Communication

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Oleg M. Usov, Vladimir M. Grigoryants, Ranitendranath Tagore, Gary W. Brudvig, and Charles P. Scholes

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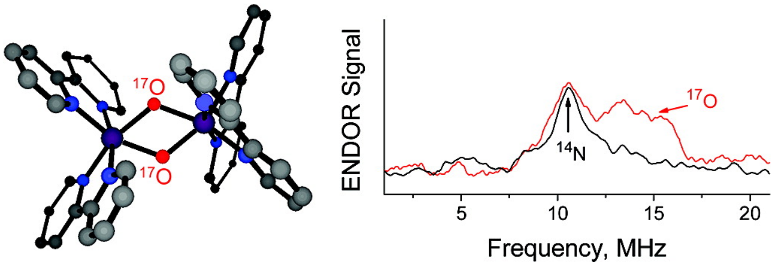

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COMMUNICATIONS

Hyperfine Coupling to the Bridging ^{17}O in the Di-μ-oxo Core of a $Mn^{III}-Mn^{IV}$ Model Significant to the Core Electronic Structure of the O_2-Evolving Complex in Photosystem II

Oleg M. Usov,[‡] Vladimir M. Grigoryants,[‡] Ranitendranath Tagore,[†] Gary W. Brudvig,*,[†] and Charles P. Scholes*,[‡]

Department of Chemistry, University at Albany, State University of New York, Albany, New York 12222, and Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

Received May 4, 2007; E-mail: cps14@albany.edu; gary.brudvig@yale.edu

It is generally accepted that Mn in the S_2 state of the oxygen-evolving center (OEC) is in the +3 and +4 oxidation states with μ-oxo linkages.[1,2] X-ray crystallography has provided the resolution to model the OEC as a Mn_3CaO_4 cube connected to a fourth Mn via a μ-oxo bridge.[3,4] ^{55}Mn electron nuclear double resonance (ENDOR) is highly consistent with the cuboidal structure.[5,6]

Di-μ-oxo-bridged $Mn^{III}-Mn^{IV}$ compounds are widely studied models for this S_2 state.[1,7,8] Such models present a manganese multiline EPR pattern from $S = 2$ Mn^{III} and $S = {}^3/_2$ Mn^{IV}, antiferrromagnetically coupled to each other to yield a net spin $S = {}^1/_2$.[6] Electron spin echo envelope modulation (ESEEM) and ENDOR of such $Mn^{III}-Mn^{IV}$ models have resolved hyperfine couplings for Mn^{IV} and Mn^{III},[9,10] protons,[9] and liganding nitrogen.[11] However, the ubiquitous μ-oxygens which physically couple the Mn^{III} and Mn^{IV} have yet to have their electronic structure and electron-spin density elucidated.

Recently Tagore et al.[1] showed incorporation of isotopically enriched oxygen into the di-μ-oxo bridges of $Mn^{III}-Mn^{IV}$ models, simply by slow exchange from trace water in dry CH_3CN. For our work the di-μ-oxo $Mn^{III}-Mn^{IV}$ bipyridyl dimer $[(bpy)_4Mn_2^{III/IV}(\mu\text{-}O)_2](ClO_4)_3$ (bpy = 2,2″ bipyridine) was synthesized according to literature methods.[1,12] A CH_3CN (HPLC grade, Fisher) solution 2.5 mM in $Mn^{III}-Mn^{IV}$ bipyridyl dimer was prepared, and trace H_2O, either as $H_2{}^{16}O$ or as isotopically enriched $H_2{}^{17}O$ (84% atomic enrichment in ^{17}O, Isotec.), was added at 1 μL of water to 200 μL of CH_3CN. The exchange time of the water oxygen into the μ-oxo cross bridges at room temperature is about 20 min.[1] An equal volume of CH_2Cl_2 (Fisher, reagent grade) was added, and the sample precooled at −80 °C for several hours. The precooled 70 μL sample, in a 2.0 mm i.d., 2.4 mm o.d. quartz EPR tube, was glassed by plunging into liquid nitrogen. A glass inhibits paramagnetic species from aggregating upon freezing to prevent these aggregates from interfering with ENDOR. ($CH_3CN-DMF$ also provided an even better glass. However, the DMF contained reductants that produced Mn^{II} artifacts but did not hamper di-μ-oxo ^{17}O hyperfine measurements (see Supporting Information).)

X-band EPR (9.525 GHz) was carried out at 15 K as previously described.[13] CW Q-band (34.1 GHz) ENDOR was performed under dispersion (χ') and rapid passage field-modulated conditions at 2 K.[13] A nucleus, Z, with $I \geq 1$, namely, ^{17}O ($I = {}^5/_2$) or ^{14}N ($I = 1$), will have first-order ENDOR frequencies given as $^Z\nu^{\pm}_{ENDOR} = |^ZA/2 \pm {}^Z\nu + 3^ZP(2m - 1)/2|$, where $-I + 1 \leq m \leq I$, ^ZA, and ^ZP are hyperfine and quadrupole coupling constants and $^Z\nu$ is the nuclear Zeeman frequency.[14] At 12200 G $^{17}\nu = 7.03$ MHz and $^{14}\nu = 3.76$ MHz. For the ^{17}O features here, $|^{17}A/2| \approx {}^{17}\nu$. The $^{17}\nu^-_{ENDOR}$ branch is close to zero frequency and is not resolved because $|^{17}A/2|$ and $^{17}\nu$ cancel. The $^{17}\nu^+_{ENDOR}$ branch occurs at a frequency of approximately $|^{17}A/2 + {}^{17}\nu|$ because as elsewhere, ^{17}O quadrupolar splittings contribute only to line broadening.[14,15] For ^{14}N, the $^{14}\nu^+_{ENDOR}$ branch, like the $^{17}\nu^+_{ENDOR}$ branch, is the one observable by rapid passage CW Q-band ENDOR.[13]

The X-band EPR signal from the di-μ-oxo $Mn^{III}-Mn^{IV}$ bipyridyl dimer (Figure 1A) was similar to that reported by Cooper et al.[12] The outer features 300−600 G above the center (at $g = 1.99$ and ∼3400 G) of the multiline pattern showed the most well-resolved structure. There was significant broadening of this structure brought on by the $H_2{}^{17}O$. In Figure 1B, we compare second-derivative X-band features, which show significant ^{17}O-induced broadening.

A comparison (Figure 2) of ENDOR signals from the $Mn^{III}-Mn^{IV}$ bipyridyl dimers, respectively, exchanged with $H_2{}^{16}O$ and with $H_2{}^{17}O$, showed a new feature from the ^{17}O sample near 13.5 ± 1.0 MHz. This feature was best resolved ∼300 to 600 G above and below the Q-band EPR line center (which occurs at $g = 1.99$ or 12240 G). The hyperfine coupling, derived from $^{17}\nu^+_{ENDOR} = |^{17}A/2 \pm {}^{17}\nu|$, was $|^{17}A| = 12.8 \pm 1.0$ MHz. A feature near 10.5 MHz occurred from all samples. We assign this as the liganding bipyridyl ^{14}N nitrogen with an approximate hyperfine coupling of $|^{14}A| = 13.5 \pm 0.3$ MHz; corresponding $|^{14}A|$ couplings of the $Mn^{III}-Mn^{IV}$ CYCLAM and TMPA complexes were, respectively, 9.2 and 11.2 MHz.[11]

Correlating EPR Line Broadening with ^{17}O Hyperfine Coupling. For *two* equivalent $I = {}^5/_2$ ^{17}O-di-μ-oxo nuclei, an eleven-line pattern is expected with peaks in the ratio of 1:2:3:4:5:6:5:4:3:2:1 and a separation between peaks of $|^{17}A|$ (in Gauss). [Note that $2.79|^{17}A|$ (in Gauss) = $|^{17}A|$ (in MHz).] This packet shape is well approximated by a Gaussian function whose peak width between derivative extrema is $4.84 \cdot |^{17}A|$ (in Gauss).[16] To replicate EPR line broadening, we convoluted the narrower second-derivative spectrum of the ^{16}O-di-μ-oxo $Mn^{III}-Mn^{IV}$ bipyridyl dimer with a Gaussian broadening function and, in the Supporting Information, with an exact 1:2:3:4:5:6:5:4:3:2:1 distribution. The convolutionally broadened EPR spectra were compared (Figure 1B) with the broadened spectrum of the ^{17}O-di-μ-oxo $Mn^{III}-Mn^{IV}$ bipyridyl dimer. Best agreement was obtained with a Gaussian broadening function having a 22 ± 3 G peak width between derivative extrema. This width corresponded to an intrinsic di-μ-oxo ^{17}O coupling of $|^{17}A| = 4.6 \pm 0.6$ (in Gauss) $= 12.9 \pm 1.8$ (in MHz). The coupling estimated from the EPR line width compares favorably with the hyperfine coupling of $|^{17}A| = 12.8 \pm 1.0$ MHz from ENDOR.

There has been little direct experimental hyperfine evidence on the oxygen hyperfine structure at μ-oxo cross bridges. There happens to be ENDOR hyperfine information from the bridging μ-oxygen between Fe(III) ($S = {}^5/_2$) and Fe(IV) ($S = 2$) in the di-Fe cluster of ribonucleotide reductase.[15] There the hyperfine

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[‡] State University of New York, Albany.
[†] Yale University.

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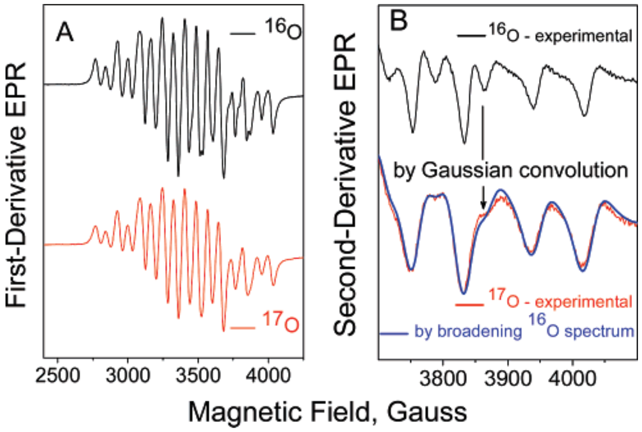

Figure 1. (Spectra A) First-derivative X-band EPR spectra of di-μ-oxo $Mn^{III}-Mn^{IV}$ bipyridyl dimers exchanged with $H_2{}^{16}O$ (black) and $H_2{}^{17}O$ (red) in $CH_3CN-CH_2Cl_2$, recorded at $T = 15$ K, 6 G field modulation, 100 s signal averaging with a 2000 G field sweep, 2 mW microwave power, EPR frequency = 9.525 GHz. (Spectra B) Experimental second-derivative X-band EPR spectra of the same dimers exchanged with $H_2{}^{16}O$ (black) and $H_2{}^{17}O$ (red) and recorded in the 3700−4100 G range using 3 G field modulation; the blue overlay shows that the EPR spectrum from the di-μ-oxo-^{17}O dimer can be obtained from the narrower line di-μ-oxo ^{16}O dimer by convolution of that narrower spectrum with a Gaussian broadening function (of 22 G width between derivative extrema) using the Origin 7.0 data analysis program.

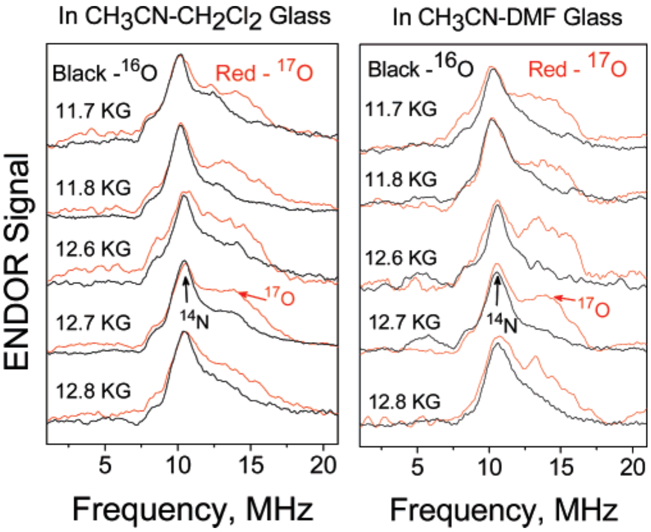

Figure 2. We present ENDOR of $Mn^{III}-Mn^{IV}$ bipyridyl dimers exchanged with $H_2{}^{16}O$ (black) and $H_2{}^{17}O$ (red) in $CH_3CN-CH_2Cl_2$ and in CH_3CN-DMF glasses. The fields in the figure from top to bottom are approximately 500 and 600 G below $g = 1.99$ and approximately 300, 400, and 500 G above $g = 1.99$. ENDOR conditions: adiabatic rapid passage, $T = 2$ K, microwave power = 0.2 μW, 100 kHz mod = 5 G ptp, time constant = 90 ms, radio frequency power ≈ 20 W, radio frequency sweep rate = 2 MHz/s, averaging time/spectrum = 1000 s, $\nu_{EPR} = 34.10$ GHz.

coupling of ~23 MHz is nearly double that measured here for the $Mn^{III}-Mn^{IV}$ bipyridyl dimer. The di-Fe cluster couplings should be larger because Fe tends to be more covalent than Mn and because the $S = {}^5/_2$ ferric ion has a spin-containing $d(x^2-y^2)$ orbital directed for σ bonding toward the oxygen 2s orbital. This σ bonding should lead to sizable ^{17}O Fermi hyperfine coupling, whereas, the di-Mn system has no such spin-containing $d(x^2\text{-}y^2)$ orbital. Antiferromagnetic coupling between paramagnetic metals depends on covalent electron-spin transfer through bridging ligands.[17] DFT (density functional theory) computations on di-μ-oxo-$Mn^{III}-Mn^{IV}$ systems indirectly utilize the μ-oxo covalent spin transfer to predict $Mn^{III}-Mn^{IV}$ antiferromagnetic coupling.[18,19] The present work provides experimental underpinnings for testing future high level DFT calculations that give a comprehensive prediction of spin density, di-μ-oxo hyperfine coupling, and $Mn^{III}-Mn^{IV}$ antiferromagnetic coupling.

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Supporting Information Available: X-band EPR spectra are provided from the $Mn^{III}-Mn^{IV}$ bipyridyl dimer in CH_3CN-DMF glassing solvent. A comparison is provided of line broadening simulations due to a Gaussian packet, a di-^{17}O 1:2:3:4:5:6:5:4:3:2:1 packet, and a mono-^{17}O 1:1:1:1:1:1 packet. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) If there are n equivalent nuclei with spin I and hyperfine coupling $|A|$ (in Gauss), the root mean square width between derivative extrema in the resultant approximate Gaussian lineshape would be $2A[n\,I(I + 1)/3]^{1/2} = 4.84\cdot|^{17}A|$, when $n = 2$ and $I = {}^5/_2$. See: McElroy, J. D.; Feher, G.; Mauzerall, D. C. *Biochim. Biophys. Acta* **1972**, *267*, 363.
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