SUPPLEMENTARY INFORMATION

Formation of CoIV=O intermediate at the Boundary of the “Oxo-wall” Induces Water Oxidation

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**SI.1 - Materials and methods.**

**Sample preparation for XAS and EPR study of water oxidation reaction catalyzed by (1) in acidic media**

To an aliquot of 200 µL of 1mM solution of (1) in mixture of acetonitrile and 0.1 M nitric acid 1:1 by volume 20 µL of 200 mM solution of the oxidizer (cerium (IV) ammonium nitrate, 20equiv) in 0.1 M nitric acid was added fast at room temperature. After quick mixing, 40 µL of the reaction mixture was immediately filled into a polycarbonate tape- supported polypropylene cryostat sample holders and frozen in liquid N2. For preparation of EPR samples, entire 200 µL amount of the reaction mixture was quickly transferred into EPR tubes and frozen immediately in liquid N2. X-band EPR measurements were conducted with Bruker EMX CW X-band spectrometer. ColdEdge- closed cycle cryostat was used for variable temperature measurements. Power dependence was measured for all detected EPR signals. We found that none of the Fe signals can be saturated with maximum available microwave power of 30 mW.

**EPR**

X-band EPR measurements were conducted at 20 K temperature with Bruker EMX X-band spectrometer and CW microwave radiation using ColdEdge- closed cycle cryostat.

The EPR samples were prepared by mixing 200 ul of 1 mM of (1) in 0.1 M HNO3 with appropriate amount of CeIV in an EPR tube, followed by freezing in liquid N2 in less than 30 seconds.

**DFT calculations**

The DFT calculations, optimizations and resulting single point frequency calculations were performed by Gaussian 16 with unrestricted BP86 Becke’s 1988 functional 1 and the gradient corrections of Perdew 2. The basis set def2tzvp was used for all atoms unless noted otherwise. The CPCM polarizable conductor model was used to model acetonitrile or water solvation. The value of the reference potential (RHE) was assigned to 4.44 V and the free energy of a solvated proton to -11.64V3.

Transition state calculations were performed using the B3LYP hybrid functional, with the def2tzvp basis set for Co and 6-31G\* for C, H, N, and O atoms, Table S6. Transition states are identified by the presence of one negative frequency. Transition state barrier and associated Δ G values were obtained by repeating optimizations and single point frequency calculations on the reactant and product in this basis set. Obtained energies for transition state were ~+0.96 eV for BP86/def2tzvp and ~+0.93 eV for B3LYP/Co-def2tzvp/O, N, C, H – 6-31G\*, Table S6. This value is similar to previous DFT studies involving WNA on transition metal=O species.4-12 Note that the reactant and product species in this reaction, CoIII2O4CoIV=O/CoIV(CH3CO2)mono / H2O and CoIII2O4CoIII-OOH/CoIII(CH3CO2H)mono, have triplet and singlet spin states respectively. Single point energy calculations along the reaction pathway revealed that the geometry at which the singlet and triplet states have equal energy is farther along the reaction coordinate than the transition state geometry; as such, the transition state was calculated in the triplet state, Figure S6.

**XAS and EXAFS Measurements**

X-ray absorption spectra were collected at the Advanced Photon Source (APS) at Argonne National Laboratory on bending magnet beamline 9 at electron energy 7810 eV and average current of 100 mA. The radiation was monochromatized by a Si (110) crystal monochromator. The intensity of the X-rays was monitored by three ion chambers (*I*0, *I*1, and *I*2) and placed before the sample (*I*0) and after the sample (*I*1 and *I*2). *I1* and *I2* were filled with 100% nitrogen. The X-ray energy was calibrated by setting the first maximum in the derivative of the Co metal K-edge XANES spectrum to 7709 eV. For in situ measurements, a custom-made electrochemical cell with 4µm mylar tape window and a magnetic stirrer was placed between *I0* and *I1* ion chambers. For the measurements of (1) oxidized with cerium (IV) ammonium nitrate the plastic (Lexan) EXAFS sample holders (inner dimensions of 12 mm × 2 mm × 3 mm) filled with frozen solutions were inserted into a cryostat pre-cooled to 20 K. The samples were kept at 20 K in a He atmosphere at ambient pressure. Data were recorded as fluorescence excitation spectra using a 13-element energy-resolving detector. In order to reduce the risk of sample damage by X-ray defocused mode (beam size 1 × 1 mm) was used and no damage was observed. The shutter was synchronized with the scan software, preventing exposure to X-rays between scans and during spectrometer movements.

**EXAFS Data Analysis**

Athena software was used for data processing13. Energy scale for each scan was normalized using potassium permanganate powder standard and scans for same samples were added. Data in energy space were pre-edge corrected, normalized, and background corrected. The processed data were converted to the photoelectron wave vector (*k*) space and weighted by *k*3. The electron wave number is defined as in equation (1),

*k* = [2*m*(*E* – *E*0)/*η*2]1/2 (1)

where *E*0 is the threshold energy. *k*-space data were truncated near zero crossings and Fourier-transformed into *R*-space. Artemis software was used for curve fitting. In order to fit the data, the Fourier peaks were isolated separately, or entire experimental spectrum was fitted. The individual Fourier peaks were isolated by applying a Hanning window. Curve fitting was performed using *ab initio*-calculated phases and amplitudes from the FEFF8 program from the University of Washington. *Ab initio*-calculated phases and amplitudes were used in the EXAFS equation (equation 2)14:

(2)

where *N*j is the number of atoms in *j*th shell; *R*j is the distance between the absorbing atoms and the atoms in *j*th shell; *f*eff j is the *ab* *initio* amplitude function for *j*, and is Debye-Waller factor for shell *j* accounting for damping due to thermal and static disorder in the shell. The mean free path term accounts for losses due to inelastic scattering. The oscillations in the EXAFS spectrum are reflected in the sin(2*kRj*+*φij*(*k*)) term, where *φij*(*k*) is the *ab initio* phase function for the shell *j*. *S*0 is an amplitude reduction factor. The EXAFS equation was used to fit experimental data using *N*, *E*0, *R* and *σ2* as variable parameters, while *S*0 was kept fixed. The quality of fit was evaluated by *R*-factor: if *R*-factor is less than 2% then the fit is good enough. Reduced *χ*2 was used to justify the addition of new absorber-backscatter shells.

**SI.2 – Calculations**

**Table S1.**

Structural parameters from *in situ* EXAFS fits*a*fora bulk electrolysis of **(1)** at pH = 12.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Fit # | Shell | R, Å | N | σ2 x 103 | R-factor | Reduced χ2 |
| Beamtime 1  DFT results for  CoIII2O4CoIV=O/CoIV(CH3CO2)mono  CoIV=O ~1.675 Å  Co-Co:  2.72, 2.73, 2.73 Å  2.86, 2.86, 2.91 Å | 1 | Co-O | 1.88 | 6 | 3.2 | 0.40 | 307 |
| 2 | Co-O  Co-Co | 1.87  2.81 | 6  3 | 3.4  9.0 | 0.07 | 70 |
| 3 | Co-O  Co-O  Co-Co | 1.68  1.88  2.81 | 0.5  5.5  3 | 2.7\*  2.7\*  9.0 | 0.05 | 52 |
| 4 | Co-O  Co-O  Co-N  Co-Co | 1.67  1.86  1.92  2.80 | 0.532.53 | 0.4\*  0.4\*  0.4\*  8.9 | 0.03 | 44 |
| 5 | Co-O  Co-O  Co-N  Co-Co  Co-Co | 1.69  1.86  1.92  2.68  2.81 | 0.532.512 | 0.5\*  0.5\*  0.5\*  4.8  4.8 | 0.02 | 41 |
| Beamtime 2 | 6 | Co-O | 1.90 | 6 | 2.4 | 0.589 | 4362 |
| 7 | Co-O  Co-Co | 1.90  2.84 | 6  3 | 2.7  4.2 | 0.028 | 271 |
| 8 | Co-O  Co-Co  Co-Co | 1.90  2.79  2.98 | 6  1.5  1.5 | 2.6  0.4\*  0.4\* | 0.022 | 254 |
| 9 | Co-O  Co-O  Co-Co  Co-Co | 1.69  1.89  2.79  2.89 | 0.5  5.5  1.5  1.5 | 2.0  2.0  0.1\*  0.1\* | 0.017 | 236 |

*a*Fits were done in *q*-space. *R* is the Co–backscatter distance. σ2 is Debye–Waller factor. *R*-factor and Reduced χ2 are the goodness-of-fit parameters (see SI). *So2* =1.0 was used in all fits. \* denotes when σ2 was set to be the same for absorber-backscatter vectors.

**Table S2.** Sum of electronic and thermal Free Energies of different species, which were computed by DFT Ubp86/ def2tzvp and CPCM in acetonitrile solution.

|  |  |  |  |
| --- | --- | --- | --- |
| Species | Spin, S | Charge | Free Energy (Hartree) |
| [(py)4(Ac)4CoIII4O4] | 0 | 0 | -7740.978555 |
| [(py)4(Ac)4CoIII3CoIVO4]+ | ½ | 1 | -7740.806429 |
| [(py)4(Ac)4CoIII2CoIV2O4]2+ | 1 | 2 | -7740.590161 |
| [(bpy)4Ac2CoIII4O4]2+ | 0 | 2 | -8272.097612 |
| [(bpy)4Ac2CoIII3CoIVO4]3+ | ½ | 3 | -8271.904128 |
| [(bpy)4Ac2CoIII2CoIV2O4]4+ | 1 | 4 | -8271.669248 |

**Table S3.** DFT approximated redox potentials\* (eV) for complexes in acetonitrile, see Table S1.

|  |  |  |
| --- | --- | --- |
| Redox reaction | Experiment | DFT |
| [(py)4(Ac)4CoIII4O4]= [(py)4(Ac)4CoIII3CoIVO4]++ e- | 0.3 | 0.24 |
| [(py)4(Ac)4CoIII3CoIVO4]+ = [(py)4(Ac)4CoIII2CoIV2O4]2+ + e- | 1.45 | 1.44 |
|  |  |  |
| [(bpy)4Ac2CoIII4O4]2+ = [(bpy)4Ac2CoIII3CoIVO4]3+ + e- | 0.71 | 0.82 |
| [(bpy)4Ac2CoIII3CoIVO4]3+= [(bpy)4Ac2CoIII2CoIV2O4]4+ + e- | n/a | 1.95 |

\* potentials are given vs ferrocene Fe+/Fe0 couple.

**Table S4.** Structural parameters from EXAFS fits*a*for(1) (starting material) and oxidized with CeIV at pH = 1.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Fit # | Shell | *R, Å* | *N*\* | σ2 x 103 | *R*-  factor | Reduced  χ2 |
| (1), powder  DFT, Co-Co:  2.723; 2.723; 2.724; 2.724; 2.849; 2.850  XRD 15, Co-Co:  2.699; 2.702; 2.806;  2.696, 2.710, 2.806 | 1 | Co-O | 1.89 | 6 | 4.3 | 0.54 | 11483 |
| 2 | Co-O  Co-Co | 1.88  2.74 | 6  3 | 4.1  7.8 | 0.086 | 2365 |
| 3 | Co-O  Co-Co  Co-C | 1.89  2.75  2.90 | 6  3  4 | 4.1  7.3\*  7.3\* | 0.069 | 2246 |
| 4& | Co-O  Co-N  Co-Co  Co-C | 1.88  1.92  2.75  2.90 | 3  3  3  4 | 2.5\*  2.5\*  7.1\*  7.1\* | 0.055 | 2177 |
| 5 | Co-O  Co-N  Co-Co  Co-Co  Co-C | 1.88  1.93  2.73  2.84  2.92 | 3  3  2  1  4 | 2.3\*  2.3\*  3.0\*  3.0\*  3.0\* | 0.020 | 1002 |
| (1) + CeIV = (1)+  DFT, Co-Co:  2.682; 2.683; 2.683;  2.683; 2.844; 2.844  XRD 16, Co-Co:  2.714; 2.730; 2.893;  2.707; 2.732; 2.893 | 6 | Co-O | 1.89 | 6 | 4.0 | 0.42 | 4219 |
| 7 | Co-O  Co-Co | 1.89  2.77 | 6  3 | 3.9  11.5 | 0.18 | 2277 |
| 8 | Co-O  Co-Co  Co-Co | 1.88  2.69  2.83 | 6  2  1 | 3.8  4.4\*  4.4\* | 0.14 | 2209 |
| 9 | Co-O  Co-Co  Co-Co  Co-C | 1.88  2.68  2.83  2.86 | 6  2  1  4 | 3.9  3.0\*  3.0\*  3.0\* | 0.07 | 1363 |
| 10 | Co-O  Co-Co  Co-Co  Co-C | 1.89  2.69  2.84  2.88 | 6  2  1  4 | 4.2  2.7  1.0\*  1.0\* | 0.014 | 258 |
| 11 | Co-O  Co-N  Co-Co  Co-Co  Co-C | 1.85  1.95  2.69  2.84  2.87 | 3  3  2  1  4 | 1.9\*  1.9\*  2.7  1.0\*  1.0\* | 0.009 | 228 |

*a*Fits were done in *q*-space. *R* is the Co–backscatter distance. σ2 is Debye–Waller factor. *R*-factor and Reduced χ2 are the goodness-of-fit parameters (see XAS/EXAFS Section in the text). *So2* =1.0 was used in all fits. \* denotes when σ2 was set to be the same for absorber-backscatter vectors.

**Table S5.** Sum of electronic and thermal Free Energies of different species, which were computed by DFT Ubp86/ def2tzvp and CPCM in water.

|  |  |  |  |
| --- | --- | --- | --- |
| Species | Spin, S | Charge | Free Energy (Hartree) |
| Two electron oxidation products of (**1**) | | | |
| CoIII2CoIV2 | 1 | +2 | -7740.591742 |
| CoIII2O4CoIV=O/CoIV(CH3CO2)mono/H2O | 1 | 0 | -7892.613188 |
| CoIII2O4CoIV=O/CoIV(CH3CO2)mono | 0 | 0 | -7816.124519 |
| CoIII2O4CoIV=O/CoIV(CH3CO2)mono | 1 | 0 | -7816.149772 |
| CoIII2O4CoIII-OOH/CoIII(CH3CO2H)mono | 0 | 0 | -7892.583524 |
| CoIII2O4CoIII-OOH/CoIII(CH3CO2H)mono | 1 | 0 | -7892.571866 |
| CoIII2O4CoIIIOOH/CoIII(CH3CO2)mono | 0 | -1 | -7892.125385 |
| CoIII2O4CoIIIOO/CoIII(CH3CO2)mono | 0 | -2 | -7891.622223 |
| CoIII3O4CoIII(OOC(O)CH3)bridging | 0 | 0 | -7816.12931 |
| Two electron oxidation products of (**1**) with one acetate ligand fully dissociated | | | |
| CoIII2O4CoIV=O/CoIV=O | 1 | -1 | -7662.943627 |
| CoIII3O4CoIIIOObridging | 1 | -1 | -7662.947915 |
| CoIII3O4CoIIIOObridging | 0 | -1 | -7662.957249 |
| Three electron oxidation products of (**1**) | | | |
| CoIIIO4CoIV=O/CoIV,CoIV(CH3CO2)mono/H2O | ½ | 1 | -7892.418265 |
| CoIII3O4CoIV=O(CH3CO2)mono | ½ | 1 | -7815.869818 |
| CoIII2O4CoIV-OOH/CoIII(CH3CO2H)mono | ½ | 1 | -7892.415831 |
| CoIII2O4CoIV-OOH/CoIII(CH3CO2)mono | ½ | 0 | -7891.974380 |
| CoIII2O4CoIV-OO/CoIII(CH3CO2)mono | ½ | -1 | -7891.518788 |
| H2O | 0 | 0 | -76.467538 |

**Table S6.** Sum of electronic and thermal Free Energies of different species, which were computed by DFT Ubp86/ def2tzvp and CPCM water solution, with 15% Hartree Fock Exchange.

|  |  |  |  |
| --- | --- | --- | --- |
| Species | Spin | Charge | Energy (Hartree) |
| CoIII2O4CoIII-OOH/CoIII(CH3CO2H)mono | 0 | 0 | -7972.387673 |
| CoIII2O4CoIV=O/CoIV(CH3CO2)mono/ H2O | 1 | 0 | -7972.380670 |
| CoIII2O4CoIV=O/CoIV(CH3CO2)mono | 1 | 0 | -7894.574203 |
| H2O | 0 | 0 | -77.793214 |

**Table S7.** DFT analysis of transition state for peroxide formation, initial and final states. Basis set is def2tzvp for Co and 6-31G\* for other atoms, using the B3LYP hybrid functional and CPCM model for water solvation.

|  |  |
| --- | --- |
| **Species** | **Free Energies (Hartree)** |
| CoIII2O4CoIV=O/CoIV(CH3CO2)mono/H2O | -7890.724977 |
| CoIII2O4CoIII-OOH/CoIII(CH3CO2H)mono | -7890.733972 |
| CoIV=O 🡪 CoIIIOOH Transition State | -7890.690654 |
|  |  |
| Barrier | +0.93 eV |
| ΔG | -0.24 eV |

**Table S8.** DFT analysis of deprotonation reaction for peroxide species at pH=12.

|  |  |
| --- | --- |
| Reaction | Delta G (eV) |
| CoIII2O4CoIII-OOH/CoIII(CH3CO2H)mono   = CoIII2O4CoIII-OOH/CoIII(CH3CO2)mono + H+ | +0.12 |
| CoIII2O4CoIII-OOH/CoIII(CH3CO2)mono = CoIII2O4CoIII-OO/CoIII(CH3CO2)mono + H+ | +1.34 |
| CoIII2O4CoIV-OOH/CoIII(CH3CO2H)mono = CoIII2O4CoIV-OOH/CoIII(CH3CO2)mono + H+ | -0.34 |
| CoIII2O4CoIV-OOH/CoIII(CH3CO2)mono = CoIII2O4CoIV-OO/CoIII(CH3CO2)mono + H+ | +0.05 |

**Table S9.** Electronic energies of the OEC models of Photosystem II computed by DFT Ubp86/ def2tzvp with 15% Hartree Fock exchange.

|  |  |  |  |
| --- | --- | --- | --- |
| S-state /Species | Spin, S | Charge | Energy (Hartree) |
| S3 Mn=O | 3 | -2 | -8479.206039 |
| S3 MnOOH (Left Bridging) | 1 | -2 | -8479.148166 |
| S3 MnOOH/H2O (Right Bridging) | 1 | -2 | -8557.01168 |
| S4 Mn=O | ½ | -1 | -8479.123254 |
| S4 MnOOH/H2O (Left Bridging) | ½ | -1 | -8556.868051 |
| S4 MnOOH\_(Right Bridging) | ½ | -1 | -8479.116616 |
| H2O | 0 | 0 | -77.8123358 |

**SI.3 - Figures**

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**Figure S1.** XANES of **(1)** as a powder (red) in comparison with 1mM **(1)** oxidized with CeIV (blue) at pH=1. Oxidized intermediate was measured inside a cryostate at 20K.

A close up of text on a white background

Description automatically generated

**Figure S2.** Fitting of EXAFS data for (1) as a powder (a), its solution during electrolysis at pH = 12 with 1.4 V potential vs Ag/AgCl after prolonged time (b)and its 1mM solution oxidized with 20 eq of CeIV at pH = 1 (c).

A close up of a mans face

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A close up of a mans face

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**Figure S3.** Cyclic voltammetry data for cubane **1** (top, green) and the analog Co4O4(bpy)4(OAc)2(ClO4)2 (bottom, brown) in 0.1 M tetrabutylammonium hexafluorophosphate electrolyte. Conditions: Glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl reference electrode with potentials referenced to ferrocene.

A screenshot of a cell phone

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**Figure S4.** Upper set: Spin densities calculated for CoIV=O states, using a, B3LYP; b, BP86; and c, BP86 plus 15% Hartree Fock exchange methodologies. Bottom set: Potential intermediates in O-O bond formation process. a, CoIII3O4CoIII(OOC(O)CH3)bridging. b, CoIII3O4CoIIIOObridging c, CoIII2O4CoIV-OOH/CoIII(CH3CO2)mono, d, CoIII2O4CoIV-OO/CoIII(CH3CO2)mono.

A screenshot of a cell phone

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**Figure S5.** EPR of bulk electrolysis of Co4O4Ac4Py4 at pH = 7.

A close up of a mans face

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**Figure S6.** Determination of intersystem crossing point for WNA reaction forming O-O bond. Electronic energies are calculated in both singlet and triplet state along the minimum energy pathway. Reaction proceeds with decreasing O-O bond distance. Transition state geometry appears near 1.9 Å.

**SI.4 - References**

1 Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A* **38**, 3098-3100, doi:10.1103/PhysRevA.38.3098 (1988).

2 Perdew, J. P. & Yue, W. Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation. *Physical Review B* **33**, 8800-8802, doi:10.1103/PhysRevB.33.8800 (1986).

3 Pushkar, Y., Moonshiram, D., Purohit, V., Yan, L. & Alperovich, I. Spectroscopic Analysis of Catalytic Water Oxidation by [RuII(bpy)(tpy)H2O]2+ Suggests That RuV=O Is Not a Rate-Limiting Intermediate. *J Am Chem Soc* **136**, 11938–11945 (2014).

4 Tong, L. *et al.* Catalytic Water Oxidation by Mononuclear Ru Complexes with an Anionic Ancillary Ligand. *Inorganic Chemistry* **52**, 2505-2518, doi:10.1021/ic302446h (2013).

5 Sala, X. *et al.* The cis-[RuII(bpy)2(H2O)2]2+ Water-Oxidation Catalyst Revisited. *Angewandte Chemie International Edition* **49**, 7745-7747, doi:10.1002/anie.201002398 (2010).

6 Angeles-Boza, A. M. *et al.* Competitive oxygen-18 kinetic isotope effects expose O–O bond formation in water oxidation catalysis by monomeric and dimeric ruthenium complexes. *Chemical Science* **5**, 1141-1152, doi:10.1039/C3SC51919H (2014).

7 Vigara, L. *et al.* Experimental and quantum chemical characterization of the water oxidation cycle catalysed by [RuII(damp)(bpy)(H2O)]2+. *Chemical Science* **3**, 2576-2586, doi:10.1039/C2SC20399E (2012).

8 Li, Y.-Y., Tong, L.-P. & Liao, R.-Z. Mechanism of Water Oxidation Catalyzed by a Mononuclear Iron Complex with a Square Polypyridine Ligand: A DFT Study. *Inorganic Chemistry* **57**, 4590-4601, doi:10.1021/acs.inorgchem.8b00333 (2018).

9 Privalov, T., Åkermark, B. & Sun, L. The OO Bonding in Water Oxidation: the Electronic Structure Portrayal of a Concerted Oxygen Atom–Proton Transfer Pathway. *Chemistry – A European Journal* **17**, 8313-8317, doi:10.1002/chem.201100901 (2011).

10 Shao, Y., de Groot, H. J. M. & Buda, F. Proton Acceptor near the Active Site Lowers Dramatically the O–O Bond Formation Energy Barrier in Photocatalytic Water Splitting. *The Journal of Physical Chemistry Letters* **10**, 7690-7697, doi:10.1021/acs.jpclett.9b02914 (2019).

11 Hughes, T. F. & Friesner, R. A. Systematic Investigation of the Catalytic Cycle of a Single Site Ruthenium Oxygen Evolving Complex Using Density Functional Theory. *The Journal of Physical Chemistry B* **115**, 9280-9289, doi:10.1021/jp2026576 (2011).

12 Rudshteyn, B. *et al.* Water-Nucleophilic Attack Mechanism for the CuII(pyalk)2 Water-Oxidation Catalyst. *ACS Catalysis* **8**, 7952-7960, doi:10.1021/acscatal.8b02466 (2018).

13 Ravel, B. & Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Rad.* **12**, 537-541 (2005).

14 Rehr, J. J. & Albers, R. C. Theoretical approaches to x-ray absorption fine structure. *Rev. Mod. Phys.* **72**, 621 (2000).

15 Sarmah, P., Chakrabarty, R., Phukan, P. & Das, B. K. Selective oxidation of alcohols catalysed by a cubane-like Co(III) oxo cluster immobilised on porous organomodified silica. *Journal of Molecular Catalysis A: Chemical* **268**, 36-44, doi:<https://doi.org/10.1016/j.molcata.2006.11.042> (2007).

16 Ullman, A. M. *et al.* Water Oxidation Catalysis by Co(II) Impurities in Co(III)4O4 Cubanes. *Journal of the American Chemical Society* **136**, 17681-17688, doi:10.1021/ja5110393 (2014).