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Journal

ACS Catalysis, 10(3)

ISSN

2155-5435

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Publication Date

2020-02-07

DOI

10.1021/acscatal.9b03281

Peer reviewed

**Observation of O-O Bond Forming Step of Molecular Co₄O₄ Cubane Catalyst for Water
Oxidation by Rapid-Scan FT-IR Spectroscopy**

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(ACS Catal., in press)

Abstract

Monitoring of water oxidation by the established Co cubane catalyst $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4$ (abbrev. Co_4O_4 , OAc = acetate, py = pyridine) by time-resolved rapid-scan ATR FT-IR spectroscopy revealed the O-O bond forming intermediate by its O-O stretch mode at 833 cm^{-1} . The catalysis was either driven in alkaline solution by a visible light sensitizer, or in hydroxide (OH^-) containing acetonitrile solution using the one-electron oxidized cubane as the sole source of charge. The μ -peroxido structure of the intermediate was established by ^{18}O isotopic labeling, and its catalytic relevancy and role in the O_2 evolving cycle revealed by the kinetic relationship with decreasing cubium ($[\text{Co}_4\text{O}_4]^+$) and recovery of Co_4O_4 complex.

Keywords: Water oxidation catalysis, cobalt oxide, cubane, time-resolved FT-IR, peroxo intermediate, O-O bond formation

1. Introduction

Detection and structural identification of transient intermediates of water oxidation at metal oxide catalyst surfaces provides the most direct mechanistic insight for this essential reaction of artificial photosystems. In situ infrared and Raman spectroscopy reveal the molecular structure of surface intermediates under photo- or electrocatalytic conditions, and temporal resolution allows elucidation of their kinetic behavior and, therefore, the role in the catalytic cycle. Using these methods, surface intermediates of several important O₂ evolving metal oxide catalysts have recently been discovered. These include Co^{IV}=O and superoxido intermediates of Co₃O₄ nanocrystals by time-resolved photosensitized ATR (attenuated total reflection) FT-IR spectroscopy,^{1,2} Fe^{IV}=O³ and superoxido intermediates of hematite films by ATR FT-IR spectrophotoelectrochemistry⁴ or of Ni oxyhydroxide by surface enhanced Raman spectroscopy.⁵ Furthermore, hydroperoxide species have been detected on Ir oxide nanoparticles by rapid-scan FT-IR,⁶ peroxido intermediates on titania nanoparticle by infrared spectroelectrochemistry,⁷ and transient titanyl species by ultrafast infrared and optical spectroscopy at SrTiO₃ crystal surfaces.⁸ Direct identification of the molecular structure of these intermediates not only revealed specific reaction steps on the catalyst surface, but is beginning to shed light on how hole charges transferred to the metal oxide drive the multi-electron catalytic cycle on its surface.⁹⁻¹¹ Recent in situ infrared monitoring of di-oxo Fe^{VI} surface intermediate of NiFe layered double hydroxide in non-aqueous media or ex situ infrared detection of Mn^{VII} oxo on a Mn oxide catalyst surface add to the growing variety of species monitored upon water oxidation catalysis at metal oxides.^{12,13}

Among Earth abundant metal oxides catalysts for water oxidation, Co oxides play a prominent role in the most stable Co₃O₄ spinel structure^{14,15} and in the form of high surface area

amorphous electrodeposits.¹⁶ For the latter, cobaltate clusters are thought to be the catalytically active structures, which led to particular interest in oxygen evolving molecular analogues featuring a Co₄O₄ cubane core.¹⁷⁻³¹ Of these, the complex Co₄O₄(OAc)₄(py)₄ (OAc = acetate, py = pyridine, abbreviated Co₄O₄) (Scheme 1) was found by the groups of Dismukes and Tilley to be a remarkably active water oxidation catalyst^{17,18} and is at this point the most extensively studied among the various molecular Co cubane complexes.^{17-24, 26-29} This includes demonstration of activity upon immobilization on a Nafion-coated fluorine-tin-oxide electrode or hematite photoanode,³⁰ and in confined environments such as metal-organic frameworks.²⁴ Co₄O₄ evolves oxygen in alkaline solution, and the catalytic cycle can be driven by the one-electron oxidized [Co₄O₄]⁺ species as the sole oxidant (1.25 V vs. NHE), as was demonstrated by UV-visible, EPR and NMR monitoring.^{17,18} [Co₄O₄]⁺ was obtained in isolated form and spectroscopically characterized by EPR, X-ray absorption spectroscopy, and resonant inelastic X-ray scattering.^{19,22} A [Co₄O₄(OH₂)]⁺ complex and its deprotonated form emerging from replacement of acetate by H₂O at a [Co₄O₄]⁺ Co center were identified by NMR.¹⁸ ¹⁸O isotopic labeling studies revealed that only terminally coordinated hydroxide ligands, not bridging oxygens, of the cubane core are incorporated into the O₂ product,^{17,18} and kinetic analysis of stopped-flow UV-visible measurements indicate that O-O bond formation occurs upon two-electron oxidation of the catalyst.¹⁸ A two-electron oxidized Co₄O₄ cubane species featuring a pair of adjacent Co^{IV} centers was observed by X-ray absorption and near infrared spectroscopy in acetonitrile solution under non-catalytic conditions.²³ While DFT studies of the cubane water oxidation mechanism conducted by several groups consistently predict the formation of bridging^{21,26,27} or side-on peroxido intermediates,^{17,28,29} experimental detection of an O-O bond forming intermediate has remained elusive.

In this work, we report the detection of a peroxido intermediate of the Co_4O_4 cubane catalyst by rapid-scan ATR FT-IR spectroscopy upon visible light sensitized reaction in alkaline aqueous solution as well as $[\text{Co}_4\text{O}_4]^+$ driven (dark) catalysis in NaOH containing acetonitrile.

Scheme 1. Structure of $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4$.

2. Experimental Section

2.1 Synthetic Materials and Methods

All chemicals were purchased from Sigma-Aldrich with purity exceeding 98% and used as received, unless noted otherwise. The $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4$ cubane compound (abbrev. Co_4O_4 , Scheme 1) was synthesized according to a well-established protocol.³² In brief, cobalt(II) nitrate hexahydrate (5.8 g, 20 mmol) and sodium acetate trihydrate (5.4 g, 40 mmol) were dissolved in 60 mL of methanol and pyridine (1.6 mL, 40 mmol) was added. The solution was heated to dissolve all components, and hydrogen peroxide (30% w/w in H_2O , 6 mL) was dropwise added. After refluxing for 3 h, an olive-green solution was obtained which was dried with anhydrous MgSO_4 , and the solvent removed with a vacuum rotary evaporator at 40°C. The crude product was dissolved in 100 mL dichloromethane, and insoluble impurities were removed by filtration. The filtrate was concentrated to 5 mL, 0.5 mL methanol was added, loaded onto a silica column, and eluted with 10% methanol in dichloromethane.²⁰ The first fraction was collected and dried

with vacuum rotary evaporator at 40°C, resulting in dark-green solid. Typically, repetition of the above purification process with silica column was required to obtain a pure Co₄O₄ product according to ¹H NMR (Figure S1), in agreement with literature.³²

[Co₄O₄(OAc)₄(py)₄]PF₆ and [Co₄O₄(OAc)₄(py)₄]ClO₄ were synthesized by dissolving Co₄O₄(OAc)₄(py)₄ (255 mg, 0.3 mmol) in 10 mL of water. Ceric ammonium nitrate (246.6 mg, 0.45 mmol) was added and the resulting solution was stirred for 10 min. Sodium perchlorate (40 mg, 0.33 mmol) or sodium hexafluorophosphate (55 mg, 0.33 mmol) was added to the reaction mixture to produce a black precipitate of [Co₄O₄]ClO₄ or [Co₄O₄]PF₆. The precipitate was extracted with 100 mL CH₂Cl₂, washed three times with 20 mL ice water, and dried with anhydrous MgSO₄. The final product [Co₄O₄]ClO₄ or [Co₄O₄]PF₆ was obtained by removing the solvent with vacuum rotary evaporator at 0°C and stored at -40 °C. The ¹H NMR spectrum shown in Figure S2 is in perfect agreement with literature reports.²⁰

2.2 Monitoring of Catalysis

Recording of O₂ evolution by Co₄O₄ in aqueous solution was conducted by visible light photosensitization of the catalyst using the [Ru(bpy)₃]²⁺/S₂O₈²⁻ light absorber/electron acceptor system (bpy = 2,2'-bipyridyl). An aqueous solution (1.5 mL) of 16 mM Co₄O₄, 5.3 mM [Ru(bpy)₃]²⁺, 8.8 mM NaS₂O₈ and 20 mM NaOH was prepared in H₂O or D₂O and deoxygenated by bubbling nitrogen gas for 10 minutes. Photolysis was conducted by irradiation of the solution with Ar ion laser emission at 476 nm laser (Coherent model Innova 90-6, 320 mW) with beam size expanded to 10 mm. Oxygen was monitored by a calibrated Clark electrode (Hansatech, Oxygraph system) composed of a platinum cathode and an Ag/AgCl anode. For operating the Clark electrode, 0.1 M KCl aqueous solution was used as electrolyte providing a

conductive path by a small piece of paper wetted with 0.1M KCl solution to bridge the platinum cathode with Ag/AgCl anode. The cathode and anode were covered by a thin, O₂ permeable polytetrafluoroethylene (PTFE) membrane to separate the Clark electrode section from the O₂ evolving catalyst solution (cathode: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{H}_2\text{O}$; anode: $4\text{Ag} + 4\text{Cl}^- \rightarrow 4\text{AgCl} + 4\text{e}^-$). For oxygen evolution measurements by dark reaction of one-electron oxidized [Co₄O₄]⁺ species, 1.4 ml of [Co₄O₄]ClO₄ solution (3.3 mM) was prepared in CH₃CN and deoxygenated by bubbling nitrogen gas for 10 minutes. 180 μL of deoxygenated aqueous NaOH solution (25 mM) was added to the [Co₄O₄]ClO₄ solution by syringe and O₂ evolution monitored by Clark electrode measurements.

Rapid-scan FT-IR monitoring using the attenuated total reflection (ATR) configuration was conducted using a Bruker model Vertex 80 spectrometer equipped with a 25 μm bandgap LN₂ cooled HgCdTe detector and a ten-reflection diamond ATR accessory Harrick model ConcentrateIR2. The spectral resolution was 4 cm^{-1} , and data were recorded in double-sided/forward-backward mode with mirror velocity of 160 kHz. For time-resolved spectroscopy of visible light sensitized reactions using the [Ru(bpy)₃]²⁺ sensitizer, Ar ion laser emission at 476 nm was used and light pulses were generated by intercepting the laser beam by a mechanical shutter with variable opening times from 0.3 ms to continuous (Vincent Associates model Uniblitz controlled by a BNC pulse/delay generator model 565). The opening of the shutter was triggered by the start of the forward motion of the interferometer mirror for precise synchronization of the FT-IR data acquisition with the initiation of photochemical reaction. The size of the laser beam was adjusted to match the 3 mm size of the diamond ATR element. A home-made cylindrical Teflon cell for controlling the gas phase of the head space above the liquid sample was installed and sealed against the ATR support plate by an O ring, as shown in

Scheme S1. The cell featured gas line connections for supply of CO₂ or N₂ (1 atm). A quartz window at the top of the cell provided entry of the photolysis laser beam normal to the ATR plate.

To avoid ambient light-induced photochemical reactions, the samples containing all the required components for photochemical water oxidation were prepared in two separate solutions and mixed just before the start of a photolysis experiment. One solution was composed of Co₄O₄ and [Ru(bpy)]₃Cl₂, the other consisted of persulfate and sodium hydroxide. In a typical measurement, 15 µL of each solution was placed onto the diamond ATR element and the Teflon cell installed immediately afterwards while avoiding exposure of the sample to room light. Prior to photolysis, the cell was swept by nitrogen or argon gas for 2-3 minutes to remove any residual oxygen. The rapid-scan FT-IR protocol consisted of 500 scans for background followed by opening of the shutter for a photolysis period of 6 s during which 10 interferograms were recorded and stored, each consisting of the average of 10 double sided interferograms of 60 ms duration. During the dark period following termination of the laser pulse, 190 subsequent spectra were recorded over a period of 114 s. The timing of each spectrum is represented by its midpoint (300 ms, 900 ms, 1500 ms,, 119700 ms, as graphically illustrated in Scheme S2).

For FT-IR monitoring of water oxidation catalysis initiated under dark conditions by one-electron oxidized catalyst species ([Co₄O₄]⁺) in wet acetonitrile (without deoxygenation), spectra were recorded with 40 kHz mirror velocity and 4 cm⁻¹ spectral resolution. After recording 35 spectra (each consisting of the average of 5 double sided interferograms of 220 ms duration) of [Co₄O₄]PF₆ or [Co₄O₄]ClO₄ in 45 µL CH₃CN solution (20 mM) over a period of 38.5 s, 5 µL of 0.5 M NaOD in D₂O/CH₃CN = 1/9 solution were added and recording of 260 spectra resumed after a waiting period for 5 s (protocol illustrated in Scheme S3). For experiments with H₂¹⁸O

(Icon, 97.6% ^{18}O), 5 μL 0.5 M Na^{18}OH in $\text{H}_2^{18}\text{O}/\text{CH}_3\text{CN} = 1/9$ solution was added to initiate catalysis. A similar protocol was used to monitor the spontaneous dark reaction after adding NaOD to $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$ photosensitized Co_4O_4 solution in neutral D_2O . Prior to initiating FT-IR spectra collection, the solution was irradiated with 476 nm laser light for 12 s to accumulate $[\text{Co}_4\text{O}_4]^+$ in the deoxygenated cell. Subsequently the cell was opened for adding NaOD to initiate water oxidation catalysis.

^1H NMR spectra were recorded on a Bruker Biospin Advance II 500 MHz High Performance Spectrometer.

3. Results and Discussion

Time-resolved rapid-scan FT-IR spectroscopy of the one-electron oxidation catalyst and formation of peroxide intermediate and its kinetics are presented and discussed in turn.

3.1 Monitoring of One-Electron Cubane Intermediate

To verify the activity of the Co_4O_4 catalyst and estimate the product buildup upon visible light photosensitization using the $[\text{Ru}(\text{bpy})_3]^{2+}$ -persulfate system, electrochemical measurements of O_2 yields were conducted with a calibrated Clark electrode by illuminating aqueous solutions of Co_4O_4 catalyst and photosensitizer at pH 12.3 with a 476 nm laser pulse of several s duration. As shown in Figure 1 and Figure S3, O_2 yields are linear with respect to photolysis pulse duration at constant laser intensity and negligible depletion of sacrificial $\text{S}_2\text{O}_8^{2-}$ electron acceptor, and no reaction is observed at neutral pH, as expected based on previous reports³³ (although some earlier studies observed water oxidation activity at neutral pH,^{34,35} subsequent investigations

revealed cobalt ion impurity as the active species²⁰). Experiments were conducted in D₂O since it provides a wider spectral window for infrared monitoring of catalytic species in aqueous solution below 800 cm⁻¹ compared to H₂O.⁶ The amount of O₂ generated for pulse durations of a few s indicated that corresponding concentrations of catalytic intermediates should be adequate for the detection of transient intermediates with infrared bands of moderate intensity by the ATR FT-IR method.

Table 1. IR frequencies of Co₄O₄ and [Co₄O₄]⁺ in CH₃CN or D₂O.

Co ₄ O ₄ in CH ₃ CN	[Co ₄ O ₄]PF ₆ in CH ₃ CN	Co ₄ O ₄ in D ₂ O	[Co ₄ O ₄] ⁺ in D ₂ O
1607	1609	1611	1610
1551		1579	
1534		1534	
		1518	
	1497	1502(sh)	1502(sh)
1484	1486	1488	1488
1453	1451	1452	1452
1413	1419	1419	1415
1340	1353	1350	1358
1213	1213	1215	1215
1154	1156	1156	1160
1073	1070	1072	1072
1047	1049	1050	1048
1020	1020	1022	1022
	880		
	848		
761	761	762	763
	702	703	702
696		696	
	692		692
646	652	*	*
633	631	*	*

*Frequencies below 650 cm⁻¹ are blocked by D₂O solvent absorption. Bands in grey areas correspond to highlighted spectral regions in Figure 2a,b.

Figure 1. Electrochemical monitoring of O₂ evolution by photosensitization of Co₄O₄ in aqueous solution. Red trace: 476 nm (320 mW) illumination of D₂O solution at pH 12.3 containing Co₄O₄ catalyst and sensitizer with 3 s, 6 s, and 30 s pulse. Grey background indicates photolysis period (Co₄O₄, 16 mM; [Ru(bpy)₃]²⁺, 5 mM; S₂O₈²⁻, 20 mM; NaOH: 20 mM). Blue trace: Same experiment at neutral pH.

Results of photosensitized rapid-scan FT-IR experiments using 476 nm light pulses of 6 s duration and identical catalyst and sensitizer concentrations in D₂O as used for the Clark electrode tests are presented in Figure 2. Panel 2a shows spectral traces in the 1700 – 600 cm⁻¹ region (omitting 1300-900 cm⁻¹, which is included in Figure S4) at 2.7 and 5.7 s during excitation of the [Ru(bpy)₃]²⁺ sensitizer solution at pH 7 (blue background) followed by 4 time slices during the subsequent dark period of 114 s. The traces shown are the average of 6 rapid-scan experiments, each with a fresh sample. For comparison, static spectra of the Co₄O₄ catalyst and [Co₄O₄]⁺PF₆⁻ one-electron oxidized compound in CH₃CN are displayed in the top two traces of Figure 2a (the latter compound is insoluble in water) omitting the 1300-900 cm⁻¹ region; corresponding complete infrared spectra are shown in Figure S5. The set of infrared bands of the two compounds in D₂O and CH₃CN is presented in Table 1.

Figure 2. Rapid-scan FT-IR monitoring of photosensitization of Co_4O_4 catalyst in neutral and basic deoxygenated D_2O solution. (a) Spectral time slices in neutral D_2O (Co_4O_4 , 16 mM; $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 5 mM; $\text{S}_2\text{O}_8^{2-}$, 20 mM) referenced against spectrum before photolysis. Spectra represent average of 9 independent experiments. Traces with blue background were recorded during the 6 s photolysis pulse period (476 nm, 600 mW). Absorption bands of $\text{Ru}(\text{bpy})_3$ sensitizer and $\text{S}_2\text{O}_8^{2-}$ acceptor were subtracted from the spectra for clarity. Static spectra of Co_4O_4 and $[\text{Co}_4\text{O}_4]\text{PF}_6$ compounds in CH_3CN solution are shown for reference (top traces). (b) Photolysis using identical sample in D_2O at pH 12.3 (20 mM NaOH). Spectra represent average of 6 independent experiments. (c) Kinetic behavior of representative Co_4O_4 and $[\text{Co}_4\text{O}_4]^+$ bands at neutral pH during photolysis (grey background) and after termination of the pulse. Error bars indicate $\frac{1}{2}$ peak-to-peak noise. (d) Kinetics of bands of the same species of at pH 12.3.

Prominent spectral changes during the 6 s photosensitization period associated with ligand as well as Co_4O_4 cubane modes are the decrease of the broad asymmetric O=C-O stretch mode of Co_4O_4 acetate ligand at 1534 cm^{-1} typical for bridging acetate ligand^{32,36} under concurrent growth of a strong $[\text{Co}_4\text{O}_4]^+$ band at 1452 cm^{-1} . An acetate ligand band of Co_4O_4 at

1350 cm^{-1} decreases while a corresponding ligand band of $[\text{Co}_4\text{O}_4]^+$ at 1358 cm^{-1} grows in (these are the peak positions as they appear in the difference spectra of Figure 2, which are slightly shifted from the maxima of the pure compounds due to spectral overlap). According to NMR investigations by Tilley, conversion of a bridging acetate ligand of the $[\text{Co}_4\text{O}_4]^+$ core to monodentate configuration is accompanied at neutral pH by coordination of a water molecule at the vacated Co site, $[\text{Co}_4\text{O}_4(\text{OH}_2)]^+$.¹⁸ While the observed infrared spectral changes of the acetate ligand modes in the 1600-1300 cm^{-1} region are consistent with bidentate to monodentate conversion, these spectral changes are always observed upon oxidation of the Co_4O_4 cubane core to $[\text{Co}_4\text{O}_4]^+$. Most relevant for monitoring change of catalyst oxidation state is the observed decrease of the intense cubane breathing mode of Co_4O_4 at 696 cm^{-1} (with shoulder at 703 cm^{-1})^{32,37} accompanied by growth of the corresponding Co-O stretch doublet of $[\text{Co}_4\text{O}_4]^+$ at 702 and 692 cm^{-1} , providing direct evidence for the formation of the one-electron oxidized cubane complex. After termination of the photolysis pulse, these spectral changes persist over the observed dark period of nearly 2 min with minimal decay as shown in the kinetic curves of Figure 2c (all curves are normalized to the same initial amplitude to facilitate comparison). We conclude that at neutral pH, visible light sensitized hole transfer to Co_4O_4 results in long-lived one-electron oxidation of the cubane core that does not induce further reaction, consistent with the absence of O_2 evolution by Clark electrode measurements and in agreement with previous findings of other labs.^{20,33} No further oxidation of Co_4O_4 beyond the one-electron intermediate $[\text{Co}_4\text{O}_4]^+$ by $[\text{Ru}(\text{bpy})_3]^{3+}$ (1.26 V vs. NHE)³⁸ was observed in either neutral aqueous or CH_3CN solution as shown by FT-IR spectroscopy of the cubane stretch modes (Figure S6).

By contrast, when conducting the rapid-scan FT-IR experiment in alkaline solution at pH 12.3 under otherwise identical conditions, the spectral changes following the 6 s

photosensitization pulse reversed completely during the 114 s dark period (Figure 2b). The spectra shown are the average of 9 rapid-scan experiments. The curves plotted in Figure 2d present the kinetics of $[\text{Co}_4\text{O}_4]^+$ loss under concurrent recovery of Co_4O_4 . The reduced buildup of $[\text{Co}_4\text{O}_4]^+$ compared to experiments at neutral pH indicates that one-electron oxidized cubane species are already beginning to be consumed by catalysis during the 6 s photolysis period. Because the Clark electrode result shows that photosensitization for a period of 6 s in alkaline solution results in O_2 evolution and, therefore, full catalytic cycles, the conversion of the catalyst from its one-electron oxidized $[\text{Co}_4\text{O}_4]^+$ state to the Co_4O_4 starting state observed by rapid-scan FT-IR is attributed to spontaneous water oxidation driven by the $[\text{Co}_4\text{O}_4]^+$ species (it is important to note that SO_4^- (sulfate radical anion) intermediate formed in the first electron transfer step of $\text{Ru}(\text{bpy})_3$ activation ($[\text{Ru}(\text{bpy})_3]^{2+*} + \text{S}_2\text{O}_8^{2-} \rightarrow [\text{Ru}(\text{bpy})_3]^{3+} + \text{SO}_4^- + \text{SO}_4^{2-}$), while potentially contributing to $[\text{Co}_4\text{O}_4]^+$ formation together with $[\text{Ru}(\text{bpy})_3]^{3+}$ during the 6 s photolysis period, cannot play any role in the spontaneous conversion of $[\text{Co}_4\text{O}_4]^+$ to Co_4O_4 under O_2 evolution after termination of the light pulse because SO_4^- is completely consumed within less than 100 microsec in the presence of mmol concentration of sensitizer molecules, as shown in previously by time-resolved optical spectroscopy).⁶ We find that the bleach of the acetate $\text{O}=\text{C}-\text{O}$ stretch mode at 1534 cm^{-1} at pH 12.3 (Figure 2b) is identical to the bleach at neutral pH (Figure 2a). Hence, the reacting Co_4O_4 species in the rapid-scan experiment at pH 12.3 possesses all four acetates even though some detachment of acetate ligands from Co_4O_4 occurs under alkaline conditions as shown in Figure S7b; however, no absorbance change is observed at 1558 cm^{-1} in Figure 2b where the intense asymmetric CO_2 stretch of free acetate occurs (Figure S7a). Therefore, the complete reversal of the catalyst to Co_4O_4 species featuring the intact ligand sphere of the starting structure (4 acetate and 4 pyridine ligands) strongly indicates that the

observed reacting catalyst does not completely detach acetate from the cubane core during the catalytic cycle, suggesting transient conversion of bi-dentate to monodentate acetate to allow for coordination of OH^- (Scheme 2). This result is in agreement with studies by Dismukes who reported reduction of $[\text{Co}_4\text{O}_4]^+$ by OH^- without net ligand loss based on UV-Vis and EPR monitoring.¹⁷

Scheme 2. Photochemical one-electron oxidation of Co_4O_4 and partial acetate ligand detachment.

3.2 Observation of O-O Bond Formation

As shown in Figure 2d, the kinetics of consumption of $[\text{Co}_4\text{O}_4]^+$ in alkaline solution as exhibited by the behavior of the 1358 and 1452 cm^{-1} bands is substantially faster than the recovery of the Co_4O_4 catalyst (growth of bands at 696, 1347, 1534 cm^{-1}), indicating that additional intermediates are formed on the early s time scale prior to release of O_2 . Therefore, we explored time-resolved FT-IR spectroscopy for the detection of subsequent catalytic intermediates. Initial attempts consisted of accumulation of $[\text{Co}_4\text{O}_4]^+$ intermediate in neutral aqueous solution using the $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$ visible light sensitization system followed by triggering of catalytic water oxidation by switching to alkaline pH. Figure 3 shows the result of such an experiment under electrochemical monitoring of O_2 (Clark electrode) and by rapid-scan FT-IR spectroscopy. For the Clark electrode experiment shown in Figure 3a, $[\text{Co}_4\text{O}_4]^+$ was accumulated by irradiating a 16 mM Co_4O_4 solution in H_2O at pH 7 containing 5 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 22 mM $\text{S}_2\text{O}_8^{2-}$ for 120 s at 476 nm (320 mW). No O_2 evolved until NaOH was added (100 μL of 0.1 M H_2O

solution), as expected. For FT-IR monitoring shown in Figure 3b (full spectrum shown in Figure S8), a D₂O solution of 80 mM Co₄O₄, 1.3 mM [Ru(bpy)₃]²⁺ and 22 mM S₂O₈²⁻ at pH 7 was illuminated for 12 s at 476 nm (600 mW) and spectra taken after adding NaOD (5 μL 0.5 M NaOD in D₂O). A broad band around 830 cm⁻¹ is observed in the first recorded time slice at 3 s after adding hydroxide, which vanishes within 20 s. Note that no SO₄⁻ intermediates are present during the reaction period shown in Figure 3b because this species is consumed by reaction with sensitizer molecules within less than 100 microsec after termination of the 12 s photosensitization period.

Figure 3. FT-IR spectroscopy of water oxidation catalysis initiated by adding NaOH to photosensitized Co₄O₄ aqueous solution. (a) O₂ evolution monitored by Clark electrode during photo-sensitization at neutral pH for accumulating [Co₄O₄]⁺ and upon addition of NaOH. (b) Time-resolved FT-IR difference spectra after adding NaOH to D₂O solution with [Co₄O₄]⁺ accumulated by photosensitization of Co₄O₄ solution at neutral pH. The Co₄O₄ bleach of the initial time slice at 3 s was computationally added to all subsequent time slices in order to

visualize the recovery of Co_4O_4 catalysts. Corresponding raw difference spectra are shown in Figure S6. Band intensities below 650 cm^{-1} are not reliable because of strong overlap with D_2O solvent absorption. The spectrum represents the result of a single experiment; no spectral averaging because manual addition of NaOD was on the same time scale as the reaction.

In order to increase the buildup of the new 830 cm^{-1} species, FT-IR experiments were conducted with chemically prepared $[\text{Co}_4\text{O}_4]\text{PF}_6$ or $[\text{Co}_4\text{O}_4]\text{ClO}_4$ compounds that enable higher starting concentrations of $[\text{Co}_4\text{O}_4]^+$. Because both $[\text{Co}_4\text{O}_4]\text{PF}_6$ and $[\text{Co}_4\text{O}_4]\text{ClO}_4$ are insoluble in neutral water, wet acetonitrile solution was used instead of neat D_2O as in the case of UV-Vis or EPR experiments reported by Dismukes.¹⁷ Clark electrode measurements were conducted to confirm oxygen evolution from $[\text{Co}_4\text{O}_4]\text{PF}_6$ and $[\text{Co}_4\text{O}_4]\text{ClO}_4$ acetonitrile solutions after adding NaOH (Figure S9), and FT-IR spectra of the solutions recorded after O_2 evolution to verify reduction to the Co_4O_4 starting catalyst (Figure S10). Figure 4a shows rapid-scan spectra recorded over a period of 4 min after adding $1\text{ }\mu\text{L}$ of 1.8 M NaOD in D_2O to $45\text{ }\mu\text{L}$ of $20\text{ mM } [\text{Co}_4\text{O}_4]\text{PF}_6$ in CH_3CN , resulting in solvent mixture of composition $2.2\text{ vol}\% \text{ D}_2\text{O}$, $97.8\text{ vol}\% \text{ CH}_3\text{CN}$. Full spectra including the $1300\text{-}1000\text{ cm}^{-1}$ region are shown in Figure S11. Since the 833 cm^{-1} band overlaps partially with a stretch mode of the PF_6^- counter ion at 848 cm^{-1} , spectral deconvolution shown in Figure 4b was required to determine the kinetic behavior. The similar intensity of the 833 cm^{-1} band when compared with $[\text{Co}_4\text{O}_4]^+$ absorptions ($880, 1020\text{ cm}^{-1}$) confirms that the observed intermediate is formed by a large fraction, if not all, reacting Co_4O_4 catalyst molecules. Note that the 848 cm^{-1} band is absent when conducting the same experiment using $[\text{ClO}_4]^-$ as counter ion of $[\text{Co}_4\text{O}_4]^+$, as shown in Figure S12. The temporal profile of the 833 cm^{-1} peak absorbance, presented in Figure 4d (red trace), indicates an intermediate formed by consumption of $[\text{Co}_4\text{O}_4]^+$ ($880, 1020\text{ cm}^{-1}$) with a rise time of around 10 s that decays under regeneration of Co_4O_4 catalyst ($696, 1534\text{ cm}^{-1}$). The kinetics for each species in Figure 4d was normalized according their maximum ΔA in the time period monitored. The 696 cm^{-1} cubane

stretch of the latter is shown on an expanded scale in Figure 4c, and its absorbance growth in Figure 4d (green trace). It should be added that there is a significant remaining concentration of peroxide intermediate at 250 s while the growth of recovered Co_4O_4 catalyst has already reached its asymptotic limit. The origin of this kinetic behavior is the fixed reservoir of $[\text{Co}_4\text{O}_4]^+$ species at the start of reaction; two $[\text{Co}_4\text{O}_4]^+$ species are consumed for each intermediate generated, and two more $[\text{Co}_4\text{O}_4]^+$ are needed to evolve O_2 and regenerate Co_4O_4 . As a result there is insufficient concentration of one-electron oxidized cubane for converting all intermediates to product.

Figure 4. FT-IR spectroscopy of water oxidation catalysis initiated by adding NaOH to $[\text{Co}_4\text{O}_4]\text{PF}_6$ acetonitrile solution. (a) Spectral time slices after adding 1 μL NaOH in D_2O to 45 μL $[\text{Co}_4\text{O}_4]\text{PF}_6$ dissolved in CH_3CN . The top traces show steady state spectra of Co_4O_4 and $[\text{Co}_4\text{O}_4]\text{PF}_6$ for reference. (b) Spectral deconvolution of band profile in the 870 – 810 cm^{-1} region. (c) Absorption at 700 cm^{-1} on expanded scale. (d) Kinetics of $[\text{Co}_4\text{O}_4]\text{PF}_6$ (1020, 880 cm^{-1}), catalytic intermediate (833 cm^{-1}), and Co_4O_4 catalyst (696 and 1534 cm^{-1}). The data points for each band were normalized with respect to the maximum ΔAbs value of the curves. Error bars represent $\frac{1}{2}$ peak-to-peak noise amplitude.

Figure 5. FT-IR spectra of water oxidation catalysis initiated by $[\text{Co}_4\text{O}_4]\text{ClO}_4$ in basic solution containing H_2^{18}O , H_2^{16}O , or D_2^{16}O . Trace (1): 5 μL 0.5 M NaOH in $\text{H}_2^{16}\text{O}/\text{CH}_3\text{CN} = 1/9$ added to 45 μL of 20 mM $[\text{Co}_4\text{O}_4]\text{ClO}_4$ in CH_3CN . Trace (2): 5 μL 0.5 M NaOD in $\text{D}_2^{16}\text{O}/\text{CH}_3\text{CN} = 1/9$ added to 45 μL of 20 mM $[\text{Co}_4\text{O}_4]\text{ClO}_4$ in CH_3CN . (Trace (3): Use of fully ^{18}O labeled water: 5 μL 0.5 M NaOH in $\text{H}_2^{18}\text{O}/\text{CH}_3\text{CN} = 1/9$ added to 45 μL of 20 mM $[\text{Co}_4\text{O}_4]\text{ClO}_4$ in CH_3CN . Trace (4): Use of partially ^{18}O labeled water: 10 μL 0.5 M NaOH in H_2^{18}O (70% $^{18}\text{O})/\text{CH}_3\text{CN} = 1/13$ added to 40 μL of 20 mM $[\text{Co}_4\text{O}_4]\text{ClO}_4$ in CH_3CN .

FT-IR experiments with ^{18}O labeled water allowed determination of the vibrational assignment of the 833 cm^{-1} mode. Because higher concentrations of the intermediate are obtained in experiments using $[\text{Co}_4\text{O}_4]^+$ compounds, and the band is free of overlaps in the case of $[\text{Co}_4\text{O}_4]\text{ClO}_4$, experiments with H_2^{18}O were conducted using the perchlorate compound. FT-IR trace (3) of Figure 5 with a band at 804 cm^{-1} represents the average of 260 spectra upon addition

of 5 μL 0.5 M NaOH in $\text{H}_2^{18}\text{O}/\text{CH}_3\text{CN} = 1/9$ to 45 μL of 20 mM $[\text{Co}_4\text{O}_4]\text{ClO}_4$ dissolved in CH_3CN . The spectrum is compared with the 833 cm^{-1} band observed upon reaction in the presence of D_2^{16}O after adding 5 μL 0.5 M NaOD in $\text{D}_2^{16}\text{O}/\text{CH}_3\text{CN} = 1/9$ to 45 μL of 20 mM $[\text{Co}_4\text{O}_4]\text{ClO}_4$ in CH_3CN (Figure 5, trace (2)), and the 834 cm^{-1} absorption when reacting in the presence of H_2^{16}O when adding 5 μL 0.5 M NaOH in $\text{H}_2^{16}\text{O}/\text{CH}_3\text{CN} = 1/9$ to 45 μL of 20 mM $[\text{Co}_4\text{O}_4]\text{ClO}_4$ in CH_3CN shown by trace (1). The absence of a pronounced D isotope shift indicates that the intermediate does not feature an OH group. The same FT-IR experiment was conducted with partially ^{18}O labeled water, adding 10 μL of 0.5 M NaOH in H_2^{18}O (70% ^{18}O)/ $\text{CH}_3\text{CN} = 1/13$ to 40 μL 20 mM $[\text{Co}_4\text{O}_4]\text{ClO}_4$ in CH_3CN . As can be seen in trace (4) of Figure 5, a new band appears at 819 cm^{-1} , which corresponds to half of the ^{18}O frequency shift of the 804 cm^{-1} band for the fully labeled intermediate and is therefore assigned to partially labeled $^{18}\text{O}^{16}\text{O}$ intermediate. The observed ^{18}O shift pattern is unique for a species featuring an O-O bond, and the frequency is in agreement with a CoOOCo μ -peroxido group of a dinuclear heteroaromatic compound.³⁹ Specifically, assignment to a $\text{Co}=\text{O}$ moiety, which for the partially labelled intermediate would only give rise to bands at 833 and 804 cm^{-1} is ruled out. In the absence of a Co_4O_4 cubane structure, the ^{18}O frequency shift for the fully labeled CoOOCo μ - O_2 moiety is 44 cm^{-1} .⁴⁰ The smaller, 30 cm^{-1} shift of the cubane peroxido intermediate observed here implies that the O-O stretch mode is coupled with $\text{Co}-^{16}\text{O}$ cubane stretch modes thereby diminishing the isotope shift of the normal mode absorbing at 834 cm^{-1} (as mentioned above, oxygens of the Co_4O_4 cubane core of the ^{16}O parent compound were shown not to exchange with water).^{17,18} ^{18}O isotope shifts of normal modes that are smaller than the ones expected for pure O-O bond modes are due to coupling with ^{16}O bond vibrations of similar frequency, which is an established phenomenon, e.g. the asymmetric stretch mode of partially labeled formate

(HC¹⁸O¹⁶O⁻).⁴¹ The observed intensity ratio of ¹⁸O-¹⁸O, ¹⁸O-¹⁶O and ¹⁶O-¹⁶O peroxido intermediate is 9.5:7.6:1.5, which agrees within the uncertainty reflected by the signal-to-noise with the theoretical ratio of 0.49:0.42:0.09. We conclude that the catalytic intermediate has a peroxido moiety.

Looking more broadly at possible peroxido structures, OO bond formation between two Co₄O₄ species is ruled out by the observation of efficient water oxidation of Co₄O₄ anchored as isolated molecule in a molecular organometallic framework,²⁴ and upon attachment on FTO or hematite electrode surfaces.³⁰ There are two conceivable cubane peroxido isomers, bridging and side-on. The infrared observations provide an argument for the bridging (Scheme 3) over side-on geometry. There is good agreement of the 833 cm⁻¹ band with bridging OO modes between two Co centers of organometallic or coordination complexes, which is in the lower frequency range of reported peroxido OO modes.^{40,42} Furthermore, literature indicates that OO modes of side-on η²-O₂ structures occur at tens to a hundred cm⁻¹ higher frequency than bridging μ-O₂ for peroxido as well as superoxido compounds. For example, Fe(II)(salen) superoxido complex has the η²-O₂ mode at 1104 cm⁻¹ compared to 1001 cm⁻¹ for the OO stretch of the bridging [(salen)Fe-OO-Fe(salen)] complex.⁴³ A likely reason is that the force constant of the OO bond is larger for the side-on than for the bridging configuration because coordination of the peroxide moiety to two low valent Fe centers (bridging) pushes more electron density into the antibonding OO orbital than a single Fe center (side-on), resulting in a weaker OO bond for the bridging geometry. However, these infrared spectroscopic arguments by themselves are not strong enough to rule out side-on geometry.

Smith *et al.*¹⁷ concluded that both O atoms are bound to one Co center (η²-O₂) based on two observations. According to NMR data only a negligible fraction of acetate ligands fully

dissociate from the Co_4O_4 core, in agreement with our rapid-scan FT-IR result. This is taken to indicate that cis geometry of adjacent Co-OH groups is not accessible thereby preventing formation of a bridging CoOOCo moiety.¹⁷ However, we do not agree with the conclusion that formation of bridging geometry requires full dissociation of an acetate ligand from the Co_4O_4 core. A switch from bidentate OAc to monodentate binding upon coordination of OH^- to Co is a facile process as evidenced by the fast reaction in alkaline solution. A second OH^- could bind in cis configuration at an adjacent Co center concurrently with OAc bidentate to monodentate conversion at that center, followed by exchange of OH and OAc coordination positions that would put OH in cis configuration. Furthermore, Nguyen et al.²¹ have proposed a mechanism for the formation of bridging peroxide intermediate that does not involve a cis $\text{Co}(\text{OH})\text{-O-Co}(\text{OH})$ pathway, but rather the formation of $\text{Co}^{\text{V}}=\text{O}$ intermediate; OH^- attack on the high valent $\text{Co}^{\text{V}}=\text{O}$ moiety is proposed to form a CoOOH intermediate whose outer O center coordinates to adjacent Co while displacing an acetate bond. The absence of a vibrational D isotope effect in our measurements (Figure 5) implies that the OO bridge is not protonated. Based on these findings, we do not consider the lack of complete acetate dissociation as precluding the formation of bridging peroxido geometry. The second observation of Smith *et al.*¹⁷ is the lack of water oxidation activity of a related cubane complex of composition $\text{Co}_4\text{O}_4(\text{OAc})_2(\text{bpy})_4$ that features only two acetate but four bidentate bipyridyl ligands. This complex has an obvious path to cis $\text{Co}(\text{OH})\text{OC}(\text{OH})$ formation, while $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4$ does not in the authors' opinion if there is no full acetate dissociation,¹⁷ yet the latter is an active water oxidation catalyst. Formation of geminal $\text{Co}(\text{OH})_2$ intermediate is proposed, leading to side-on peroxido geometry (geminal $\text{Co}(\text{OH})_2$ is not feasible in the case of the $\text{Co}_4\text{O}_4(\text{OAc})_2(\text{bpy})_4$ complex). While this explanation is consistent with the absence of reactivity of $\text{Co}_4\text{O}_4(\text{OAc})_2(\text{bpy})_4$ under the assumptions made,

there are other factors that might be responsible for the inactivity of this complex, of which two have been raised.¹⁷

Neither these nor the infrared spectroscopic findings allow a firm conclusion regarding bridging versus side-on structure, which awaits direct observation of transient 2-electron intermediates prior to O-O bond formation under catalytic conditions. Because there is no precedent for symmetric organo binuclear complex forming side-on peroxide OO geometry to our knowledge,⁴⁴ and in light of the points made above, our preferred assignment is the bridging OO structure.

Scheme 3. Role of intermediates observed by FT-IR spectroscopy in the catalytic cycle. Charge transfer between two encountering $[\text{Co}_4\text{O}_4]^+$ species (B) (right hand side of catalytic cycle) results in a doubly oxidized cubane species subject to nucleophilic attack by hydroxide to form the observed peroxide intermediate (C).

The catalytic scheme featuring the intermediates observed in the rapid-scan FT-IR experiments reported here is presented in Scheme 3. One-electron oxidized $[\text{Co}_4\text{O}_4]^+$ complexes (B), whether generated by visible light sensitized oxidation of Co_4O_4 (A) or by direct addition of $[\text{Co}_4\text{O}_4]^+\text{PF}_6^-$ or $[\text{Co}_4\text{O}_4]^+\text{ClO}_4^-$, react with another $[\text{Co}_4\text{O}_4]^+$ species and OH^- to form the μ -

peroxido intermediate (C). While structures have been proposed for two-electron oxidized cubane intermediates that react with OH^- , our preferred mechanism, or by internal O-O coupling to form the peroxido intermediate observed here,^{17,18,21,23} such species have not yet been spectroscopically observed under catalytic water oxidation conditions and are therefore not included in Scheme 3. Continued transfer of two holes by encounters of the $\mu\text{-O}_2$ intermediate (C) with $[\text{Co}_4\text{O}_4]^+$ results in elimination of O_2 under regeneration of the starting Co_4O_4 catalyst. Intermediates of the elementary steps of the conversion of transient (C) to O_2 and regenerated catalyst have yet to be uncovered. Nevertheless, we found that the quality of kinetic fits according to Scheme 3, shown Figure 4d as solid traces (DynaFit simulation program),⁴⁵ is only mildly sensitive to the detailed reaction pathway, such as sequential transfer of 2 holes involving superoxide formation vs. spontaneous elimination of O_2 from peroxide, or spontaneous elimination of O_2 from superoxide.

4. Conclusions

The formation of an O-O bonded intermediate of the $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4$ cubane catalyst for water oxidation has been uncovered under reaction conditions by rapid-scan ATR FT-IR spectroscopy and identified as a μ -peroxido species by its vibrational frequency and ^{18}O isotope shifts. The intermediate, predicted by DFT calculations of several groups, was observed by visible light photosensitization of the oxygen evolving cycle in alkaline aqueous solution, and by (dark) catalysis when adding hydroxide to an acetonitrile solution of the one-electron oxidized cubane. The kinetic behavior of the species obtained by time-resolved FT-IR monitoring confirms its role as a two-electron oxidation intermediate of the catalytic cycle. Knowledge of the peroxido

intermediate of a molecular Co cubane catalyst will guide future vibrational spectroscopic studies for elucidating details of the ligand dynamics and likely additional transient species formed in the catalytic cycle prior to O₂ release.

Supporting Information

ATR sample cell; measurement protocols for time-resolved rapid-scan FT-IR spectroscopy; electrochemical monitoring of oxygen evolution; additional rapid-scan FT-IR data; FT-IR and NMR characterization of catalyst compounds in neutral and alkaline solution.

Acknowledgment

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical, Geological and Biosciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Portions of this work (NMR spectroscopy) were performed as a User Project at The Molecular Foundry, Lawrence Berkeley National Laboratory, which is supported by the Office of Science, Office of Basic Energy Sciences. Hongfei Liu acknowledges Early Postdoc Mobility fellowship support by the Swiss National Science Foundation (Grant No. P2ZHP2_168445).

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