Oxygen Generation

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An All-Inorganic, Stable, and Highly Active Tetraruthenium Homogeneous Catalyst for Water Oxidation**

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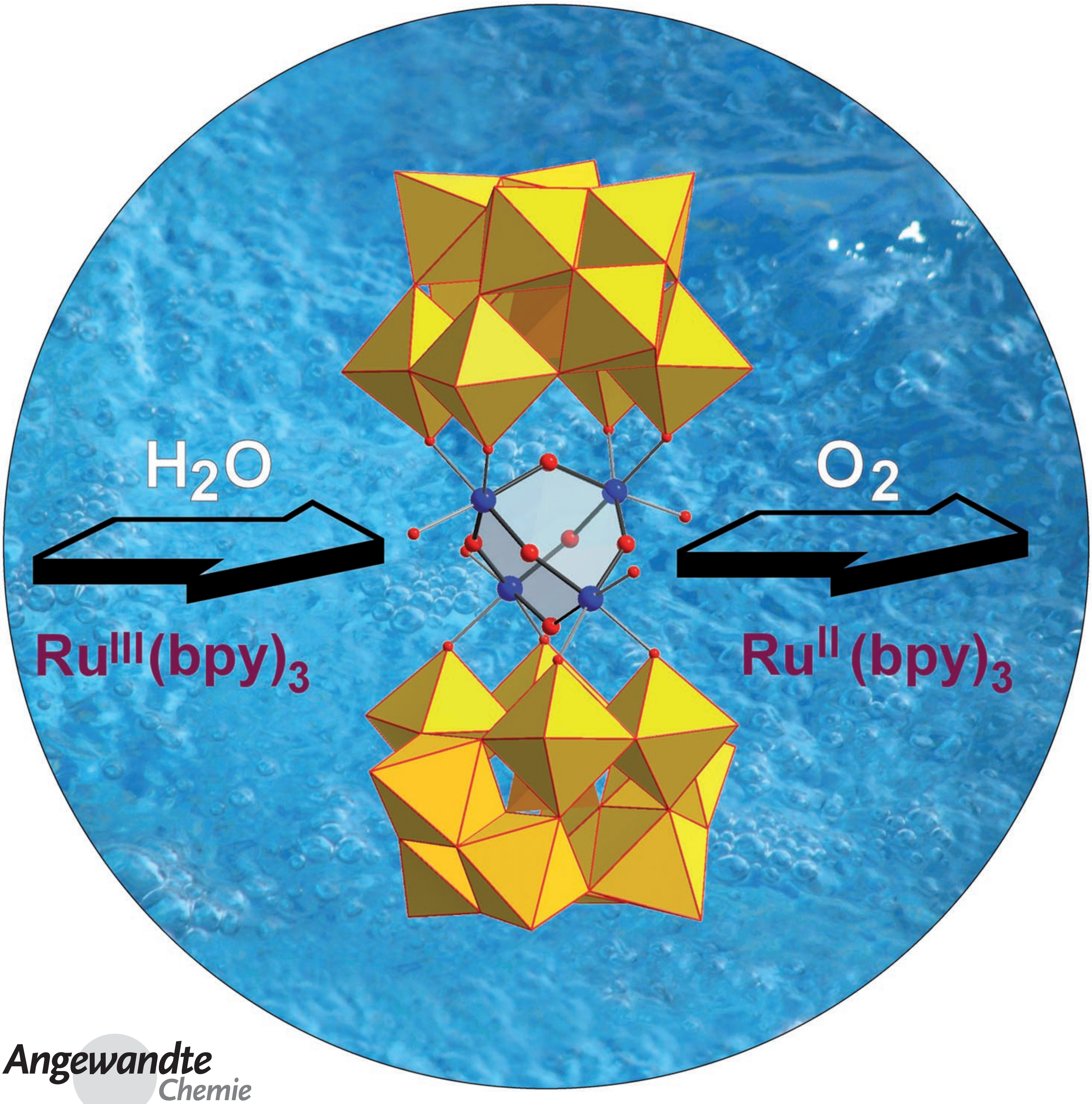

The design of viable and well-defined molecular catalysts for water oxidation in conjunction with the conversion of solar into chemical energy is both intellectually and practically important.[1–19] Increasingly, high-resolution crystal structures and physicochemical investigations of the Mn_4Ca-centered water oxidation–oxygen evolving center (OEC) in photosystem II, and studies of model compounds, are providing more insight into the properties of this multimetal biocatalyst.[11,14,16–18,20–25] In early work, Shafirovich and co-workers documented that several nonmolecular materials (metal oxides/hydroxides) catalyzed H_2O oxidation to O_2 over a wide pH range.[1,2] Classic work by Meyer and co-workers on the soluble and structurally defined functional H_2O oxidation catalyst, $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$,[3] and subsequent work by several groups[15–17,19] has clarified some mechanistic aspects of water oxidation and defined key challenges. Despite all these achievements and ongoing research, however, stable and rapid molecular and homogeneous catalysts for H_2O oxidation and O_2 generation have yet to be achieved. Some organic ligands are adequately stable in photovoltaic devices (for example, $[Ru(bpy)_3]^{3+/2+}$ units in Grätzel cells last 10000+ h),[10] but they are not stable in water-splitting devices. Extensive homogenous catalytic oxidation studies suggest that likely intermediates in H_2O oxidation would degrade all organic ligands, a point consistent with the findings involving molecular H_2O oxidation catalysts reported to date.[3,7,8,14–17,19] Thus, the need to develop highly active and stable H_2O oxidation catalysts remains of considerable importance. Based on the reported $\{Ru_2\}$ catalysts for H_2O oxidation, documented polyoxometalate (POM) complexes with multinuclear d-electron-containing centers capable of accepting several electrons needed for H_2O oxidation,[26–31] and the report by Shannon and co-workers of electrocatalytic O_2 evolution by the Neumann–Khenkin complex, $[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$,[32] we initially prepared $[\{Ru^{III}_2(OH)_2(H_2O)_2\}(\gamma\text{-}SiW_{10}O_{36})]^{4-}$ [33] and demonstrated that it did catalyze H_2O oxidation.[34] Unfortunately, this complex is unstable in aqueous solution, and transforms to as yet unknown products,[34] but these findings led us to further, related studies. Herein we report the synthesis and characterization of $Rb_8K_2[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]\cdot 25\,H_2O$ (**1**), an oxidatively and hydrolytically stable complex that addresses some of the core challenges: it catalyzes the rapid oxidation of H_2O to O_2, does so in aqueous solution at pH 7, and is quite stable under turnover conditions.

Reaction of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with two equivalents of Ru^{III} in acidic aqueous solutions (pH 1.6) at ambient temperature, followed by addition of RbCl, affords crystals of polyanion salt **1** in ca. 40% yield. The X-ray crystal structure of **1** reveals the same "out-of-pocket" d-metal coordination polyhedra observed in water-soluble γ-diiron derivatives;[35,36] namely, the ruthenium centers are corner-sharing and not ligated to the central SiO_4 unit (Figure 1). The two "out-of-pocket" γ-$\{SiW_{10}Ru_2\}$ monomeric units are rotated by 90° around the vertical C_2 axis relative to one another, defining overall D_{2d} symmetry for the polyanion. The staggered structure facilitates incorporation of a $\{Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4\}^{6+}$ core, in which the four ruthenium centers span a slightly distorted tetrahedron with Ru···Ru distances of 3.47–3.66 Å. The adjacent ruthenium centers within each γ-$\{SiW_{10}Ru_2\}$ unit are bridged by hydroxo ligands (bond valence sum 1.29), and oxo ligands bridge the ruthenium centers of different monomeric units.

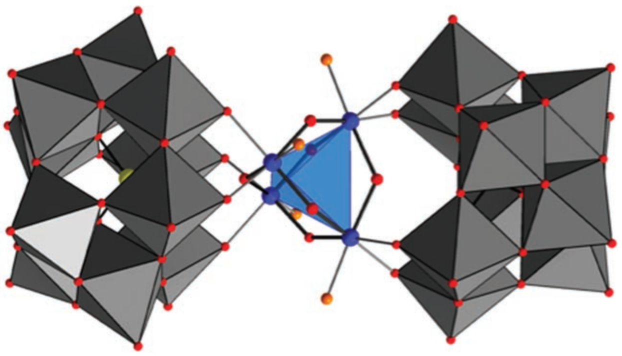

Figure 1. Structure of the polyanion in **1**, highlighting the central $\{Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4\}^{6+}$ core (ball-and-stick representation, Ru blue, μ-O red, $O(H_2)$ orange; hydrogen atoms omitted for clarity) and the slightly distorted $\{Ru_4\}$ tetrahedron (transparent blue). The polytungstate fragments are shown as gray polyhedra, and Si as yellow spheres.

The presence of μ-oxo Ru–O–Ru bridges (indicated by a band at 487 cm^{-1} in the Raman spectrum) is consistent with other structural reports on dimeric ruthenium-containing POMs.[31,37–39] Five lines of evidence indicate that, during the synthesis of **1**, Ru^{III} ($RuCl_3\cdot H_2O$ reactant) is oxidized by O_2 to give a $\{Ru^{IV}_4\}$ complex: 1) magnetic properties are consistent with diamagnetic d^4 Ru^{IV} and not paramagnetic d^5 Ru^{III} centers; 2) bond valence sums on the Ru–O bond lengths yield oxidation states of 4.04 and 4.17 for the two crystallographically independent ruthenium atoms; 3) elemental analysis (number of countercations) and charge balance considerations are in accord with a $\{Ru^{IV}_4\}$ core; 4) **1** is EPR silent;

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and 5) the rest potentials of the cyclic voltammograms are consistent with a $\{Ru^{IV}_4\}$ core. In addition, the oxidation of Ru^{III} in aqueous solution to give a Ru^{IV}-containing POM is known.[31,38]

In preparation for catalytic studies, several techniques were used to further characterize oxidation states and potentials of the ruthenium centers and the protonation states of the $\{Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4\}^{6+}$ core. Repeated acid–base titrations in both directions and monitored both by pH values and the UV/Vis spectra indicate that **1** has two pK_a values in the pH range 3.5–4.5, and these titrations are reversible from pH 2.5–7.5. Thermogravimetric analysis and differential thermal calorimetry indicate the anion in **1** is stable to 450 °C.

Cyclic voltammograms (CVs) of aqueous solutions of **1** are pH-dependent (Figure 2a). At pH 1.0, two oxidation peaks, at ca. 940 and at 1050 mV are observed in a scan from the rest potential (800 mV) to positive potentials and corresponding reduction peaks at ca. 750 and 965 mV are observed on the reverse scan. These are assigned to two $Ru^{V/IV}$ couples in **1**. At potentials lower than the rest potential, three reduction peaks at 530, 370, and −170 mV and the corresponding re-oxidations at 640, 480, and 290 mV, respectively, are observed, which is consistent with three $Ru^{IV/III}$ reductions in **1**. A peak for a fourth $Ru^{IV/III}$ reduction at ca. −350 mV overlaps with an intense peak for $W^{VI/V}$ reduction at ca. −460 mV (not shown in Figure 2a). Thus, under acidic conditions, two Ru^{IV} centers are electrochemically oxidized to Ru^{V}, while all four Ru^{IV} centers can be reduced to Ru^{III}. At higher pH, the rest potentials are lower, but the CV traces are less informative because the ruthenium complexes exhibit complex acid–base equilibria under these conditions (Figure 2a). Significantly, at pH 7.0 there is a very sharp increase in current at $E > 900$ mV; a very weak peak at circa 930 mV is hardly seen. The currents at 950–1050 mV are several-fold higher in the presence of 0.6 mM **1**; this behavior is consistent with electrocatalytic H_2O oxidation at these unusually low potentials (Figure 2a). This result led us to evaluate **1** as a catalyst for homogeneous H_2O oxidation in aqueous solution.

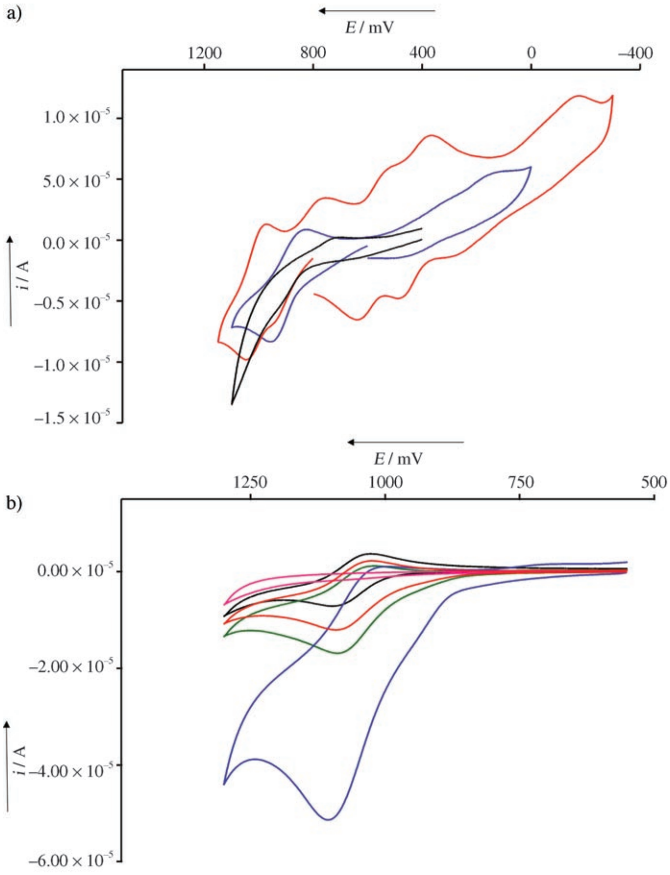

Figure 2. a) CVs of 1 mM **1** in 0.1 M HCl (pH 1.0, red curve), in 0.4 M sodium acetate buffer (pH 4.7, blue curve), and of 0.6 mM **1** (pH 7.0, black curve). Scans start at the rest potentials (800, 600, and 400 mV, respectively), and potentials are relative to a Ag/AgCl (3 M NaCl) reference electrode. b) CVs of 1 mM $[Ru(bpy)_3]^{2+}$ at different concentrations of **1** (0, 0.006, 0.012, and 0.029 mM: black, red, green, and blue curves, respectively) and of 0.029 mM **1** in the absence of $[Ru(bpy)_3]^{2+}$ (pink curve), pH 7.0. Conditions: scan rate 25 mV s^{-1}, in 0.025 M sodium phosphate buffer and 0.15 M NaCl for pH 7.0.

The test reaction for H_2O oxidation was the well-studied process in Equation (1).[2,11,14] A CV of $[Ru(bpy)_3]^{2+}$ at pH 7.0

$$4\,[Ru(bpy)_3]^{3+} + 2\,H_2O \rightarrow 4\,[Ru(bpy)_3]^{2+} + O_2 + 4\,H^+ \qquad (1)$$

shows reversible behavior ($E_a = 1100$, $E_c = 940$ mV, and $I_a/I_c \approx 1$, Figure 2b), and this potential is higher than both the most-positive peak observed for **1** (at pH 1.0) and the standard potential for the four-electron oxidation of H_2O to O_2 ($E^o = 0.82$ V vs. NHE at pH 7).

At a very low concentration of **1**, 0.006–0.029 mM, catalytic currents are observed at potentials corresponding to the oxidation of $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_3]^{3+}$ [see Equation (1) and Figure 2b]. The peak current increases almost linearly with [**1**]. An increase in the anodic peak is accompanied by a complete disappearance of a cathodic peak. The contribution of **1** to the catalytic current in the absence of $[Ru(bpy)_3]^{3+}$ is negligible (Figure 2b).

These promising electrochemical findings led us to investigate catalysis of Equation (1) by **1**, monitored by both accumulated $[Ru(bpy)_3]^{2+}$ spectrophotometrically and O_2 chromatographically (GC with TC detector). In the absence of **1** the typical reaction time, $\tau_{1/2}$, for Equation (1) is > 30 min. Addition of very small amounts of **1** (ca. 0.5–1.5 μM) considerably shortens the reaction time. The reaction does not obey a simple exponential law (the apparent rate constant decreases with time) and is complete in 30–40 s after addition of 1.5 μM **1**. In a typical (unoptimized) reaction, 1.2 mM (12 μmol) $[Ru(bpy)_3]^{3+}$ in the presence of 10 μM (0.1 μmol) of **1** gives 1.07 mM (10.7 μmol) $[Ru(bpy)_3]^{2+}$ (ca. 90 % based on initial $[Ru(bpy)_3]^{3+}$) and 1.78 μmol of O_2 (ca. 66 % based on initial $[Ru(bpy)_3]^{3+}$). To rule out catalysis by RuO_2, a well-known catalyst for H_2O oxidation[5] and a conceivable decomposition product of **1**, we examined the activity of $RuCl_3$ under otherwise identical conditions. The lifetime of $[Ru(bpy)_3]^{3+}$ was only half as long in the presence of 10 μM $RuCl_3$ than with no catalyst. At the equivalent ruthenium concentration of **1** (2.5 μM), the rate of Equation (1) was ca. 10^2 times higher. The data are consistent with catalysis by **1** and not RuO_2. Addition of 10 µм $K_8[\gamma\text{-}SiW_{10}O_{36}]$ to a 10 µм solution of $RuCl_3$ (precursors of **1**) has no effect on the reaction rate, because **1** forms more slowly at this high buffered pH. Although the turnovers (TON) and stoichiometries (ratios of oxygen atoms present in the system) make it clear that the oxygen atoms in O_2 must derive from H_2O and not another sources, we nonetheless, conducted a reaction according to Equation 1 using isotopically labeled water (^{18}O, 5 and 10%). A proportionally enriched O_2 was confirmed by gas chromatography using EI-mass spectrometric detection (see the Supporting Information, Figure S9 for details). In addition, the ratio of $^{16}O^{18}O$:$^{18}O^{18}O$ (m/z ratio 34:36) also confirmed that the oxygen atoms in O_2 were from H_2O.

Thus, the present study clearly documents the formation of O_2 from H_2O, confirmation of which has been a major issue for most of the reported water oxidations by soluble complexes.[8,11,14,15] This work demonstrates that H_2O is not only the solvent but also the source of oxygen atoms in O_2. Indeed, the number of oxygen atoms in the O_2 produced far exceeds the number of oxygen atoms in **1**.

Although the kinetics of H_2O oxidation catalyzed by **1** are complicated, which might indicate involvement of multiple intermediates, four lines of evidence indicate that **1** stays intact in many oxidation states in neutral aqueous media: 1) the acid–base titrations are fully reversible up to pH 7.5; 2) the cyclic voltammograms are reproducible and show reversible oxidation and reduction of multiple ruthenium centers; 3) the $RuCl_3$ control experiment shows H_2O oxidation activity two orders of magnitude lower than **1**; and 4) the turnover number for **1** in the catalytic H_2O oxidation experiments is ca. 18 (moles O_2/mol **1**) or 120 (moles $[Ru(bpy)_3]^{3+}$/mol **1**). In summary, we document a rapid and stable catalyst for H_2O oxidation to O_2 that is operational in H_2O under ambient conditions.

Experimental Section

$Rb_8K_2[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]\cdot 25\,H_2O$ (**1**): The synthesis of **1** and its characterization by single crystal X-ray diffraction and eight other techniques are described in detail in the Supporting Information.

Catalytic water oxidation and O_2 generation: The kinetics of Equation (1) monitored by production of both $[Ru(bpy)_3]^{2+}$ at 454 nm and O_2 by GC are described in detail in the Supporting Information.

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