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Electrocatalytic Water Oxidation Beginning with the Cobalt Polyoxometalate $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$: Identification of Heterogeneous CoO_x as the Dominant Catalyst

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S *Supporting Information*

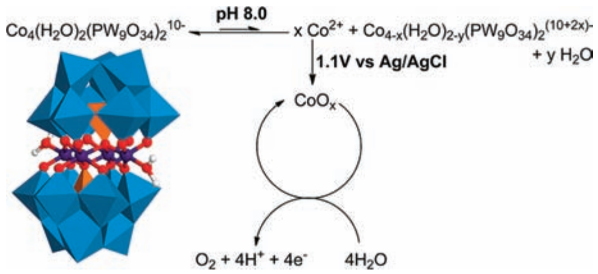
ABSTRACT: The question of "what is the true catalyst?" when beginning with the cobalt polyoxometalate (POM) $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ in electrochemical water oxidation catalysis is examined in pH 8.0 sodium phosphate buffer at a glassy carbon electrode. Is $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ a true water oxidation catalyst (WOC), or just a precatalyst? Electrochemical, kinetic, UV−vis, SEM, EDX, and other data provide four main lines of compelling evidence that, under the conditions used herein, the dominant WOC is actually heterogeneous CoO_x and not homogeneous $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$.

Efficient storage of energy is requisite for the broad implementation of solar energy technologies, since photon energy input is available only while the sun is shining.[1] The storage of energy in chemical bonds is one arguably superior solution to the energy storage problem.[1] Conversion of solar to chemical energy can be achieved by oxidation of water to oxygen and protons with simultaneous reduction of protons to hydrogen fuel.[2] Of these two half-reactions, the oxidation of water is more demanding because it encompasses the transfer of four electrons and four protons and often requires large electrochemical overpotentials in order to drive the reaction at appreciable rates.[3]

In-situ-formed CoO_x water oxidation catalysts (WOCs) have been reported by Nocera and co-workers and others;[4,5] these catalysts are formed under oxidizing conditions from aqueous Co(II) salts, operate at moderate overpotentials, and are oxidatively stable.[4] The CoO_x formula is used herein to indicate a cobalt−oxo/hydroxo-based solid that can incorporate additional countercations and -anions (e.g., we observed herein a CoO_x catalyst with the empirically observed formula $Co_aO_bNa_cP_d$; see below).

A 2010 *Science* paper and a 2011 *JACS* paper reported that the cobalt-containing polyoxometalate (POM) $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ is an extremely active, stable, homogeneous WOC with either chemical or photochemical oxidants.[6,7] However, no detailed study of this cobalt POM as an electrochemical WOC has previously appeared. Two standard electrochemical studies of $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ round out what is known about the redox activity of this POM,[8,9] work which did not report any type of WOC.

Scheme 1. Proposed Heterogeneous CoO_x Catalyst Formation Pathway and a Polyhedral Plus Ball-and-Stick Model of the Cobalt POM Starting Material (WO_6, blue polyhedra; PO_4, orange polyhedra; Co, purple; H, white; O, red)



We report herein experimental results providing compelling evidence that CoO_x, and not the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ POM precatalyst, is the dominant WOC when the oxidizing equivalents are supplied by a glassy carbon electrode in 0.1 M sodium phosphate buffer at pH 8.0 under air (Scheme 1). This conclusion is supported by the following four primary lines of evidence: (1) $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ degrades in pH 8.0 sodium phosphate buffer, as determined by UV−vis spectroscopy and by electrochemical measurement of the aqueous, leached Co(II) concentration; (2) a CoO_x WOC film is formed in situ from $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solutions on a glassy carbon working electrode under oxidizing conditions (1.1 V vs Ag/AgCl), as shown by electrochemical, UV−vis, scanning electron microscopy (SEM), and energy-dispersive X-ray analysis (EDX) methods; (3) 58 μM Co(II) [or its functional equivalent, hereafter denoted as "apparent Co(II)"; see below] is detectable in solution by two independent methods; and (4) authentic $Co(NO_3)_2$, at the 58 μM level leached into solution from the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, *quantitatively* accounts for *all* of the water oxidation activity within experimental error.

The $Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ POM was synthesized according to the procedure of Weakley[10] as modified by Hill and co-workers[6] and recrystallized twice from water. Its basic structure was confirmed by IR spectroscopy [see the Supporting Information (SI)]. The purity of the cobalt POM, especially the absence of any detectable excess Co(II) present as a simple countercation, was confirmed by elemental analysis (see the SI).

Initial investigations of the catalytic activity of $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solutions were conducted using a standard three-electrode electrochemical setup; unless otherwise noted, the solutions were in contact with air and a glassy carbon working electrode ($A = 0.071$ cm^2), a Ag/AgCl reference electrode, and a platinum wire counter electrode were used for all of the

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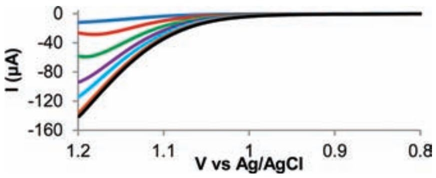

Figure 1. Linear sweep voltammetry of 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ in pH 8.0 sodium phosphate buffer monitored for the first 3 h after dissolution of the electrolyte; scans were taken at $t = 0.02$ (blue), 0.5 (red), 1.0 (green), 1.5 (purple), 2.0 (light-blue), 2.5 (orange), and 3.0 (black) h. The scan rate was 20 mV/s.

electrochemical measurements (full experimental details are given in the SI). One minute after $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (500 μM) was dissolved in 0.1 M sodium phosphate buffer at pH 8.0, linear-sweep voltammetry showed an oxidation wave (onset at 1.05 V). As this solution was aged over a 3 h period, the oxidation wave *increased by greater than 10-fold in magnitude and shifted to lower onset potentials* (Figure 1). Since the catalytic oxidation wave increased over time, the most active catalyst cannot be the initially present $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ but must instead be a derivative of the cobalt POM. In other words, *$[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ is a precatalyst to the most active WOC.*

Cyclic voltammetry of a 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solution initially showed a small quasi-irreversible oxidation wave at ~1.1 V with a maximum anodic current of 11 μA (Figure 2a; an expanded view is shown in Figure S1 in the SI). When a constant potential of 1.1 V vs Ag/AgCl was applied to the cell, the oxidation current increased rapidly and bubbles (O_2; see below) formed at the working electrode. Concomitant with the increase in current, a film (identified as CoO_x by UV–vis, SEM, and EDX; see below) was deposited onto the glassy carbon electrode. When the electrode was then removed from solution, rinsed with water, and placed into a solution containing only 0.1 M sodium phosphate buffer at pH 8.0 (i.e., with no $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$), the catalytic activity was maintained at the previously observed levels in both cyclic voltammetry and controlled-potential electrolysis experiments (Figure 2a,b). The slow decrease in catalytic activity of the film is attributed to poor adhesion of the film to glassy carbon, resulting in dissolution of the film in pH 8.0 sodium phosphate buffer; that poor film adhesion also prevented longer electrodeposition times.

SEM of the electrodeposited catalytic film on a glassy carbon plate showed complete coverage of the substrate plus sporadic nodules that measured ~100 nm in diameter (Figure S2). EDX revealed that these catalytic films contained O, Co, Na, and P (with an approximate Co:Na:P ratio of 4:1:1) as well as carbon from the substrate (Figure S3). In comparison, for their authentic CoO_x catalyst films, Nocera and co-workers observed a similar Co:P ratio ranging from 2:1 to 3:1 for films deposited from 1 mM $Co(NO_3)_2$ in 0.1 M potassium phosphate buffer (pH 7.0).[4a]

Notably, *no tungsten* is observed in our CoO_x film (i.e., no detectable W-containing cobalt POM). As a control, SEM of a drop-coated $Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ film showed different, micrometer-sized blocklike crystallites (Figure S2). EDX analysis confirmed a film composed of oxygen, tungsten, sodium, and cobalt (although phosphorus was presumably present, it could not be identified because the tungsten Mγ line overlaps with the phosphorus Kα,β lines shown in Figure S4). This control confirms that the cobalt POM would have been observed by SEM/EDX in our hands had it been present. Comparison of the $Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ and CoO_x films in Figure S2 demonstrates that the electrodeposited heterogeneous catalyst is fundamentally different than the cobalt POM starting material.

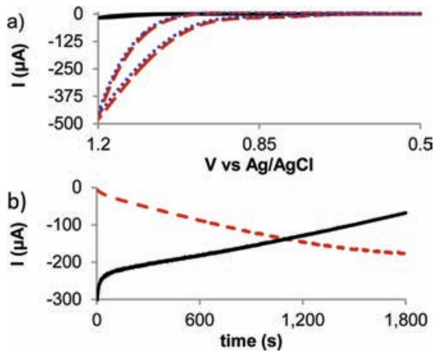

Figure 2. (a) Cyclic voltammograms of 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ immediately after dissolution (black solid curve), after 30 min of electrolysis at 1.1 V vs Ag/AgCl (red dashed curve) and of the catalytic film formed during the 30 min of electrolysis after the working electrode was washed with water and placed into a pure sodium phosphate electrolyte (i.e., no added $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$) (blue dotted curve). The scan rate was 100 mV/s. (b) Controlled-potential electrolysis of 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (red dashed curve) and of the catalytic CoO_x film in sodium phosphate electrolyte without added POM (black solid curve). Electrolysis experiments were stirred at 600 rpm; the supporting electrolyte was 0.1 M sodium phosphate buffer (pH 8.0) in all of the experiments.

The CoO_x film could also be deposited onto a transparent indium tin oxide (ITO) electrode under the conditions given above. UV–vis of the resultant CoO_x film on ITO showed no evidence of the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ POM (Figure S6). Since $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ could not be observed in the catalytic film by EDX or UV–vis spectroscopy and the catalytic film was more active than the initial $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solution, the evidence again implies that CoO_x and not $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ is the dominant catalyst. A caveat here is that because ITO was used as an electrode, the system is not rigorously comparable to the studies using glassy carbon.

An important question is how is the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ transformed into CoO_x under the reaction conditions? Is the POM converted directly to the CoO_x catalyst, or does it release freely diffusing Co(II) [or its functional equivalent, denoted apparent Co(II), wide infra], which in turn is transformed/oxidized into the heterogeneous catalyst? Relevant here is the fact that the Co(II) dissociation constants of several cobalt-substituted POMs have been measured by Contant[11] and Hamlaoui et al.[12] and found to be both nonzero and in a range that could yield catalytically viable amounts of Co(II), vide infra. Specifically, the dissociative equilibrium constants for Co(II)-substituted $\alpha_1\text{-}P_2W_{17}O_{61}{}^{10-}$, $\alpha_2\text{-}P_2W_{17}O_{61}{}^{10-}$, and $\alpha\text{-}PW_{11}O_{39}{}^{7-}$ are approximately $10^{-7.5}$, $10^{-5.5}$ and $10^{-4.5}$ in 1 M $LiClO_4$[11] and $10^{-5.6}$ in 1 M $NaClO_4$ for $\alpha_2\text{-}P_2W_{17}O_{61}{}^{10-}$.[12] This in turn means that leaching of Co(II) from the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ POM in aqueous solution is a plausible and arguably the simplest (i.e., Ockham's razor) *hypothesis* en route to the observed CoO_x.

Hence, the solution stability of $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ was determined next by UV–vis spectroscopy and electrochemical methods. Upon dissolution of 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ in 0.1 M sodium phosphate buffer at pH 8.0 in air, the absorbance band at 580 nm decreased by 4.3 ± 0.6%

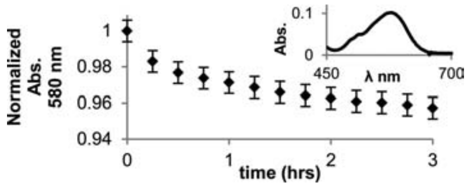

Figure 3. Normalized peak absorbance at 580 nm for a 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solution in 0.1 M sodium phosphate solution (pH 8.0). Inset: absorption spectrum ~1 min after dissolution of the POM, which is defined as $t = 0$. The decrease over 3 h was 4.3 ± 0.6%.

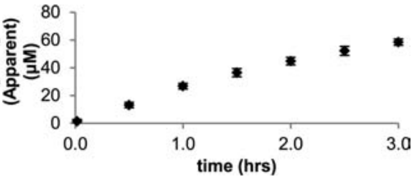

Figure 4. Apparent $[Co^{2+}]$ in $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solution vs time based on the anodic current at 1.1 V for a 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solution (Figure 1) and the $[Co^{2+}]$ calibration curve (Figure S8). The supporting electrolyte was 0.1 M sodium phosphate (pH 8.0).

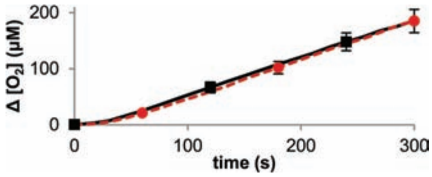

Figure 5. Changes in O_2 solution concentration ($\Delta[O_2] = [O_2]_t - [O_2]_{t=0}$) produced during controlled-potential electrolysis at 1.1 V for a 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solution aged for 3 h (red ●) and a 58 μM $Co(NO_3)_2$ solution (■). The supporting electrolyte was 0.1 M sodium phosphate buffer (pH 8.0). $[O_2]$ was recorded every 15 s; for clarity, only the points at 60 s intervals are displayed. The solid and dashed lines are provided solely as guides for the eye (i.e., no curve fitting was done). The glassy carbon working electrode ($A = 1.92 \pm 0.07$ cm^2) and Ag/AgCl reference electrode were separated from the Pt auxiliary electrode via a fine frit; the working compartment was stirred at 600 rpm. The short induction period at the start of the experiment is due to both a slow response of the O_2 sensor and initially slower water oxidation (the CoO_x film activity increases as more material is electrodeposited).

over the course of a 3 h period (Figure 3). This decrease in the absorbance corresponds to degradation of ca. 21.5 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [≤86 μM Co(II), or ~64 μM Co(II) for $x = 3$; Scheme 1 and Figure S11).[13]

In contrast, the aforementioned 2010 *Science* paper reported that 0.75–1.0 mM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solutions did not vary with age or pH when the electrolyte was sodium acetate (50 mM, pH 3.5, 1 day), sodium phosphate (11 mM, pH 8.0, 1 month), or sodium borate (50 mM, pH 9.0, 1 month).[6] In a separate study, Ohlin et al.[14] found that decreasing the pH from 7.2 to 4.0 in 1.1 mM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solutions yielded a decrease in the 580 nm absorption band and an increase in the absorption below ~475 nm; however, Co(II) EPR measurements did not detect any POM decomposition over this pH range, albeit over an unspecified time scale. In short, and as is already known,[15] these types of inorganic POM ligands are *not* immune to hydrolytic degradation under acidic ($pH < 4$) or basic ($pH \geq 8$) conditions. Indeed, the expected hydrolytic instability of $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, with which we have worked before,[16] was one primary reason we were drawn to examine the question "what is the true WOC?" for this cobalt POM.

In order to determine whether cobalt was being released by $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ in pH 8.0 solutions, the apparent $[Co^{2+}]$ was determined via catalytic oxidative linear-sweep voltammetry [the apparent Co(II) was determined, since we do not know unequivocally whether it is just aqueous Co^{2+}, a Co(II)–POM fragment, or conceivably some other Co(II)-containing species; see below). A Co(II) calibration curve was constructed using $Co(NO_3)_2$ as a standard precursor for a CoO_x catalyst (Figure S8); linear-sweep voltammetry of $Co(NO_3)_2$ solutions showed that the oxidation wave current was directly proportional to $[Co^{2+}]$ over the range ~1.0–1.1 V; the resultant calibration curve was linear over the concentration range and scan rates used herein ($[Co^{2+}] \leq 75$ μM; 20 mV/s ≤ scan rate ≤ 100 mV/s). Noteworthy here is the fact that the oxidation wave (~1.0 V onset vs Ag/AgCl) in these scans corresponds to catalytic water oxidation by the CoO_x film, as reported previously by Nocera and co-workers and as reproduced herein, vide supra.[4a]

Using the authentic $[Co^{2+}]$ calibration curve in Figure S8 in conjunction with linear-sweep voltammetry of $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (Figure 1) allowed calculation of the apparent $[Co^{2+}]$-versus-time curve for a 500 μM cobalt POM solution (Figure 4). Over the course of 3 h, the calculated apparent $[Co^{2+}]$ increased from 1 ± 1 to 58 ± 2 μM. In order to verify that the oxidation wave was caused by a Co(II) species, the apparent $[Co^{2+}]$ was confirmed by a modified procedure for cathodic-stripping voltammetry reported by Krolicka et al.[17] (experimental details are given in the SI); this complementary method showed that after 3 h of aging, an initially 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solution contained an apparent $[Co^{2+}]$ of 56 ± 2 μM. The excellent agreement between the apparent $[Co^{2+}]$ values obtained from the two methods, along with the observed decrease in the 580 nm absorption band of the POM, provides compelling evidence that the starting $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ slowly degrades in 0.1 M phosphate buffer solution at pH 8.0.

Direct comparison of the catalytic activities of authentic $Co(NO_3)_2$ and $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solutions was made next in order to quantify how much of the catalytic water oxidation reaction could be attributed to the Co(II) or its functional equivalent available in aged cobalt POM solutions. Significantly, and to verify that WOC activity was being measured, the WOC product O_2 was measured in the solution during catalytic controlled-potential electrolysis by using a fluorescence-based O_2 sensor (Neofox/FOXY phase-measurement system).

As shown in Figure 5, the O_2 generated over a 5 min period during controlled-potential electrolysis (1.1 V vs Ag/AgCl) of a 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solution aged for 3 h *is identical within experimental error to the O_2 generated by the amount of leached, apparent Co(II) independently determined above, that is, by a 58 μM $Co(NO_3)_2$ solution (1.09 ± 0.13 vs 1.10 ± 0.12 μmol of O_2)*. The theoretical O_2 yields (i.e., the moles of electrons passed during electrolysis divided by the stoichiometric factor of 4) are 1.05 ± 0.14 and 1.06 ± 0.03 μmol of O_2 for solutions containing 500 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and 58 μM $Co(NO_3)_2$, respectively. This result indicates that the low (58 μM) apparent concentrations of Co(II) present in $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solutions in pH 8.0 sodium phosphate buffer *quantitatively account for all of the observed catalytic water oxidation activity within the stated ±12% experimental error.*

In conclusion, we have provided four main lines of compelling evidence that *under the conditions used in this study*, the

Co-containing POM in $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ solutions at pH 8.0 partially decomposes to release Co(II) or its functional equivalent, which in turn forms a well-precedented active CoO_x WOC under oxidizing conditions. Our results reveal the important insight that $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ is *not* the most active WOC under the conditions examined herein.[18] Our results are also consistent with a growing trend in the literature that claims of water oxidation by homogeneous molecular complexes must attempt to disprove the often facile catalysis by what can be low levels of the corresponding known M_xO_y WOCs.[19] Such mechanistic studies are central to a better understanding and rational improvement of both the present, as well as all other, WOCs since catalyst activity, stability, selectivity, isolability, and regeneration of these—indeed of all—catalysts depend on the identity of the true catalyst.[20]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, additional data, and additional citations for ref 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) The 2010 *Science* paper reported that when $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ was combined with the sacrificial oxidant tris(2,2′-bipyridyl)ruthenium(III) in pH 8.0 sodium phosphate solution (0.03 M), rapid water oxidation to O_2 was observed at rates of up to 5 s^{-1} [mol of O_2 (mol of catalyst)$^{-1}$ s^{-1}], and turnover numbers (TONs) of $\sim 10^3$ (total mol of O_2/mol of POM) were reported. See: Yin, Q.; Tan, J. M.; Besson, C.; Geletii, Y. V.; Musaev, D. G.; Kuznetsov, A. E.; Luo, Z.; Hardcastle, K. I.; Hill, C. L. *Science* **2010**, *328*, 342.

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(9) In contrast to the studies of Gao et al.,[8] Balula et al. found that $[(C_4H_9)N]_7H_3[Co_4(H_2O)_2(PW_9O_{34})_2]$ in acetonitrile showed sequential one-electron oxidation waves at 0.811 and 1.123 V vs Ag/Ag^+ at a Pt electrode with 0.1 M $[N(C_4H_9)_4]ClO_4$ electrolyte. See: Balula, M. S.; Gamelas, J. A.; Carapuca, H. M.; Cavaleiro, A. M. V.; Schlindwein, W. *Eur. J. Inorg. Chem.* **2004**, 619.

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(18) We emphasize that the present studies have not examined either the system or the precise conditions utilized in the 2010 *Science* paper, i.e., water oxidation beginning with 3.2 μM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ using tris(2,2′-bipyridyl)ruthenium(III) as an oxidant in 0.03 M sodium phosphate (pH 8).[6] In addition, further study of the (slightly) different conditions in the present and prior study is needed before one could have any firm basis for believing that the instability of the cobalt POM observed herein discredits the central claim made in ref 6 that the POM is stable at pH 8 under their specific conditions.

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