter termed as an O_2-evolving potential) is affected by the electron-donating ability of the substituent R; the stronger electron-donating group gives rise to the larger negative shift in the O_2-evolving potential (Figures 1 and S1).[10] The O_2-evolving potential for complex **6** (E = ca. 1.35 V) is quite similar to that for **1** (E = ca. 1.3 V).[6] On the other hand, the O_2-evolving potentials for **4** and **5** are rather shifted to the positive potential (E = ca. 1.4 V for **4** and ca. 1.45 V for **5**), despite that the Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV} couples for **4** and **5** are largely shifted to the lower potential compared with those of **1** (vide supra).

The oxygen evolution from water catalyzed by **4**–**6** is investigated by employing cerium(IV) ammonium nitrate [$Ce(NH_4)_2(NO_3)_6$] as an oxidant (Figure 2). An aqueous solution (0.10 mL) of each catalyst was added to an aqueous 0.21 M Ce^{4+} solution (1.9 mL; 400 μmol of Ce^{4+}) at 20 °C. The O_2 evolved was monitored using an oxygen probe (YSI 5331/5300), as previously discribed.[6] The total amounts of O_2 evolved after 40 h for **4**–**6** are in the range of 37–62 μmol. The turnover numbers (TON) after 40 h, estimated from the total amount of O_2 evolved (O_2 μmol) and the amount of each Ru complex (0.25 μmol), are also depicted in Figure 2. The results clearly indicate that the stronger electron-donating group on the 4,4′-positions of R_2bpy gives rise to the higher catalytic activity, consistent with the results of electrochemical studies described above. Although we expected that the lowering in the Ru-based redox couples may lead to the lowering in the overpotential for O_2 evolution, compounds **4**–**6** are found to be lower in activity in comparison with **1** (TON per 40 h = 310, Figure 2).

Finally, a reaction between **4** and 82 equiv of $Ce(NH_4)_2(NO_3)_6$ was monitored spectrophotometrically to ascertain the stability of the catalyst during the reaction (Figure S2).[10] After addition of $Ce(NH_4)_2(NO_3)_6$ to an aqueous solution of **4**, the metal-to-ligand charge-transfer (MLCT) band of **4** centered at 500 nm immediately disappeared. Standing of the solution for 1 h similarly resulted in O_2 evolution from water with TON = 4.5 (Figure S3).[10] At this point, an excess of ascorbic acid (82 equiv with regard to the catalyst) was added to the reaction mixture to regenerate the MLCT band with quantitative recovery in absorbance (Figures S2a and S2d).[10] This is a clear indication that **4** is substantially robust during the catalysis for at least 1 h, even though the prolonged reaction up to 90 h has been confirmed to result in gradual decomposition of the complex (Figure S4).[10]

In this study, we have shown that mononuclear ruthenium complexes with tmtacn ligated in a facial fashion serve as O_2-evolving catalysts, revealing that the aqua ligand attached to the trans position of a N(tmtacn) in **4**–**6** rather than a N (bpy derivatives) in **1**–**3** can also serve as an active site for the oxidation from water. It is also found that the O_2-evolving activity of $[Ru(tmtacn)(R_2bpy)(OH_2)]^{2+}$ becomes higher with increasing electron-donating character of the substituent groups on the 4,4′-positions of R_2bpy. The use of tmtacn instead of terpy results in dramatic shifts of the Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV} couples to the lower potential, but does not lead to the lowering in the overpotential for the electrocatalytic O_2 evolution from water. Since the rate of O_2 formation catalyzed by **1** was found to be linear to both the catalyst and Ce^{4+} concentrations,[6] the rate-determining step could be, for example, a reaction between the $Ru^{V}{=}O$ species and Ce^{4+} as the final step for O_2 formation. A possible interpretation is that the redox potential for the $Ru^{IV}{=}O/Ru^{V}{=}O$ couple is not much affected by the introduction of tmtacn in place of terpy. Mechanistic studies on the present system are now in progress.

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