Structural and mechanistic studies of tunable, stable, fast multi-cobalt water oxidation catalysts

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ABSTRACT

New multi-cobalt-containing polyoxometalates (POMs) are soluble, fast and tunable water oxidation catalysts (WOCs). We report additional studies of $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (**1**), a very fast, soluble and oxidative stable WOC: new kinetics data further indicate that Co^{2+} is not kinetically important in water oxidations catalyzed by **1**. Second, we report a new WOC, $[\{Co_4(\mu\text{-}OH)(H_2O)_3\}(Si_2W_{19}O_{70})]^{11-}$ that coexists in a 1:1 ratio in the solid state (**2a** and **2b**), and while it is oxidatively stable, it is not hydrolytically stable, rearranging to $[Co(H_2O)SiW_{11}O_{39}]^{6-}$ in aqueous solution. All these studies provide insights relating structural, electronic and other features of these WOCs to their reactivity and stability.

Keywords: water oxidation catalysts, water splitting, artificial photosynthesis

1. INTRODUCTION

The development of effective water oxidation catalysts (WOCs) is a central challenge in the production of green energy using water as electron source, including the solar splitting of water and reduction of CO_2 by water. “Effective” means very fast, selective and stable. All catalysts for production of solar fuels will ultimately need to be based on earth-abundant and inexpensive elements.[1] Soluble catalysts facilitate a more thorough study and thus comprehension of the water oxidation process at the atomic and molecular levels than heterogeneous catalysts. Since POMs model metal oxides in several respects[2-4] but are well-defined molecular species whose compositions and structures can be extensively altered synthetically, we turned our attention to WOCs comprising multi-d-electron-metal centers (e.g. Ru and Co) that strongly ligated by multi-dentate POM ligands.

In 2008, our group[5] and that of Bonchio (Padova, Italy)[6] reported the synthesis and catalytic water oxidation activity of $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ (Ru4POM), although under quite different conditions. Their group prepared the compound starting with a multi-Ru-oxo precursor and $\gamma\text{-}SiW_{10}O_{36}^{10-}$,[6] while our group dimerized the di-ruthenium “monomer”, $\{\gamma\text{-}[(H_2O)Ru^{III}(\mu\text{-}OH)_2Ru^{III}(H_2O)][SiW_{10}O_{36}]\}^{4-}$ by oxidation. They conducted water oxidation using Ce(IV) as the sacrificial electronic acceptor (SEA) in strong acid;[6] whereas, we conducted this reaction using $[Ru(bpy)_3]^{3+}$ as the SEA in phosphate buffered water at pH 7.2. Subsequent studies by both groups clarified several of the redox and catalytic features of Ru4POM and showed that water oxidation could be driven by light-sensitized systems.[7-10] The isostructural phosphorus-centered Ru4POM was also prepared and shown to be very good WOC in light-driven reactions.[11]

Subsequently, the tetra-cobalt polytungstate, $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, **1**, was prepared, thoroughly characterized and shown to be an even faster WOC than Ru4POM with a turnover frequency of 5 s^{-1} (versus ca. 1.0 s^{-1} for Ru4POM). Subsequent studies revealed that **1** is highly effective at catalyzing homogeneous visible-light driven water oxidation to O_2 with persulfate as the SEA and $[Ru(bpy)_3]^{2+}$ as the photosensitizer.[12] Extensive spectroscopic, electron microscopic, voltammetric, scattering and other methods indicated that **1** was stable under these conditions (no evidence of decomposition, including formation of cobalt oxide or cobalt oxide phosphate nanoparticles).

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2. EXPERIMENTAL SECTION

2.1 Materials and methods

The preparative precursors and the protocols for synthesis and characterization of Ru4POM and **1** were those already described.[7, 8, 12, 13] The ligand $[\alpha\text{-SiW}_9O_{34}]^{10-}$ was used as its Na_{10} salt as described in the literature.[14] The purities of all samples were checked by IR spectroscopy as 2% samples in KBr pellets using a NicoletTM 6700 FT-IR spectrometer. All other reagents were commercially available and used as received. Galbraith Laboratories in Knoxville, Tennessee performed the elemental analyses for K, Na, Co, Si and W. The UV-visible spectra were taken on an Agilent 8453 UV-vis spectrometer. Thermogravimetric analysis (TGA) data were collected using ISI TGA 1000 instrument. The electrochemical data were obtained at room temperature using a BAS CV-50W electrochemical workstation equipped with a glassy-carbon working electrode, a Pt-wire auxiliary electrode, and a Ag/AgCl (3 M NaCl) BAS reference electrode. All oxidation potentials are reported relative to this reference electrode.

2.2 The mixed sodium, potassium salt of $[\{Co_4(\mu\text{-OH})(H_2O)_3\}(Si_2W_{19}O_{70})]\cdot 31H_2O$.

The well known lacunary ligand $[\alpha\text{-SiW}_9O_{34}]$ as its Na_{10} salt (0.8 g, 0.3 mmol) was dissolved in 15 mL of water. Addition of 1 M HCl brought the pH to 6.8 at which point, $CoCl_2\cdot 6H_2O$ (190 mg (0.8 mmol) was added which further lowered the pH to *ca.* 5. After heating the resulting solution to 80 °C for 1 hr, a precipitate appeared. The solution was cooled to room temperature, and 0.5 M HCl was added until the pH was 5.8. The resulting suspension was treated with 2 mL of saturated KCl, stirred for an additional 10 min and the product precipitate removed by filtration. After sitting for 24 h, red crystals of a prism morphology were collected in 18% yield based on W. IR (2% in KBr, cm^{-1}): 992 (m), 946 (m), 888 (s), 786 (s), 703 (s), 668 (sh), 600 (m), 536 (sh), 523(m). Elemental analysis: Calcd for $Na_{0.8}K_{10.2}[\{Co_4(\mu\text{-OH})(H_2O)_3\}(Si_2W_{19}O_{70})]\cdot 31H_2O$: Co: 3.96; K: 6.70; Na: 0.309; Si: 0.944; W: 58.7%; Found: Co: 3.76; K: 6.60; Na: 0.296; Si: 0.938; W: 58.4 %.

2.3 X-Ray crystal structure determintion.

Crystals suitable for X-ray structure analysis based on optical microscopic examination and preliminary diffraction data were coated with Paratone-N oil, suspended on a small loop and placed on a Bruker D8 APEX II CCD sealed tube diffractometer. The goniometer head was cooled by nitrogen gas stream at 173 K and graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation was used. A combination of φ and ω scans were used to collect the data with 10 s frame exposure and 0.3° frame widths. The SMART software was used for data collection, indexing and initial cell refinements.[15] The SAINT was used for frame integration and final cell refinements.[16] The molecular structure of each complex was determined using direct methods and Fourier techniques; refinement was by the full-matrix least-squares procedure. SADABS was used to make multiple absorption corrections and index faces.[17] The largest residual electron density for each structure was located less than 1.0 Å from the W atoms and most likely derives from imperfect absorption corrections. These are common in X-ray structure determinations of polytungstate complexes. Anomalous dispersion corrections and scattering factors were taken from the International Tables for X-ray Crystallography. SHELXTL, v 6.14, software was used for structure solution, refinement, and production of graphics.[18]

2.4 Catalytic experiments

The reaction vessel for catalytic water oxidation (typically a 10-mL Schlenk flask) was filled with 8 mL of a solution containing 1.0 mM $[Ru(bpy)_3]Cl_2$, 5 mM $Na_2S_2O_8$, 25 mM buffer solution and the catalyst at its indicated concentration (see Figure captions). Prior to reaction, argon was bubbled through the solution to thoroughly deairate it. Reaction was initiated when a Xe-lamp equipped with a 420-520 nm band-pass filter was used to irradiate the solution. The reactions were temporarily stopped after the specific illumination times by blocking the light. The reaction flasks were vigorously shaken to facilitate equilibration of O_2 between the solution and the head-space. The headspace gas was analyzed by gas chromatography using argon as the carrier gas. Typically a 0.1 mL aliquot of gas was withdrawn from the headspace and injected into a Agilent 7890A gas chromatograph equipped with a 5Å molecular sieve capillary column to separate O_2 and N_2. Products were quantified using a thermal conductivity detector and built-in integration system. The consumption of persulfate ($Na_2S_2O_8$) marked reaction completion.

3. RESULTS AND DISCUSSION

3.1. Kinetics and stability studies of water oxidation catalyzed by $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, 1, and $Co^{2+}(aq)$.

We conducted 7 different experiments in our initial report on the potent WOC, **1**, that collectively provide very strong evidence that **1** is stable under the conditions used in that study (typically runs up to 20 minutes in phosphate-buffered H_2O at pH 8).{Yin, 2010 #8752} However, it is well known that POMs containing one or more d-electron-containing metal centers (3d metals such as Mn, Fe, Co as well as 4d and 5d metals) are in equilibrium with their defect forms (eq 1 is an exemplary case). The three preceding 3d metals may ultimately all be relevant to water oxidation in POM systems based on their ground state redox potentials in such ligand environments in aqueous media (desired) and other media (less desired).

$$\text{Defect POM (e.g. } PW_{11}O_{39}^{7-}) + Co^{2+}(aq) = Co^{II}PW_{11}O_{39}^{7-} \qquad (1)$$

The equilibrium constants are very large for such processes. Nonetheless, it is possible that Co^{2+} loss from **1** could lead to water oxidation catalyzed by $Co^{2+}(aq)$ or by subsequently-formed cobalt oxide nanoparticles, and/or in phosphate buffer, the Kanan-Nocera (KN) catalyst, a solid cobalt oxide phosphate phrase. Even though the latter heterogeneous cobalt-containing oxide materials have been evaluated and are far less active than **1** under the conditions of our initial catalytic WOC studies by **1**, we wanted to probe the kinetics of water oxidation by $Co^{2+}(aq)$ and **1** under identical conditions and also under initial conditions before either have a significant chance to rearrange to another species.

An examination of the kinetics of water oxidation (monitored by the rate of O_2 evolution by GC; see experimental section) catalyzed by $Co^{2+}(aq)$ and **1** reveals that both are highly effective catalysts. Significantly however, $Co^{2+}(aq)$ exhibits an induction period implicating that another species, very likely very small particles of insoluble hydrated cobalt hydroxide or cobalt oxide, is the actual catalyst. In contrast, O_2 evolution in the presence of **1** shows no induction period. In the presence of phosphate buffer which could lead to production of cobalt hydrogen phosphate, cobalt phosphate and/or the KN catalyst in addition to cobalt hydroxide/oxide particles, $Co^{2+}(aq)$ shows an induction period while **1** does not.

A full kinetics study will be submitted for publication in the coming months.

3.2. A new multi-cobalt polytungstate WOC, $[\{Co_4(\mu\text{-}OH)(H_2O)_3\}(Si_2W_{19}O_{70})]^{11-}$ (2).

Another ongoing effort to better understand the equilibria and dynamics of our multi-d-electron-substituted POMs is to systematically prepare other structural families of d-electron-metal-substituted POMs (particularly Co and Ru derivatives) and investigate the kinetics and thermodynamics of their rearrangements (if any) to other POMs and/or metal oxides.

To this end we have prepared **2**, a new tetra-cobalt POM. The X-ray structure of **2**, shown Figure 1, is complicated. This complex is present in the solid state as two similar isomers that co-crystallize (**2a** and **2b**). Like **1**, both isomers of **2** contain four Co(II) ions in the center of the molecule; however, these cobalt ions are ligated differently by the adjacent oxygen and tungsten atoms. Significantly, these cobalt ions have fewer bonds to the POM oxygens and this is equivalent to the fact they have more coordination positions open to the solvent or species in solution. This is a potentially attractive feature for catalyzing the multi-electron oxidation of H_2O to O_2. However, it is a potentially unattractive feature in terms of stability because these cobalt ions are more accessible to species in solution that might compete with the POMs as ligands. Any such competition could result in extraction of these d-electron centers from the structure and hydrolytic decomposition of **2**.

3.3. The reactivity properties of 2 (WOC activity and decomposition).

Figure 2 shows that **2** catalyzes water oxidation under light-driven conditions (conditions in the caption). However, Figure 3 shows that **2**, in contrast to **1**, also undergoes fairly rapid decomposition to the well-known mono-substituted Keggin POM, $[Co(H_2O)SiW_{11}O_{39}]^{6-}$ in the same medium (25 mM borate, pH 9 used in both studies).

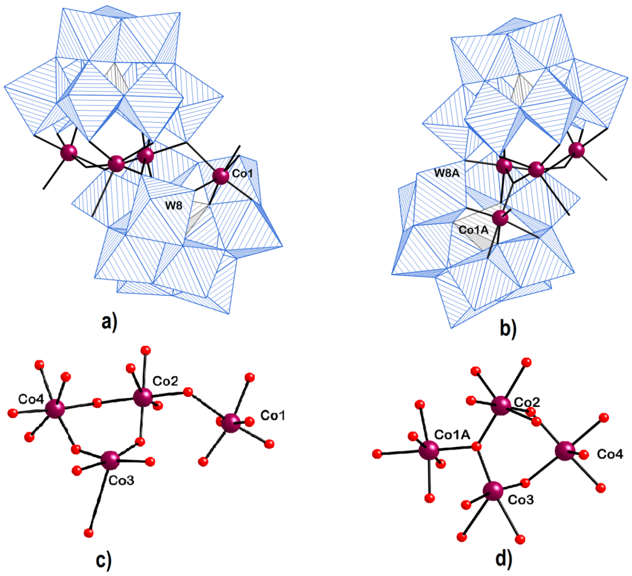

Figure 1. The two isomers (**2a** and **2b**) of $[\{Co_4(\mu\text{-}OH)(H_2O)_3\}(Si_2W_{19}O_{70})]^{11-}$ as they co-exist in a 1:1 ratio in the single-crystal structure of **2** (the $K_{10.2}Na_{0.8}$ salt). The POM framework is in polyhedral notation (WO_6 octahedra: blue, SiO_4 tetrahedra: grey). The cobalt centers (plum) are in ball-and-stick notation; all hydrogen atoms are omitted for clarity. In the (c) and (d) lower panels the μ-oxo connection motifs of the cobalt sites in **2a** and **2b**, respectively are evident.

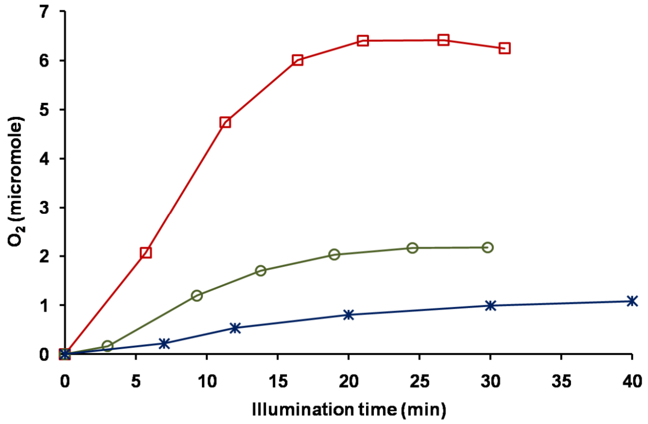

Figure 2. (a) Kinetics of water oxidation by persulfate catalyzed by 2 in a light-driven systems using different buffer solutions. Conditions: 1.0 mM $[Ru(bpy)_3]Cl_2$, 5 mM $Na_2S_2O_8$, 25 mM buffer, 10.0 µM **2**, total solution volume 8 mL; Xe lamp, 420-520 nm band-pass filter. Blue stars: sodium phosphate buffer, pH 7.2; olive green circles: 1:1 mixture of sodium phosphate and sodium borate buffers, pH 8; red squares: sodium borate buffer, pH 9.

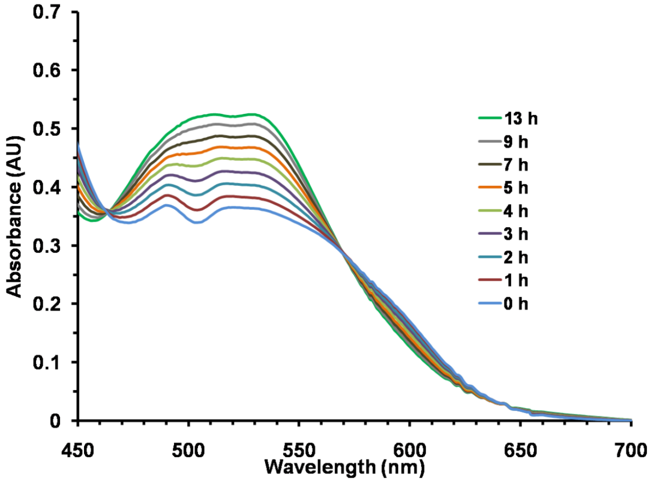

Figure 3. Evolution in UV-Vis spectra of **2** (6.2 mM) in pH 9.0 Na borate buffer (25 mM).

4. CONCLUDING REMARKS

Kinetic studies on Co^{2+}(aq) and $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (**1**), our previously reported POM-based WOC, indicate the former is not an important WOC under the catalytic conditions in our initial publications; whereas, **1** is. Reaction of Si-centered polytungstates and Co^{2+}(aq) forms other tetra-cobalt POM-based WOCs. Unlike **1**, however, **2** is not hydrolytically stable and rearranges to the long-known Keggin polytungstate, $[Co(H_2O)SiW_{11}O_{39}]^{6-}$.

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6. REFERENCES

1. Kanan, M. W.; Nocera, D. G. In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co^{2+}. *Science* **2008,** *321*, 1072-1075.
2. Pope, M. T.; Müller, A. Chemistry of polyoxometallates. Actual variation on an old theme with interdisciplinary references. *Angew. Chem.* **1991,** *103* (1), 56-70.
3. Borrás-Almenar, J. J.; Coronado, E.; Müller, A.; Pope, M. T., *Polyoxometalate Molecular Science*. Kluwer Academic Publishers: Dordrecht, 2003; Vol. 98.
4. Hill, C. L., Polyoxometalates: Reactivity. In *Comprehensive Coordination Chemistry-II: From Biology to Nanotechnology*, Wedd, A. G., Ed. Elsevier Ltd.: Oxford, UK, 2004; Vol. 4, pp 679-759.
5. Geletii, Y. V.; Botar, B.; Kögerler, P.; Hillesheim, D. A.; Musaev, D. G.; Hill, C. L. An All-Inorganic, Stable, and Highly Active Tetraruthenium Homogeneous Catalyst for Water Oxidation. Selected as the VIP Article by the reviewers and editor. . *Angew. Chem. Int. Ed.* **2008,** *47*, 3896-3899.
6. Sartorel, A.; Carraro, M.; Scorrano, G.; Zorzi, R. D.; Geremia, S.; McDaniel, N. D.; Bernhard, S.; Bonchio, M. Polyoxometalate Embedding of a Tetraruthenium(IV)-oxo-core by Template-Directed Metalation of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$: A Totally Inorganic Oxygen-Evolving Catalyst. *J. Am. Chem. Soc* **2008,** *130* (15), 5006–5007.
7. Geletii, Y. V.; Huang, Z.; Hou, Y.; Musaev, D. G.; Lian, T.; Hill, C. L. Homogeneous Light-Driven Water Oxidation Catalyzed by a Tetraruthenium Complex with All Inorganic Ligands. *J. Am. Chem. Soc.* **2009,** *131*, 7522-7523.
8. Geletii, Y. V.; Besson, C.; Hou, Y.; Yin, Q.; Musaev, D. G.; Quinonero, D.; Cao, R.; Hardcastle, K. I.; Proust, A.; Kögerler, P.; Hill, C. L. Structural, Physicochemical and Reactivity Properties of an All-Inorganic, Highly Active Tetraruthenium Homogeneous Catalyst for Water Oxidation. *J. Am. Chem. Soc.* **2009,** *131* (47), 17360-17370.
9. Sartorel, A.; Miro, P.; Salvadori, E.; Romain, S.; Carraro, M.; Scorrano, G.; Valentin, M. D.; Llobet, A.; Bo, C.; Bonchio, M. Water Oxidation at a Tetraruthenate Core Stabilized by Polyoxometalate Ligands: Experimental and Computational Evidence To Trace the Competent Intermediates. *J. Am. Chem. Soc.* **2009,** *131*, 16051-16053.
10. Puntoriero, F.; Ganga, G. L.; Sartorel, A.; Carraro, M.; Scorrano, G.; Bonchio, M.; Campagna, S. Photo-induced water oxidation with tetra-nuclear ruthenium sensitizer and catalyst: A unique 4X4 ruthenium interplay triggering high efficiency with low-energy visible lightw. *Chem. Commun.* **2010,** *46*, 4725-4227.
11. Besson, C.; Huang, Z.; Geletii, Y. V.; Lense, S.; Hardcastle, K. I.; Musaev, D. G.; Lian, T.; Proust, A.; Hill, C. L. $Cs_9[$(®-$PW_{10}O_{36})_2Ru_4O_5(OH)(H_2O)_4]$, a new all-inorganic, soluble catalyst for the efficient visible-light-driven oxidation of water. *Chem. Commun.* **2010**, 2784-2786.
12. Huang, Z.; Luo, Z.; Geletii, Y. V.; Vickers, J.; Yin, Q.; Wu, D.; Hou, Y.; Ding, Y.; Song, J.; Musaev, D. G.; Hill, C. L.; Lian, T. Efficient Light-Driven Carbon-Free Cobalt-Based Molecular Catalyst for Water Oxidation. *J. Am. Chem. Soc.* **2011,** *133*, 2068-2071.
13. Yin, Q.; Tan, J. M.; Besson, C.; Geletii, Y. V.; Musaev, D. G.; Kuznetsov, A. E.; Luo, Z.; Hardcastle, K. I.; Hill, C. L. A fast soluble carbon-free molecular water oxidation catalyst based on abundant metals. *Science* **2010,** *328*, 342-345.
14. Tézé, A.; Hervé, G., 〈-, β-, and ©-Dodecatungstosilicic Acids: Isomers and related Lacunary Compounds. In *Inorg. Synth.*, Ginsberg, A. P., Ed. John Wiley and Sons: New York, 1990; Vol. 27, pp 85-96.
15. Bruker AXS, I. *SMART, ver. 5.628*, Analytical X-ray Sysems: Madison, WI, 2003.
16. Bruker AXS, I. *SAINT, ver. 6.28*, Analytical X-Ray Sytems: Madison, WI, 2003.
17. Sheldrick, G. *SADABS*, 2.10 edition; 2003.
18. Bruker AXS, I. *SHELXTL, ver 6.14 ed.*, Madison, WI, 2003.