

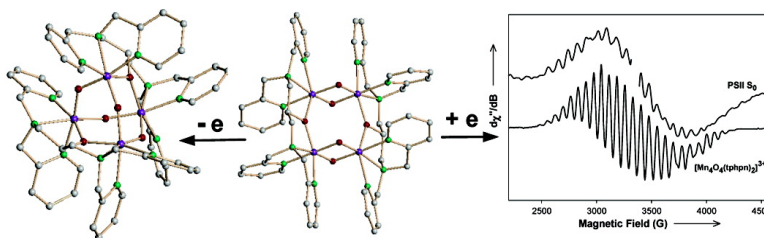
Communication

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 Relevance to Photosystem II Water Oxidase Active Site**

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Shape-Shifting Tetranuclear Oxo-Bridged Manganese Cluster: Relevance to Photosystem II Water Oxidase Active Site

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Aggregates of transition metal ions bridged by either oxide/hydroxide (O^{2-}/OH^-) or sulfide (S^{2-}) ligands are plentiful and well characterized. Some of these compounds are of known biological relevance and many are redox-active. Examples of redox-active sulfide-bridged complexes include different types of iron–sulfur clusters. While subtle structural variations occur upon oxidation or reduction of these complexes, reflected by changes in bond distances and angles, the overall three-dimensional shape remains unchanged. In other words, the same structural isomer is observed for all oxidation states. The $[Fe_4S_4]^{n+}$ (where $n = 1, 2,$ and 3) clusters exhibit a cubane-type geometry.¹ Heterometallic $[MFe_3S_4]$ clusters, where $M = V,$ ^{2a} Co, Ni, Zn, Cd,^{2b} or Mo,^{2c} also have been shown to undergo redox processes with no pronounced change in the cubane geometry.² Both $[Fe_6S_6]^{n+}$ (where $n = 3$ and 4)^{3a} and $[Fe_4Mo_2S_9]^{n+}$ (where $n = 0$ and 1)^{3b} complexes exhibit edged-bridged double cubane cores in both oxidized and reduced forms.

We reported redox behavior of the oxo-bridged tetramanganese complex $[Mn_4O_6(bpea)_4]^{4+}$ (where $bpea = N,N$ -bis(2-pyridylmethyl)ethylamine), which retains its adamantane-type core structure upon reduction by one electron.⁴ The overall cubane topology of the $[Mn_4O_4(O_2PPh_2)_6]$ complex remains unaffected when oxidized by one electron.⁵ Examining these and a large body of additional data, it is natural to conclude that chalcogenide-bridged multinuclear clusters are structurally rigid upon oxidation state changes. We have recently discovered an important exception to this general observation.

As documented here, a complex we reported previously, $\{[Mn^{III,IV}_2(\mu-O)_2(tphpn)]_2\}^{4+}$ (**1**) (where $Htphpn = N,N,N',N'$ -tetra-(2-methylpyridyl)-2-hydroxypropanediamine),⁶ undergoes dramatic structural changes when oxidized or reduced by one electron. We also demonstrate that the structure determined for **1** in the solid state is not stable in solution and that a rearrangement occurs, albeit slowly, without redox “triggering”. As shown below, the observations described here have important implications regarding our understanding of Photosystem II.

The solid-state structure of **1** was previously established to be a stacked pair of $\{Mn_2(\mu-O)_2\}^{3+}$ units linked together by two heptadentate ligand anions, $tphpn^-$.⁶ The first indication that **1** is not structurally rigid in solution arose from electronic absorption spectra, as shown in Figure 1. The data for **1** imply that a structural isomerization or “shape-shifting” occurs over time in solution, proceeding through isosbestic points at ~ 640 and ~ 728 nm. Confirmation comes from mass spectral data that show one parent-ion mass before and after the isomerization process is complete. Attempts to isolate the second isomer, compound **2**, were thwarted because the species isolated in high yield by crystallization was **1**. Thus, this isomerization process can be reversed by crystallization. This isomerization and its reversibility were also confirmed by ¹H

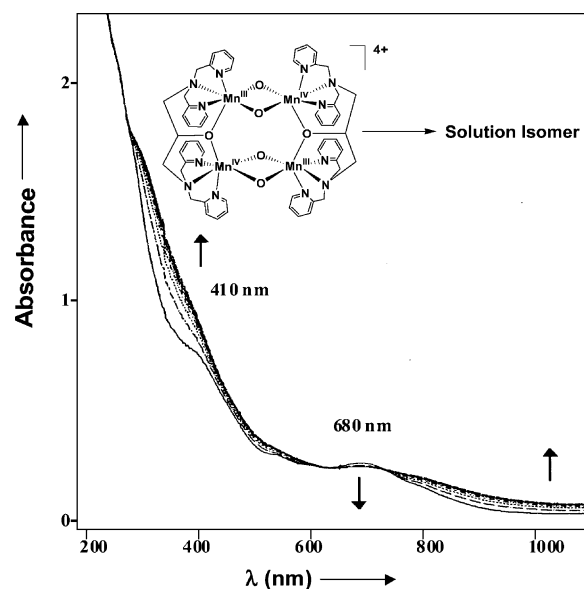


Figure 1. Conversion of **1** to **2** in acetonitrile over time as observed in electronic absorption spectra, taken at every 30 min over 12 h.

NMR and EPR measurements (see Figures S1 and S2, Supporting Information). We conclude that the “dimer-of-dimers” structure for **1** is the most stable isomer in the solid state, whereas **2**, whose structure is yet to be determined, is the isomer stable in solution.

Our early attempts to obtain reproducible electrochemical behavior of **1** were futile, as we were not aware of the isomerization mentioned above and because the solutions used must have had varying amounts of **1** and **2** present. Cyclic voltammograms of **1**(CF₃SO₃)₄ as freshly dissolved crystals and after being in solution for ~ 12 h are shown in Figure 2. Species **1** has a broad quasi-reversible one-electron oxidation at an $E_{1/2}$ value of 1.23 V ($\Delta E_p = 130$ mV) vs Ag/AgClO₄.⁷ A second well-defined reversible redox couple at $E_{1/2} = 0.92$ V ($\Delta E_p = 70$ mV) in the anodic scan begins to appear slowly in solution. This has been assigned as one-electron oxidation of **2**. It is interesting to note the relatively large shift (~ 300 mV) in the $[Mn^{IV}_3, Mn^{III}]/[Mn^{IV}_2, Mn^{III}]$ reduction potential upon isomerization. This shift is related to the energy “stored” in the dimer-of-dimers architecture.

Noting that a Mn^{IV}_3, Mn^{III} oxidation state of our tetranuclear species appeared to be accessible, we set out to isolate it in order to explore its structural and electronic properties. We were successful in oxidizing $[Mn_4(\mu-O)_4(tphpn)_2](OTf)_4$ in acetonitrile quantitatively by one electron employing a high-potential oxidant, $[Mn^{IV}(HB(3,5-Me_2pz)_3)_2](ClO_4)_2$ (where $pz =$ pyrazolyl), developed in our laboratory.⁸ We were surprised to find that the crystal structure of $[Mn_4(\mu-O)_4(tphpn)_2](OTf)_2(ClO_4)_3$, **3**(OTf)₂(ClO₄)₃, shown in Figure 3, revealed that a large change in shape of the dimer-of-dimers aggregate accompanies oxidation, resulting in an

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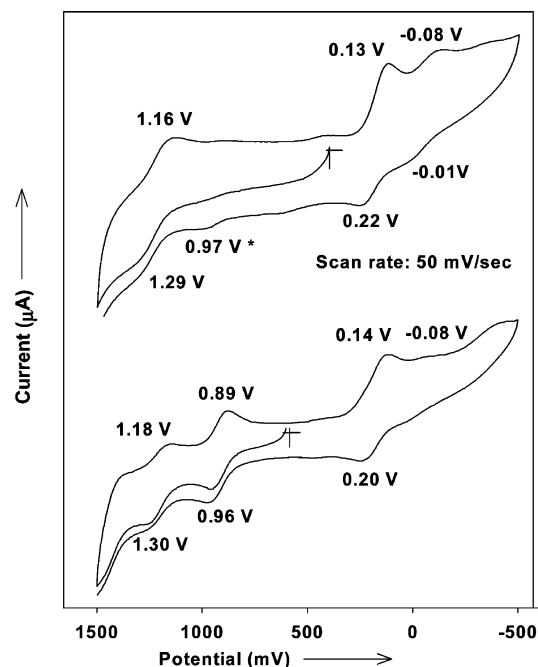


Figure 2. Cyclic voltammogram of **1**(OTf)₄ (top) and a mixture of **1**(OTf)₄ and **2**(OTf)₄ (bottom) in acetonitrile. Potentials are vs Ag/AgClO₄.

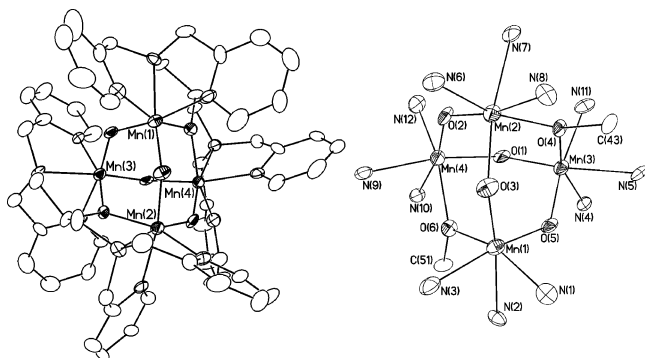
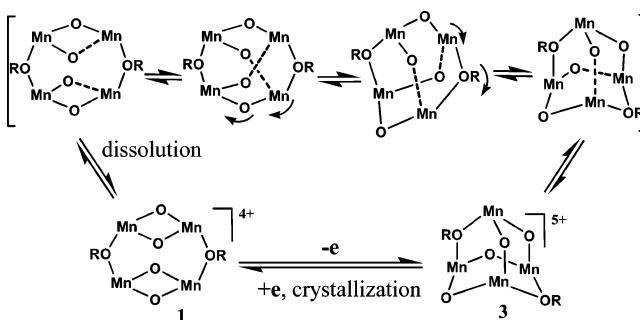


Figure 3. ORTEP views of the full cation (left) and the tetramanganese core (right) of **3**(OTf)₂(ClO₄)₃, showing 30% probability thermal ellipsoids (H atoms are omitted for clarity).

adamantane-like core complex.⁹ It is possible that compound **2** also has an adamantane core, yet this remains to be established owing to the difficulty of isolating **2** in crystalline form.

In terms of metrical parameters, the most dramatic change upon oxidation is that the average Mn–O_{oxo}–Mn angle increases from ~94.2° in **1** to ~132–135° in **3** (Figure S4). Consequently, the Mn···Mn separations are greatly increased. There are two discernible sets of distances between adjacent Mn atoms bridged by an oxide group. The average of distances Mn(2)···Mn(4) and Mn(1)···Mn(3) is 3.29 Å, whereas the same between Mn(1)···Mn(2) and Mn(3)···Mn(4) is 3.36 Å. The average bond distance between two adjacent Mn centers bridged by an alkoxo group (Mn(2)···Mn(3) and Mn(1)···Mn(4)) is 3.45 Å. The average Mn–O_{alkoxo}–Mn angle is 124°. The average Mn···Mn distance increase from **1** (2.65 Å)⁶ to **3** is of particular interest with regard to the tetranuclear manganese complex (Mn₄) found in the Photosystem II (PSII) water oxidase (WO) active site, which is responsible for catalytic conversion of water to dioxygen. The structure of WO Mn₄ is available in its “S₁” oxidation state.¹⁰ In the first two reports (3.7 and 3.8 Å),^{10a,b} no detailed structural assignment is ventured for the manganese region’s electron density. The most recent structure is at marginally higher resolution (3.5 Å),^{10c} yet the authors assign

Scheme 1



the active-site cluster as a Mn₃Ca cubane with an appended fourth Mn atom. In any event, none of the X-ray analyses to date shed light on the higher S states. EXAFS measurements reveal 2.7 Å and >3.3 Å Mn···Mn distances in the S₁ and S₂ states.^{11a,b} According to one group, advancement to the S₃ form is accompanied by marked Mn···Mn separation increases (from 2.7, 2.7, and 3.3 Å to 2.8, 3.0, and 3.3–3.5 Å),^{11c} although one might have expected shortened distances at a higher oxidation state due to shorter Mn–O_{oxo} bonds. However, this latter expectation is based on an assumption of relative structural rigidity for the PSII Mn₄. Our work demonstrates that a synthetic Mn₄ species readily rearranges at higher oxidation states, preferring a structure with more open Mn–O_{oxo}–Mn angles and thus larger Mn···Mn distances. On this basis, we put forward the hypothesis that the increase in metal–metal distance observed for the PSII Mn₄ when advancing from S₂ to S₃ states is consistent with a significant structure rearrangement or “shape-shift” rather than just lengthening of the Mn–O_{oxo} bonds.^{11b}

Analysis of the electrochemical properties (Figure S3) of **3** confirms that it is the one-electron oxidation product of **2**. The reduction of **3** by one electron was observed at $E_{1/2} = 0.90$ V ($\Delta E_p = 80$ mV), matching adequately with the one-electron oxidation of complex **2** ($E_{1/2} = 0.92$ V). Also, the second one-electron reduction of complex **3** is observed at $E_{1/2} = 0.17$ V ($\Delta E_p = 70$ mV), which is in agreement with the first one-electron reduction of complex **2** (Mn^{III}₂Mn^{IV}₂ → Mn^{III}₃Mn^{IV}). A reversible redox couple at $E_{1/2} = 1.42$ V ($\Delta E_p = 60$ mV) was observed in the oxidative scan of **3**, which corresponds to one-electron oxidation of **3** (Mn^{III}Mn^{IV}₃ → Mn^{IV}₄). The Mn^{IV}₄ species is yet to be isolated; however, adamantane structures containing only Mn^{IV} ions are known.^{4,12} The chemical reduction of complex **3** by one electron was performed with an equimolar amount of Fe(cp*)₂. The course of reduction was studied by ¹H NMR spectroscopy, demonstrating that the addition of 1 equiv of Fe(cp*)₂ to **3** generates complex **2** in solution (Figure S5), followed by crystallization to regenerate **1** in nearly quantitative yield. The conversion of **1** to **3** and vice versa likely involves several intermediates, as depicted in hypothetical Scheme 1, one of which may represent the structure of **2**.

The observation of quasi-reversible [Mn^{III}₂Mn^{IV}₂]/[Mn^{III}₃Mn^{IV}] reduction in the cathodic scans of **1** (or **2**) at $E_{1/2} = 0.17$ V ($\Delta E_p = 75$ mV), as shown in Figure 2, begged the question of whether a reduced form could be isolated as well. The one-electron reduced form of **1** is thought to have the same oxidation state as the PSII S₀ state (IV,III₃).^{11a} The latter species is known to have a hyperfine-rich EPR spectrum¹³ that can serve as a reference point for attempting to mimic the structural properties of the Mn₄ cluster at the S₀ state. In fact, complex **1** exhibits a parallel polarization EPR signal similar to that of the PSII S₁ state.⁶ Chemical reduction of **1** (and/or **2**) by one electron was carried out in acetonitrile solution using an equimolar amount of either Fe(cp*)₂ or sodium naphthalinide under inert atmosphere. Again, as for the oxidation reaction, an unexpected result was encountered; namely, we

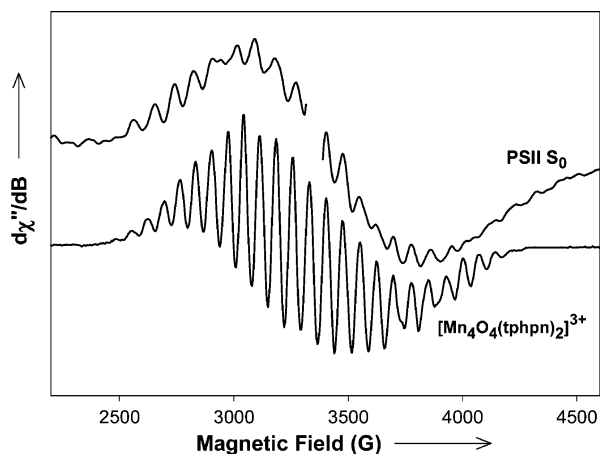


Figure 4. Comparison of the 4 K EPR spectra between the PSII S_0 state and complex **4** in acetonitrile.

observed two different species with the formulation $[\text{Mn}^{\text{III}}_3\text{Mn}^{\text{IV}}(\mu\text{-O})_4(\text{tphpn})_2]^{3+}$ (**4** and **5**), which have easily distinguishable EPR spectra. One of them (**5**) exhibits a 16-line EPR signal at $g \approx 2$ (Figure S8), consistent with a dimer-of-dimers geometry, because in the one-electron reduced form of the dimer-of-dimers structure, the antiferromagnetically coupled $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ dinuclear unit would give rise to an $S = 0$ state, whereas the $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ dinuclear unit would result in an $S = 1/2$ ground state, giving rise to a 16-line EPR spectrum.¹⁴ An analogous 16-line spectrum was observed by Kawasaki et al. when their dimer-of-dimers-type complex, possessing a $[\{\text{Mn}^{\text{III,IV}}_2(\mu\text{-O})_2\}]^{6+}$ core, supported by a similar heptadentate polypyridyl ligand, was oxidized by one electron to yield $[\{\text{Mn}^{\text{III,IV}}_2(\mu\text{-O})_2\}\{\text{Mn}^{\text{IV}}_2(\mu\text{-O})_2\}]^{7+}$, which gives rise to an $S = 1/2$ ground spin state.¹⁵

The spectrum of species **4**, shown in Figure 4, contains a hyperfine-rich signal centered at $g \approx 2$ that bears a strong resemblance to the PSII S_0 state multiline signal.¹³ Mass spectrometry confirms a tetranuclear formulation $[\text{Mn}^{\text{III}}_3\text{Mn}^{\text{IV}}(\mu\text{-O})_4(\text{tphpn})_2]^{3+}$ for **4** (Figure S6) that must have arisen from an isomerization or “shape-shift” process. Cyclic voltammetric (Figure S7) and ^1H NMR studies of **4** indicate that this is most likely the one-electron reduced product of **2**. The close correspondence between EPR spectral properties of **4** and the PSII $\text{Mn}_4 S_0$ state suggests that they possess the same electronic spin topology, and perhaps the same 3D structure as well. To date, only two other tetranuclear model complexes, both generated by γ -irradiation reduction of a Mn_4O_n core complex ($n = 4$ or 6) at 77 K, displayed EPR “multiline” signals with overall spectral width comparable to the multiline signals observed for the Mn_4 cluster in PSII S_0 and S_2 states.¹⁶ However, these complexes are unstable, decaying at temperatures above 190 K. For the first time, our work provides a synthetic multiline cluster, which is stable at room temperature indefinitely in the solid state under inert atmosphere. Structural characterization of **4** has eluded us until now because it slowly transforms in solution to yet a third reduced isomer (**6**) possessing a broad EPR signal (see Figure S9) upon crystallization. The lifetime of **4** in solution is long enough that crystallographic characterization is promising, and this is one central aim of our continuing work.

Our work described here raises the possibility of “shape-shifting” for the PSII Mn_4 cluster. Complex **4** closely replicates the well-resolved hyperfine-structured multiline EPR signal with strikingly similar spectral width and intensity pattern compared to those of

the PSII S_0 state. We have also shown that the dimer-of-dimers structural framework in the $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{IV}}_2$ oxidation state is not stable in solution, as indicated from the spectroscopic studies, and an intramolecular non-redox rearrangement occurs. Upon one-electron oxidation of **1**, an adamantane-shaped complex was isolated and structurally characterized. This transformation accompanies an overall increase in the $\text{Mn}\cdots\text{Mn}$ bond distances, which also occurs during the oxidation of the S_2 state to the S_3 state. While we do not propose the adamantane complex as a structural model for the S_2 state, we do suggest that an intramolecular core conversion process may accompany S_2 -to- S_3 state advancement.

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Supporting Information Available: Crystallographic data of **3** and experimental preparation of the complexes; NMR of **1–3**, ESI-MS of **4**, and electrochemistry of **3** and **4**; EPR spectra of complexes **1**, **2**, **5**, and **6** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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