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A New Dinuclear Ruthenium Complex as an Efficient Water Oxidation Catalyst

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A dinuclear ruthenium complex, which acts as a molecular catalyst for water oxidation, has been synthesized and characterized. The electronic and electrochemical properties were studied by UV−vis spectroscopy and cyclic voltammetry. The oxidation potentials of the complex are significantly lowered by introducing a negatively charged carboxylate ligand, in comparison with those of the reported complexes that have neutral ligands. The catalytic activity of the complex toward water oxidation using $Ce(NH_4)_2(NO_3)_6$ as a chemical oxidant was investigated by means of an oxygen electrode and mass spectrometry. The turnover number of this catalyst with Ce^{IV} as the chemical oxidant was found to be ca. 1700. The mass spectroscopic analysis of the isotopomer distribution in oxygen evolved from ^{18}O-labeled water indicates that O atoms in the evolved oxygen originate from water.

Much effort has been devoted to developing molecular catalysts capable of oxidizing water, to mimic the oxygen-evolving complex in PSII.[1−4] The model systems have mainly focused on manganese-based[1−3,5,6] and ruthenium-based[1,2,4,7] complexes as homogeneous catalysts, although some iridium-based aquo complexes have also been reported.[8] Both all-inorganic ruthenium-containing polyoxometalate[9] and ruthenium complexes with organic ligands[7,10,11] have been shown to be efficient catalysts for water oxidation.

Among these ruthenium-based catalysts, Thummel's dinuclear ruthenium complexes containing pyridazine-based

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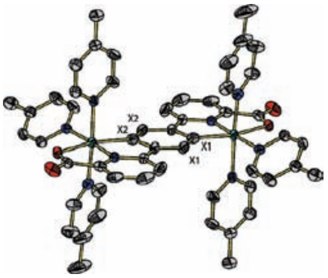
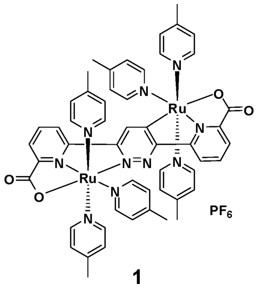


Figure 1. ORTEP view of the cation of **1** with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity. The X1 and X2 atoms of the central six-membered ring are either C and N or N and C, respectively, with 50% probability.

ligands show high efficiencies in catalytic water oxidation with turnover numbers (TNs) of up to ca. 700.[11a,b] These dinuclear ruthenium complexes containing neutral ligands, however, usually have high oxidation potentials, and strong chemical oxidants such as $Ce(NH_4)_2(NO_3)_6$ are needed when water is oxidized by these catalysts. In order to drive water oxidation by light, the oxidation potentials of the catalysts should be lower to allow oxidation by common oxidized photosensitizers. Generally, the redox potentials of metal complexes can be tuned by the ligand modification. It has been found that negatively charged ligands can lower the oxidation potentials of the corresponding metal complexes and, thus, stabilize the higher oxidation states of the metal ions.[12] With the aim of lowering oxidation potentials and improving the performance of the ruthenium complexes, we have prepared a new dinuclear ruthenium catalyst **1** (Chart 1) with a negatively charged dicarboxylate ligand **2**.

Chart 1. Structure of Complex **1**



1

Ligand **2** was synthesized according to Scheme S1 in the Supporting Information, starting from 2-cyano-6-methylpyridine. Complex **1** was then prepared by treating **2** with Et_3N in acetonitrile and reacting with $Ru(DMSO)_4Cl_2$ and 4-methylpyridine, followed by the addition of NH_4PF_6 (Scheme S1 in the Supporting Information). The crude product was collected by filtration and purified by column chromatography on Al_2O_3 to provide **1** in low yield (23%). Complex **1** was characterized by X-ray diffraction analysis, ^1H and ^{13}C NMR, and mass spectrometry (MS). It was surprisingly found from X-ray analysis (Figure 1) that, unlike Thummel's dinuclear ruthenium complexes, **1** has an "anti" structure and contains no μ-Cl bridge between the two Ru ions. Instead, the two Ru ions occupy positions on opposite sides of the central pyridazine ring and are octahedrally coordinated with a slight distortion. Structure data for **1** and bond lengths and bond angles are given in Tables S1 and S2 in the Supporting Information. Because the pyridazine ring is positioned at an inversion center, it is not possible to distinguish the two bonds between ruthenium and that ring.[13] However, it is, nonetheless, clear that one Ru ion is coordinated to a N atom and the other to a C atom in the central ring. The ^1H NMR spectrum of **1** (Figure S1 in the Supporting Information) further supports this structural assignment by showing that the two pyridyl moieties, which are attached to the central pyridazine, are nonequivalent. Thus, the protons at the b, c, and d positions (see the inset in Figure S1 in the Supporting Information) are clearly distinguished from those at the b′, c′, and d′ positions. In addition, only one proton (Ha) associated with the pyridazyl moiety can be observed as a singlet at 8.90 ppm. The high-resolution MS result also proves this structure. A monocharged peak corresponding to $[M - PF_6]^+$ was found at *m/z* 1081.1985 (calcd *m/z* 1081.2025). We have considered the possibility that this special anti structure of **1** could be due to the different procedures of preparation, but variations of the procedure gave product **1** only. Actually, this type of anti structure has also been found by Lahiri et al. for dinuclear ruthenium complexes containing a substituted pyridazine as a bridging ligand.[14]

The UV−vis spectrum of **1** in acetonitrile is shown in Figure S2 in the Supporting Information. In the UV region, there are three absorption maxima at 247 ($\epsilon = 3.34 \times 10^4$ M^{-1} cm^{-1}), 301 ($\epsilon = 4.13 \times 10^4$ M^{-1} cm^{-1}), and 310 nm ($\epsilon = 3.87 \times 10^4$ M^{-1} cm^{-1}), which are due to the ligand-centered $\pi - \pi^*$ transitions. In the visible region, three metal-to-ligand charge-transfer bands with absorption maxima at 370 ($\epsilon = 3.13 \times 10^4$ M^{-1} cm^{-1}), 453 ($\epsilon = 2.16 \times 10^4$ M^{-1} cm^{-1}), and 532 nm ($\epsilon = 1.35 \times 10^4$ M^{-1} cm^{-1}) were observed.

The electrochemistry of **1** was studied by cyclic voltammetry (CV). The CV of **1** in dry acetonitrile (Figure 2) exhibits two reversible one-electron-oxidation waves at $E_{1/2} = 0.294$ and 0.797 V vs saturated calomel electrode (SCE), which are assigned to the oxidations of $Ru_2^{II,II}$ to $Ru_2^{II,III}$ and $Ru_2^{II,III}$ to $Ru_2^{III,III}$, respectively, and two reversible ligand-based one-electron-reduction waves at $E_{1/2} = -1.461$ and -1.915 V vs SCE. In addition, one irreversible oxidation was observed for **1** at ca. 1.83 V vs SCE, probably due to the formation of a species with a higher oxidation state than $Ru_2^{III,III}$. In comparison with those of Thummel's dinuclear ruthenium complexes that have neutral ligands,[11b] corresponding oxidation potentials of **1** are significantly decreased

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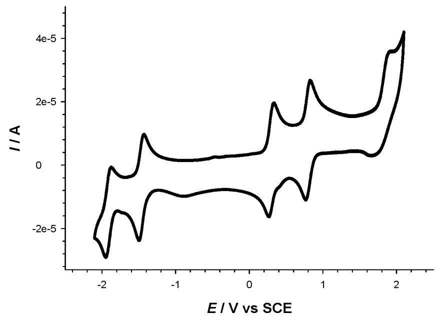

Figure 2. Cyclic voltammogram ($\nu = 0.1$ V s^{-1}) of **1** (1.3 mM) in acetonitrile, with Bu_4NPF_6 (0.1 M) as the supporting electrolyte, glassy carbon disk as the working electrode, and $Ag/AgNO_3$ as the reference electrode.

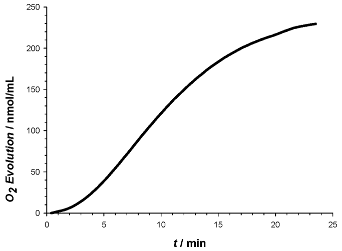

Figure 3. Oxygen evolution catalyzed by **1** (0.49 nmol) in a water solution (pH 0.8, 2.0 mL) using $Ce(NH_4)_2(NO_3)_6$ (92 μmol) as the chemical oxidant. The curve was recorded by a Clark-type oxygen electrode.

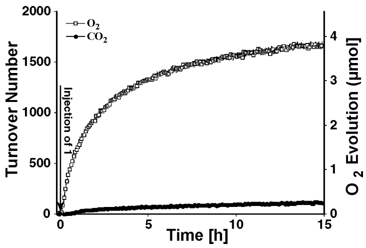

Figure 4. Oxygen and carbon dioxide evolution recorded by MS. The reaction mixture contains **1** (2.28 nmol), acetonitrile (0.1 mL), $Ce(NH_4)_2(NO_3)_6$ (95 μmol), and water (2.5 mL, pH 1.0 adjusted with CF_3SO_3H).

because of the negatively charged ligand in **1**. In an aqueous solution of **1** at pH 7, a catalytic current for water oxidation was observed, starting at ca. 1.25 V vs SCE (Figure S3a in the Supporting Information); at pH 1, this catalytic current is stronger but starts at a higher potential (ca. 1.4 V vs SCE), as shown in Figure S3b in the Supporting Information.

The catalytic activity of complex **1** for water oxidation was investigated by the chemical method, using Ce^{IV} as the oxidant, employing both the Clark-type oxygen electrode and MS. When a degassed solution of **1** in acetonitrile was added to a degassed aqueous solution (pH 0.8, adjusted with CF_3SO_3H) containing $Ce(NH_4)_2(NO_3)_6$, gas evolution was observed, which was confirmed to be oxygen by both the oxygen electrode and MS, as shown in Figures 3 and 4. In a control experiment, no oxygen evolution was found under the same conditions but without **1**. To exclude catalysis by a trace amount of RuO_2 formed during the reaction, $Ru(bpy)_3Cl_2$ and $Ru(bpy)_2Cl_2$ were used instead of **1** under the same conditions, but no oxygen evolution was observed in any reaction mixture. Commercial RuO_2 can, on the other hand, catalyze water oxidation under the same conditions but with much lower TNs (see Figure S4 in the Supporting Information), which is similar to the results reported recently by Thummel.[11c]

As shown in Figure 4, the TN of oxygen evolution catalyzed by **1** at pH 1.0 in the presence of $Ce(NH_4)_2(NO_3)_6$ as the oxidant was found to be ca. 1700 after a reaction time of 15 h. This TN is considerably higher than those reported by Thummel for related neutral complexes.[11b] A first-order rate constant (2.6×10^{-4} s^{-1}) was obtained by exponential fitting of the oxygen evolution versus time (see Figure S5 in the Supporting Information), which is similar to the rates reported earlier for related complexes.[11a]

Interestingly, CO_2 formation with a low TN (ca. 120) was simultaneously observed during catalytic water oxidation by **1**, as shown in Figure 4. Because the formation of CO_2 is catalytic and not stoichiometric, it is perhaps due to oxidation of the solvent. However, a general oxidation of the ligand by Ce^{IV}, as observed by Brudvig[15a] and Hurst,[15b] cannot be excluded. We are currently studying this in more detail.

The origin of the O atoms in the evolved oxygen was investigated with MS by evaluating the ratio of isotopes in oxygen evolved from a reaction mixture containing ^{18}O-enriched water. Figure S6 in the Supporting Information shows traces of $^{16,16}O_2$ and $^{16,18}O_2$ evolved upon the addition of a solution of **1** in acetonitrile to an aqueous solution containing isotope-enriched water (10% ^{18}O), CF_3SO_3H, and $Ce(NH_4)_2(NO_3)_6$. The observed ratio of evolved oxygen with masses 34 and 32 was found to be 2:10, which is very close to the theoretical ratio (2:9) assuming both O atoms of oxygen come from the isotope-enriched water. This result indicates that water is the main source of the evolved oxygen during water oxidation catalyzed by **1**.

In conclusion, we have prepared and characterized a new dinuclear ruthenium complex that can efficiently catalyze water oxidation in the presence of $Ce(NH_4)_2(NO_3)_6$ as the chemical oxidant. The ^{18}O-labeled isotopomer studies by MS give clear evidence that the O atoms in the evolved oxygen come from water. Moreover, we have demonstrated that, by the introduction of a negatively charged ligand, the oxidation potentials of the dinuclear ruthenium complex **1** are significantly lowered relative to those of the reported ones,[11b] which have neutral ligands. The goal for the future work is to oxidize water with this complex by using a chemical oxidant that has a lower oxidation potential than $Ce(NH_4)_2(NO_3)_6$ and eventually to drive the water oxidation reaction with light.

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Supporting Information Available: Experimental details, synthesis procedures, scheme, figures, tables, and an X-ray crystallographic file for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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