Homogeneous Catalysis

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Oxygen Evolution Catalyzed by a Mononuclear Ruthenium Complex Bearing Pendant SO_3^- Groups**

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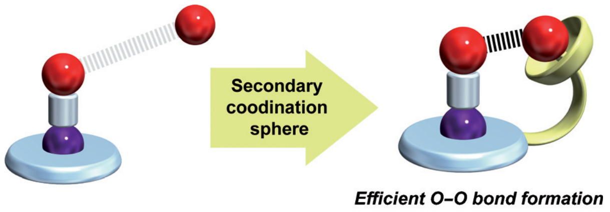
Abstract: *Rational molecular design of catalytic systems capable of smooth O–O bond formation is critical to the development of efficient catalysts for water oxidation. A new ruthenium complex was developed, which bears pendant SO_3^- groups in the secondary coordination sphere: [Ru(terpy)(bpyms)(OH_2)] (terpy = 2,2′:6′,2″-terpyridine, bpyms = 2,2′-bipyridine-5,5′-bis(methanesulfonate)). Water oxidation driven by a Ce^{4+} oxidant is distinctly accelerated upon introduction of the pendant SO_3^- groups in comparisons to the parent catalyst, $[Ru(terpy)(bpy)(OH_2)]^{2+}$ (bpy = 2,2′-bipyridine). Spectroscopic, electrochemical, and crystallographic investigations concluded that the pendant SO_3^- groups promote the formation of an O–O bond via the secondary coordination sphere on the catalyst, whereas the influence of the pendant SO_3^- groups on the electronic structure of the $[Ru(terpy)(bpy)(OH_2)]^{2+}$ core is negligible. The results of this work indicate that modification of the secondary coordination sphere is a valuable strategy for the design of water oxidation catalysts.*

The utilisation of the secondary coordination sphere of metal centres is a powerful strategy for designing efficient molecular catalysts for chemical conversion processes, as well as mimicking the reaction centres of natural metalloenzymes.[1] In the typical approaches, functional groups are placed proximal to transition metal ions to cooperatively assist metal-centred transformation reactions through noncovalent interactions such as hydrogen bonding, coordination bonding, and acid–base interactions. To date, numerous molecular systems with functional groups attached to the secondary coordination sphere have been reported for various chemical conversion processes.[2]

The oxidation of water to molecular oxygen ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is one of the most important chemical processes, and the development of artificial O_2-evolving catalysts has attracted considerable interest in recent years.[3] One of the major challenges in this area of research is to establish a rational design for molecular catalysts capable of smooth O–O bond formation because the O–O bond formation step is often the slowest step (the rate-determining step, RDS) in the catalytic reaction.[4] Because O–O bond formation in photosynthesis is proposed to proceed through the heterometallic reaction between Mn^{V}=O species and Ca^{II}–OH species[5] in the Mn_4CaO_5 cluster,[6] the fabrication of a heterometallic reaction centre in artificial systems should be an interesting and important target. In this context, modification of the secondary coordination sphere is considered a simple and useful method for creating such a reaction centre (Scheme 1).[7] However, with respect to O_2-evolving catalysts, the literature contains no reports of the construction of a heterometallic reaction centre through modification of the secondary coordination sphere.

Herein, we report the first demonstration of the utilisation of the secondary coordination sphere for heterometallic O–O bond formation. The key to the success of this work is the employment of a mononuclear Ru catalyst in Ce^{4+}-driven water oxidation. Ce^{4+} is commonly used as a sacrificial oxidant in many catalytic water oxidation systems (Net reaction: $2H_2O + 4Ce^{4+} \rightarrow O_2 + 4H^+ + 4Ce^{3+}$).[3,4,8,9] Further-



Scheme 1. A schematic illustration of efficient O–O bond formation through modification of the secondary coordination sphere.

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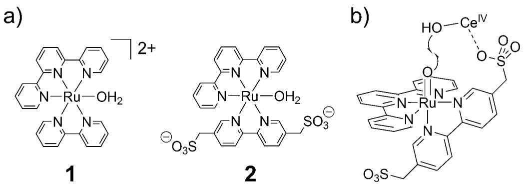
more, we[8] and other groups[9] have suggested that heterometallic O–O bond formation between $Ru^V{=}O$ species and Ce^{IV}–OH (or Ce^{IV}–ONO_2) species is the critical step in O_2 evolution catalyzed by the mononuclear ruthenium complex $[Ru^{II}(terpy)(bpy)(OH_2)]^{2+}$ (**1**, terpy = 2,2′:6′,2″-terpyridine, bpy = 2,2′-bipyridine; Scheme 2 a) and related ruthenium complexes. Our previous work also suggested that the RDS in the O_2 evolution catalyzed by **1** is O–O bond formation.[8] To accelerate this O–O bond formation reaction (as the rate-determining step in O_2 evolution), we designed a new ruthenium complex bearing SO_3^- groups, $[Ru(terpy)(bpyms)(OH_2)]$ (**2**, bpyms = 2,2′-bipyridine-5,5′-bis(methanesulfonate); Scheme 2), for which the SO_3^- groups are expected to serve as a functional group to capture Ce^{4+} as a result of the strong ability of SO_3^- groups to coordinate Lewis-acidic metal ions.[10] Notably, one of the two SO_3^- groups of **2** is located at a position appropriate for the formation of an O–O bond between Ru and Ce (Figure S2 in the Supporting Information).



Scheme 2. a) Structures of the mononuclear aquaruthenium catalysts **1** and **2**. b) Schematic of the working hypothesis.

The new ruthenium complexes bearing SO_3^- groups were prepared through a modified version of the reported methods. The precursor complex $[Ru^{II}(terpy)(bpymsH_2)Cl]^+$ was obtained by reacting $[Ru(terpy)Cl_3]$[11] and 2,2′-bipyridine-5,5′-bis(methanesulfonic acid) dipotassium salt ($bpymsK_2$) in the presence of ascorbic acid in aqueous medium. We prepared complex **2** by reacting $[Ru^{II}(terpy)(bpymsH_2)Cl]^+$ and $AgNO_3$ in aqueous medium. Their compositions were confirmed by elemental analysis, ^{1}H NMR, and X-ray crystallography.[12]

The crystal structure of **2** is shown in Figure S1 in the Supporting Information. The coordination geometry at the Ru atom is that of a distorted octahedron composed of a meridionally coordinated terpy ligand, a bidentate bpyms ligand, and an aqua ligand. All of the bond lengths and angles around the Ru atom are similar to those reported for **1** (Table S2 in the Supporting Information).[13] The UV/Vis absorption spectrum of **2** in water (Figure S3) shows an intense absorption band centred at 482 nm ($\varepsilon = 9.65 \times 10^3\,\text{M}^{-1}\,\text{cm}^{-1}$), which is assigned to a metal-to-ligand charge-transfer (MLCT) transition. The MLCT band of **2** is similar to that of **1** centred at 477 nm ($\varepsilon = 9.60 \times 10^3\,\text{M}^{-1}\,\text{cm}^{-1}$).[14] The square-wave voltammogram of **2** in an aqueous 0.5 M H_2SO_4 solution (pH 0.4) shows two redox couples at $E_{1/2} = 0.82$ V and 1.18 V vs. SCE; these couples correspond to the Ru^{III}–OH_2/Ru^{II}–OH_2 and $Ru^{IV}{=}O$/Ru^{III}–OH_2 couples, respectively (Figure S4). These potentials are similar to those for **1** ($E_{1/2} = 0.81$ V and 1.12 V; Table 1).[14] In addition to these two redox couples, the cyclic voltammogram of **2** exhibits strong irreversible anodic currents at more positive potentials, which are attributed to the electrocatalytic oxidation of water to molecular oxygen. The O_2-evolving potential for **2** (ca. 1.3 V) is also similar to that for **1** (ca. 1.3 V).[9a] These results indicate that the effect of peripheral SO_3^- substituents on the electronic structure of the $[Ru(terpy)(bpy)(OH_2)]^{2+}$ core in **2** is negligible.

Table 1: UV/Vis absorption data and redox potentials for **1** and **2** in water at room temperature.

	MLCT transitions		Redox potentials at pH 0.4 (V vs. SCE)		
	λ_{max} [nm]	ε [$10^3\,\text{M}^{-1}\,\text{cm}^{-1}$]	Ru^{III}/Ru^{II}	Ru^{IV}/Ru^{III}	O_2 evolution
1	477	9.60	0.81	1.12	ca. 1.3
2	482	9.65	0.82	1.18	ca. 1.3

We investigated the O_2 evolution catalyzed by **1** and **2** when using $(NH_4)_2[Ce^{IV}(NO_3)_6]$ as an oxidant (Figure 1 and Figure S5). An aqueous solution (0.15 mL) of each catalyst was added to an aqueous Ce^{4+} solution (2.85 mL) at 20 °C. The amount of O_2 evolved was monitored by using an oxygen probe. As shown in Figure 1, complex **2** exhibits high catalytic activity for O_2 evolution. The turnover number (TON) of **2** in the reaction with 75 µmol (25 mM) of Ce^{4+} was estimated to be 47 after the reaction completely ceased (Figure 1 a). The conversion efficiency for catalysis by **2** was estimated to be 94 %, thus indicating that this reaction proceeded almost quantitatively. Notably, complex **1** also promotes O_2 evolution under the same conditions,[8,9] and the activity of **2** is only slightly higher than that of **1**. The nearly equal activity of **1** and **2** is reasonable given the similarities between their electronic structures, as previously described.

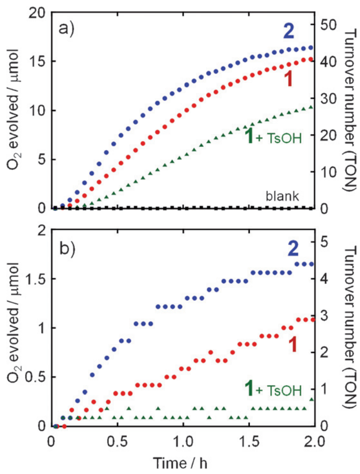


Figure 1. Oxygen evolution from an aqueous 1.0 M $HClO_4$ solution (3.0 mL) at 20 °C under Ar atmosphere with 25 mM (a) or 4 mM (b) $(NH_4)_2[Ce(NO_3)_6]$ in the presence of 0.125 mM **2** (blue dots), 0.125 mM **1** (red dots), 0.125 mM **1** and 0.25 mM TsOH (green triangles), or in the absence of any catalyst (black squares).

In contrast, a clear difference in activity between **1** and **2** was observed at the lower Ce^{4+} concentration (4 mM), where the rate of O_2 evolution in the case of catalyst **2** was much higher than that with the nonsubstituted complex **1** (Figure 1b). Because the reaction conditions were almost the same except for the presence or absence of the two pendant SO_3^- groups on the catalyst, control experiments for elucidating the significance of coexisting SO_3^- groups were performed. Importantly, the addition of 2 equiv of *p*-toluenesulfonic acid (TsOH) effectively suppressed the catalytic activity of **1** (Figure 1, green triangles). We thus concluded that the pendant SO_3^- groups on the catalyst enhance its activity, whereas the presence of free SO_3^- groups suppresses it.

The two contradictory effects of the coexisting SO_3^- groups can be explained by considering the ability of the SO_3^- group to coordinate to a Ce^{4+} ion. The formal potential of the Ce^{IV}/Ce^{III} couple is known to be lowered by the coordination of anions such as sulfate.[9b,15] The presence of TsOH lowers the oxidising ability of Ce^{4+}, thus resulting in the suppression of O_2 evolution.[8a,9b] In the case of **2**, the pendant SO_3^- groups give rise to higher catalytic activity despite the fact that the oxidising ability of Ce^{4+} must be lowered by the pendant SO_3^- groups. Because previous studies have suggested that the association between the Ru catalyst and Ce^{4+} is the RDS in the catalysis,[8,9] the increased catalytic activity of **2** indicates an enhancement of this association as a result of the the Ce^{4+}-capturing ability of the pendant SO_3^- groups. This interpretation is consistent with the small difference in activity between **1** and **2** at the higher Ce^{4+} concentration because a large excess of Ce^{4+} facilitates the association between the Ru catalyst and Ce^{4+} without the assistance of the pendant SO_3^- groups.

To confirm the ability of the SO_3^- groups of complex **2** to capture Ce^{4+}, we attempted to co-crystallise **2** with an excess of $(NH_4)_2[Ce(NO_3)_6]$. An aqueous 30 mM solution of **2** (1 mL) was added to 10 equiv of $(NH_4)_2[Ce(NO_3)_6]$ (0.164 g, 0.3 mmol), and O_2 bubbles immediately evolved. After O_2 evolution ceased, slow vapour diffusion of acetone into the reaction mixture was performed in a refrigerator. Green crystals (hereafter termed composite **3**) suitable for X-ray crystallography were obtained from the mixture after several weeks. The X-ray crystallographic structure of **3** is shown in Figure 2 and Figures S6 and S7.[12] In the crystals of composite **3**, two Ru-complex moieties undergo dimerization to form an oxo-bridged dinuclear Ru^{III} complex.[16] Furthermore, we observed that the dinuclear Ru units are linked through the coordination of the SO_3^- groups to Ce^{3+} ions to form an infinite network. The coordination bonds between the SO_3^- groups and the Ce^{3+} ions are considered evidence of the ability of the pendant SO_3^- groups to capture Ce ions.

In conclusion, we have demonstrated that the rate of O_2 evolution in Ce^{4+}-driven water oxidation can be accelerated by the introduction of pendant SO_3^- groups onto a mononuclear Ru catalyst. This finding is interesting because coexisting SO_3^- groups commonly tend to suppress Ce^{4+}-driven water oxidation. The acceleration of the reaction rate in the present system is consistent with our strategy based on the capture Ce^{4+} ions by the pendant SO_3^- groups and consequent enhancement of heterometallic O–O bond formation. The ability of the pendant SO_3^- groups to coordinate Ce^{4+} ions was confirmed by X-ray crystallography. Our findings indicate that modification of the secondary coordination sphere is a promising strategy for the creation of efficient catalysts for water oxidation.

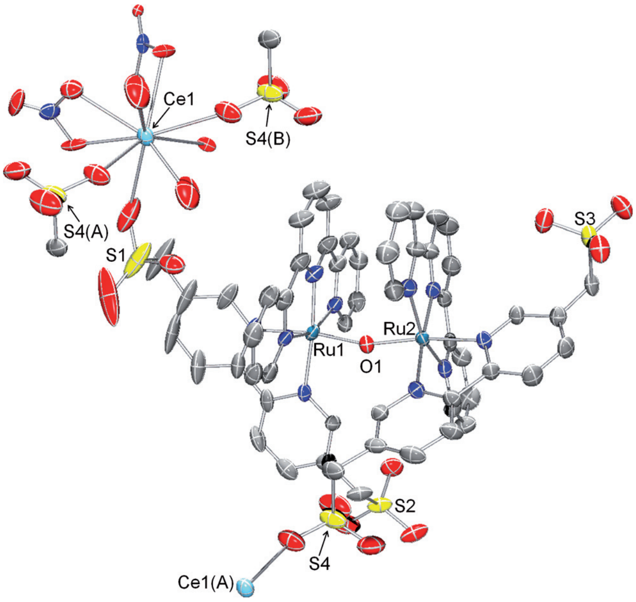


Figure 2. ORTEP drawing of the partial structure of composite **3**, showing the atom-labelling scheme. Thermal ellipsoids are displayed at the 50% probability level. For clarity, only one of the two disordered sites is plotted for the $\{Ce(NO_3)_2O(OH)\}$ group and one of the SO_3^- groups. H atoms have been omitted for clarity.

Keywords: cerium · cooperative effects · homogeneous catalysis · ruthenium · water oxidation

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[12] The crystal data have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1036455 and 1036456 for **2** and **3**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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