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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

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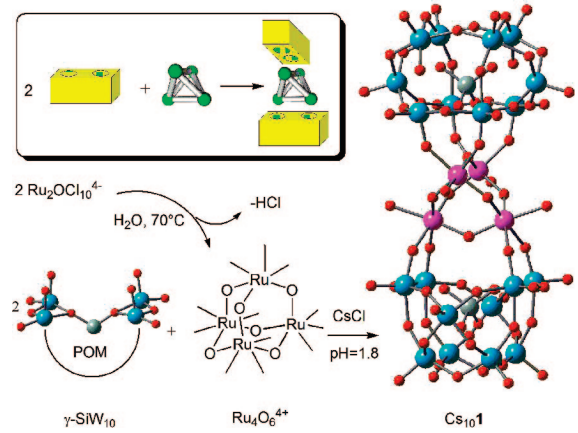
The synthesis of tailored multimetal catalysts is becoming increasingly important for high efficiency and multifunctionality in various applications. In particular, polyoxometalates (POMs) provide unique models for the investigation of structure–activity relationships at the borderline between molecules and extended solids.[1,2] In this respect, a research frontier is POM encapsulation of transition metal clusters, whereby redox-active substituents give rise to heterometal-oxo phases, interconnected with the polyoxometalate framework.[1,2] Stabilization of adjacent d-electron centers through multiple-μ-hydroxo/oxo bridging units is one of the most powerful strategies adopted by natural enzymes to effect multiple/cascade transformations.[3] In the quest for functional, bioinspired catalysts, ruthenium analogues occupy a prominent role, vis-à-vis its unmatched range of accessible oxidation states coupled with some unique mechanistic and selective performance.[4,5] Moreover the electron-withdrawing nature of the POM ligand is predicted to stabilize high-valent intermediates and assist deprotonation equilibria on the poly-oxygenated surface.[6,7] Despite their appeal, the synthesis of Ru-substituted POMs poses a major challenge, owing to the inertness of ligand exchange and to purification issues.[8]

We report herein the facile isolation of a new di-γ-decatungstosilicate embedding a tetra-ruthenium(IV)-oxo core which shows promise as a water oxidation catalyst.[5] $Cs_{10}[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]$ (Cs_{10}**1**) is obtained by reacting the divacant POM, $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ (γ-SiW_{10}) with μ-oxo-bis-pentachlororuthenate(IV), $Ru_2OCl_{10}^{4-}$, in aqueous solution (Scheme 1). POM metalation is fostered by the in situ generation of the tetranuclear ruthenium(IV) aqua-ion, $[Ru_4O_6(H_2O)_n]^{4+}$, whose existence and adamantane-like solution structure have been proposed on the basis of EXAFS studies.[9] The unprecedented entrapment of the Ru_4O_6 fragment occurs readily by the complementary assembly of two γ-SiW_{10} units under mild temperature conditions. Both the templated vicinal substitution and the lability of the aqua ligands at the ruthenium core,[10] are instrumental for the straightforward formation of **1**. The product precipitates with CsCl in 85% yield; single-crystals suitable for X-ray diffraction are obtained upon recrystallization at pH = 2. The XRD analysis shows a skewed dimeric structure for **1**, where two γ-SiW_{10} units are connected in a 90° staggered arrangement, by an electrophilic $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4]^{6+}$ central core. The polyanion has an overall D_{2d} symmetry

Scheme 1. Metalation of SiW_{10} by Complementary Lego Assembly of $[Ru_4O_6(H_2O)_n]^{4+}$



(Scheme 1). The tetraruthenate core displays the expected adamatane-like arrangement, with four ruthenium and six oxygen atoms at the apexes of a tetrahedron and of an octahedron, respectively. The bond valence sum (BVS)[11] calculations, of 4.08(12) for Ru atom, support this description and indicate that two oxygen atoms of the $Ru_4O_6^{4+}$ core are monoprotonated (average bond length of 2.00(2) Å with a BVS of 1.27(4)).

These two symmetry related hydroxo bridges are bent and connect the two adjacent Ru(IV) centers linked to the POM binding site (Ru−O−Ru bond angle of 131.2(9)°). Moreover, they each give rise to a strong three-center H-bond with two proximal Si−O−W bridges (average O−O distance: 2.89(3) Å) (Figure 1). The small BVS values calculated for the terminal oxygen atoms bound to each Ru(IV) center (average coordination length of 2.09(2) Å with BVS of 0.50(4)) are consistent with aqua ligands. Significantly, the γ-$SiW_{10}Ru_2$ unit adopts an "out-of-pocket" structural motif, whereby the two adjacent d-electron metals are corner sharing and ligated only by the four oxygen sites of the POM lacuna, with no direct bonding interaction from the internal O−Si tetrahedron.[12] The maintenance of the POM structure in aqueous solution is confirmed by converging evidence, provided by electrospray ionization mass spectra (ESI-MS), resonance Raman (rR), and UV–vis spectroscopy. The ESI-MS spectrum of the water soluble Li_{10}**1** complex shows envelopes at m/z = 1798 and m/z = 1348 which can be assigned respectively to ions $[H_9Ru_4Si_2W_{20}O_{78}]^{3-}$ and $[H_8Ru_4Si_2W_{20}O_{78}]^{4-}$, containing the tetraruthenate core after loss

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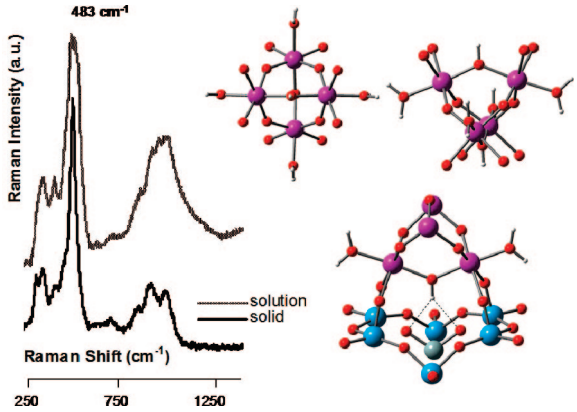

Figure 1. The rR spectra of **1**, in the solid state and in H_2O (pH = 2, excitation at 488 nm). The structures show the top-front views of the central $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4]^{6+}$ fragment.

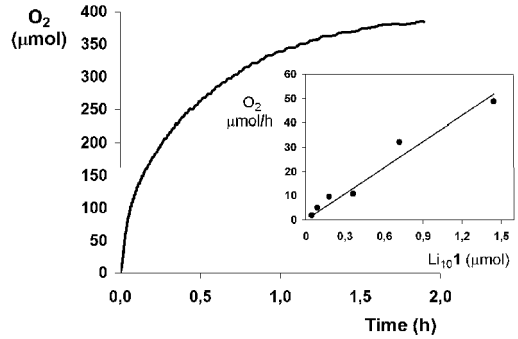

Figure 2. Kinetics of O_2 evolution by Li_{10}**1**, (4.3 μmol) with Ce(IV) (1720 μmol), in H_2O (10 mL) at 20 °C. The inset shows a plot of initial rates vs Li_{10}**1** (0.045–1.45 μmol), with Ce(IV) (10.9 mmol).

of the four labile water ligands (Supporting Information, Figure S7). Direct evidence for retention of the multiple μ-oxo-ruthenium connectivity is provided by superimposable rR experiments performed for **1**, on a solid sample and in water (pH = 2). Both rR spectra exhibit a prominent feature at 483 cm^{-1}, which falls in the range expected for a ν_{sym}(Ru−O−Ru) vibrational mode (Figure 1).[5c,13]

The UV–vis spectrum collected in water (pH = 0.6–2.0) shows a sharp absorption band at $\lambda = 443$ nm ($\log \epsilon^{443} = 4.57$).[9] Acid–base, spectrophotometric titration of Li_{10}**1** at $\lambda = 443$ nm, and fitting of the ϵ^{443} variation, indicates a reversible mono-protonation equilibrium with a pK_a of 3.62 (Supporting Information, Figures S4−S6). Structurally related Ru(H_2O) functions exhibit pK_a in the range 1.8–3.3.[14] Furthermore, the acid–base equilibrium is not concentration-dependent, thus ruling out POM dissociation or aggregation phenomena. Moreover, the FT-IR spectra are unchanged upon titration of **1**, confirming the maintenance of the POM framework. Multiple-redox states associable to the $Ru(IV)_4$ core[15,16] and reversible protonation equilibria are critical components for efficient oxygen evolving catalysis, whereby deprotonation of ligated H_2O triggers the formation of OH^-/O^{2-} reactive sites.[5] Thus, the catalytic activity of Li_{10}**1** toward water oxidation has been evaluated by reacting it (4.3 μmol) with an excess of Ce(IV) (1720 μmol), in H_2O (pH = 0.6) at 20 °C. GC sampling of the reactor headspace, with continuous monitoring of the pressure variation, confirms evolution of molecular oxygen in the system, generating 385 μmol of O_2 in 2 h, with an overall 90% yield on the added oxidant.[16b] A recharge of Ce^{IV} induces an equivalent evolution of oxygen. The water-oxidation rate exhibited by Li_{10}**1** is remarkable (maximum TOF > 450 h^{-1}, see Figure S9). A linear dependence of the initial rate on [Li_{10}**1**] is observed, with a pseudo-first-order kinetic constant of 9.92×10^{-3} s^{-1}, (up to 500 turnovers based on the evolved oxygen, inset in Figure 2 and Figure S10). Its high efficiency is indicative of a very robust catalyst, compared to other previously reported ruthenium systems, bearing classical organic ligands.[5,16b,17] IR, rR spectra confirm the integrity of the POM structure after treatment with Ce(IV) excess (Figures S11–S12). Future studies will investigate the insertion of the Ru_4O_6 fragment within other POM structures, with the final goal of optimizing the oxygen evolving catalytic performance of the system, in the quest for a modular approach to artificial photosynthesis.[18]

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Supporting Information Available: Full procedures, spectra, crystallographic data of Cs_{10}**1** and kinetics. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) *Polyoxometalate Chemistry from Topology via Self-Assembly to Applications*; Pope, M., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001.
(2) Long, D.; Burkholder, E.; Cronin, L. *Chem. Soc. Rev.* **2007**, *36*, 105–121.
(3) (a) Que, L.; Tolman, W. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 1114–1137. (b) DeGrado, W. F.; Di Costanzo, L.; Geremia, S.; Lombardi, A.; Pavone, V.; Randaccio, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 417–420. (c) McEvoy, J. P.; Brudvig, G. W. *Chem. Rev.* **2006**, *106*, 4455–4483.
(4) (a) Naota, T.; Takaya, H.; Murahashi, S-I. *Chem. Rev.* **1998**, *98*, 2599–2660. (b) Neumann, R.; Dahan, M. *Nature* **1997**, *388*, 353–355.
(5) (a) Ruttinger, W.; Dismukes, C. *Chem. Rev.* **1997**, *97*, 1–24. (b) Yagi, M.; Kaneko, M. *Chem. Rev.* **2001**, *101*, 21–35. (c) Hurst, J. K. *Coord. Chem. Rev.* **2005**, *249*, 313–328.
(6) Shaik, S.; Hirao, H.; Kumar, D. *Acc. Chem. Res.* **2007**, *40*, 532–542.
(7) (a) Sartorel, A.; Carraro, M.; Bagno, A.; Scorrano, G.; Bonchio, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3255–3258. (b) Fang, X.; Hill, C. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 3877–3880.
(8) (a) Bi, L.-H.; Chubarova, E. V.; Nsouli, N. H.; Dickman, M. H.; Kortz, U.; Keita, B.; Nadjo, L. *Inorg. Chem.* **2006**, *45*, 8575–8583. (b) Artero, V.; Laurencin, D.; Villanneau, R.; Thouvenot, R.; Herson, P.; Gouzerh, P.; Proust, A. *Inorg. Chem.* **2005**, *44*, 2826–2835. (c) Quinonero, D.; Wang, Y.; Morokuma, K.; Khavrutskii, L. A.; Botar, B.; Geletii, Y. V.; Hill, C. L.; Musaev, D. G. *J. Phys Chem. B* **2006**, *110*, 170–173.
(9) (a) Osman, J. R.; Crayston, J. A.; Richens, D. T. *Inorg. Chem.* **1998**, *37*, 1665–1668. (b) Heerman, L.; Van Nijen, H.; D'Olieslager, W. *Inorg. Chem.* **1988**, *27*, 4320–4323.
(10) The k_{ex} values of water exchange are 7 order of magnitude higher with respect to the mononuclear aqua ion. Patel, A.; Richens, D. T. *Inorg. Chem.* **1991**, *30*, 3792–3793.
(11) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192–197.
(12) This coordination mode is an emerging feature documented only for Fe(III) and Cr(III) POMs, see: (a) Botar, B.; Kogerler, P.; Hill, C. L. *Inorg. Chem.* **2007**, *46*, 5398–5403. (b) Botar, B.; Geletii, Y. V.; Kogerler, P.; Musaev, D. G.; Morokuma, K.; Weinstock, I. A.; Hill, C. L. *J. Am. Chem. Soc.* **2006**, *128*, 11268–11277.
(13) Crystals of Cs_{10}-**1** are EPR silent, indicating a diamagnetic behavior. Further investigation will address the catalyst evolution to competent species in solution (vide infra).
(14) Sadakane, M.; Higashijima, M. *Dalton Trans.* **2003**, 659–664.
(15) The CV of Li_{10}**1** in H_2O (pH = 0.6) shows four anodic and cathodic waves in a potential range from +1.4 to −0.0 V (vs Ag/AgCl) observed at $E_{1/2}$ = +1.12, +0.70, +0.53, and +0.29 V with a peak separation of ΔE_p (= $E_{pa} - E_{pc}$) of 89, 98, 59, and 166 mV (Figure S7).
(16) (a) Electrocatalytic water oxidation by a sandwich-type Ru-POM, (mixture of isomeric clusters) has been reported. Howells, A. R.; Sankarraj, A.; Shannon, C. *J. Am. Chem. Soc.* **2004**, *126*, 12258–12259. (b) $K_4Ru_2OCl_{10}$, shows a sluggish reactivity, featuring ca. 20 min induction time, followed by slow oxygen evolution (1 order of magnitude slower than the POM-catalyzed reaction) and soon leveling off to a plateu yield, at <10% of Ce(IV) conversion.
(17) (a) Sens, C.; Romero, I.; Rodriguez, M.; Llobet, A.; Parella, T.; Benet-Buchholz, J. *J. Am. Chem. Soc.* **2004**, *126*, 7798–7799. (b) Zong, R.; Thummel, R. P. *J. Am. Chem. Soc.* **2005**, *127*, 12802–12803. (c) Liu, F.; Cardolaccia, T.; Hornstein, B. J.; Schoonover, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 2446–2447.
(18) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. *Inorg. Chem.* **2005**, *44*, 6802–6827.

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