Modeling the Photosynthetic Water Oxidation Center: Chloride/Bromide Incorporation and Reversible Redox Processes in the Complexes Mn₄Oₓ(X(OAc))₃(dbm)₃ (X = Cl, Br) and (pyH)₃[Mn₄O₃Cl₇(OAc)]

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Synthetic procedures are described that allow conversion of [Mn₄O₂(OAc)₆(py)₂(dbm)₂] (1, dbmH = dibenzoylmethane) to [Mn₄Oₓ(X(OAc))₃(dbm)₃] (X = Cl, 2; X = Br, 3). Treatment of 1 with NBu₄Cl in CH₂Cl₂ or hot MeCN leads to 2 in 5–8% and 35–43% yields (based on dbm), respectively. A higher yield (~88%) is obtained by treating 1 with 4 equiv of Me₂SiCl in CH₂Cl₂. An analogous procedure with 4 equiv of Me₂SiBr in CH₂Br₂ gives 3 in 55% yield. Complexes 2 and 3 are isomorphous, monoclinic space group P2₁/n, T = −155 °C, Z = 4. For 2, a = 13.900(3), b = 22.038(5), and c = 16.518(5) Å and β = 107.80(1)°; for 3, a = 13.644(2), b = 22.190(4), and c = 16.548(3) Å, and β = 106.64(1)°. The structures were solved by direct methods (MULTAN78) and refined on F to R(F) values of 7.85 (7.38) and 7.37 (6.89)% using 2267 and 2809 unique reflections with F > 2.33σ(F) for 2 and 3, respectively. Treatment of [MnₓO₄(OAc)ₓ(py)ₓ](ClO₄)ₓ in MeCN with Me₂SiCl followed by addition of H₂O and acetic acid results in crystallization of (pyH)₃[Mn₄O₃Cl₇(OAc)]·2MeCN (4) in 75% yield (based on Mn). Complex 4 crystallizes in monoclinic space group C2/c with the following cell parameters at −157 °C: a = 37.420(5), b = 13.752(1), and c = 16.139(2) Å, β = 110.33(1), V = 7787.9 Å³, and Z = 8. The structure was solved by direct methods (MULTAN78) and refined on F to R(F) values of 5.74 (7.58)% using 2612 unique reflections with F > 3.0σ(F). The complexes possess a [Mn₄(M₄−O₃−X)₃] distorted cubane core and a 3MnIII,MnIV trapped-valence oxidation-state description. Three AcO− groups bridge each MnIII/MnIV pair, and a chelating dbm− (2 and 3) or two Cl− ions (4) on each MnIII complete peripheral ligation. The pyridinium cations of 4 are involved in hydrogen-bonding interactions with the μ₃−O− and the terminal Cl− ions of the anion.

Variable-temperature solid-state magnetic susceptibility studies show that the magnetic properties of 2 and 3 are very similar: μeff values steadily rise from ~9 μB at room temperature to ~10 μB at 30.0 K and then drop rapidly to ~9.5 μB at 5 K. Fitting of the experimental data for the two complexes to the appropriate theoretical equation yield the following fitting parameters, in the format 2/3: J = J(MnIII⋯MnIV) = −28.4(−30.1) cm⁻¹, η = J(MnIII⋯MnIII) = +8.3(+7.4) cm⁻¹, and g = 1.98(2.0). Both 2 and 3 have S = 9/2 ground states that are well-separated (~180 cm⁻¹) from an S = 7/2 first excited state. The ground state was confirmed by magnetization vs magnetic field studies at several fields and temperatures; fitting of the data allowed the zero-field splitting parameter D to be determined for both complexes. The magnetochemical properties of 4 are very similar to those of 2 and 3, and the fitting parameters were J = −29.1 cm⁻¹, η = +10.2 cm⁻¹, and g = 1.97, giving an S = 9/2 ground state and showing that the hydrogen-bonding interactions of the μ₃−O⁻ ions do not cause a significant change to the exchange parameters or to the electronic structure of the [Mn₄O₄Cl]⁶⁺ core. ¹H NMR spectra of 2−4 in CDCl₃ or CD₃CN solution at ~23 °C are similar and show that the Mn₄ complexes retain their solid-state structure on dissolution in this solvent. X-band EPR spectra of 2 and 3 in CH₂Cl₂/toluene (1:1) glasses at 5 K are also extremely similar, with three main features at g = 11.0, 5.2, and 1.96. Cyclic voltammetry at 100 mV/s and differential pulse voltammetry at 5 mV/s show that both 2 and 3 support a reversible oxidation and two reductions, the first of which is reversible. The reversible processes are at 1.09/1.06 and −0.25/−0.21 V vs ferrocene and show that the [Mn₄O₄X] core can exist at three oxidation levels spanning the 4MnIII to 2MnIII, 2MnIV range. The combined results from 2 and 3 show that the identity of X has minimal influence on the resultant structures, magnetic properties, ¹H NMR and EPR spectral properties, or the redox behavior. Such observations are of interest with regard to the ability of Br⁻ to successfully substitute for Cl⁻ at the photosynthetic water oxidation center and thus maintain the activity of the tetranuclear Mn aggregate toward oxygen evolution.

Introduction

Water oxidation to oxygen gas by the photosynthetic apparatus of green plants and cyanobacteria represents the origin of this gas in the atmosphere and provides a source of protons and reducing equivalents for photosynthesis.¹ ² The site of water oxidation is a tetranuclear, oxide-bridged, manganese cluster with primarily O-based (carboxylate) and low levels of N-based (imidazole) peripheral ligation provided by amino acid side-chain groups (Asp, Glu, His).¹ ² This redox-active water oxidizing complex (WOC) acts as an electron donor to photo-
The Photosynthetic Water Oxidation Center

system II (P680) via the intermediacy of redox-active tyrosine Y₇₅. When four electrons have been transferred, in four one-electron steps, the WOC is reduced back to its lowest oxidation level by the oxidation of water to O₂ and four protons, and is ready for recycling. The oxidation states of the WOC involved in the catalytic cycle are called the Sₙ states (n = 0–4), the subscript n referring to the number of reducing equivalents transferred vis-à-vis the most reduced state S₄.

One intriguing property of the WOC is its absolute requirements for two or three Ca²⁺ ions and several Cl⁻ ions for activity.¹,²,⁴,⁵ The precise roles of these cofactors are unknown. Restricting further discussion to Cl⁻, this ion has been suggested to be bound to the Mn₄, bound to a nearby site such as Ca²⁺, involved in charge neutralization, or involved in some other function not involving binding to Mn.⁴ Interestingly, inactive preparations that lack Cl⁻ cannot be reactivated by addition of Br⁻.⁴,⁵ Whatever the function of Cl⁻ is, it thus appears that it can also be carried out by Br⁻. Other anions will also restore activity, but only to a much lesser extent.⁴,⁵

The high Cl⁻ content of these complexes was clearly inconsistent with available data on the WOC, and therefore we have since sought to alter the peripheral ligation at the MnIII sites of the [Mn₄O₃Cl] core. Although carboxylate variation is readily accomplished by ligand substitution reactions of preformed [Mn₄O₃Clₓ(OAc)ₙ(py)] with more acidic carboxylic acids (e.g., benzoic acid),¹₁ variation of the terminal ligands at the MnIII sites by ligand substitution reactions on preformed [Mn₄O₃Clₓ(OAc)ₙ(py)] has proven difficult, and alternate procedures have been sought.

We herein report the development of a new type of [Mn₄O₃Cl₆]⁺ complex containing completely O-based peripheral ligation, namely, carboxylate and dbm⁻ (dbmH = dibenzoylmethane) groups. In addition, we show that this ligation environment supports reversible redox chemistry in both the oxidizing and reducing directions, behavior not seen with our previous family of [Mn₄O₃Clₓ]⁺ complexes. Further, we have successfully sought the substitution of Br⁻ for Cl⁻ in the [Mn₄O₃Cl⁺] core to probe the effect of the halide identity on the properties of these complexes and to thereby gain some insight into the known ability of Br⁻ to substitute for Cl⁻ in the WOC. We also include, for comparison purposes, the new complex (pyH)₃[Mn₄O₃Cl₆(OAc)]₃ possessing only Cl⁻ terminal ligation at the MnIII. Portions of this work have been previously communicated.¹²,¹³

Experimental Section

Syntheses. Unless otherwise noted, all manipulations were performed under aerobic conditions at ambient temperature using reagents

which is best described as a “tetra-face-capped Mn₄ trigonal prism” or, for convenience, a (highly) “distorted cubane”. The core has C₃ᵥ, virtual symmetry with MnIII⁺...MnIV and MnIII⁺...MnIII distances of ~2.81 and ~3.3 Å, respectively, emphasizing the severe deviation from true cubane (T₃) symmetry. The [Mn₄O₃] trigonal-pyramidal unit was one of the topologies presented by De Rose et al. in their considerations of units consistent with WOC EXAFS data. Our initial products with the above [Mn₄O₃Cl₆]⁺ core were the complexes [Mn₄O₃Clₓ(OAc)ₙ(py)] (R = various), and related species,¹⁰ containing bridging RCO₂ groups across each MnIV-MnIII pair and terminal Cl⁻ and py groups on each MnIII. The WOC EXAFS data have been extremely useful in providing insights into the structure of the WOC.⁵,⁶

EXAFS data for plants and cyanobacteria are very similar.⁶,⁷,⁸,⁹,¹⁰,¹¹

De Rose et al. recently considered topological possibilities for [Mn₄O₃] cores that would be consistent with their most recent EXAFS data and presented 10 structural possibilities ranging from a linear disposition of four Mn atoms to a variety of more condensed arrangements. The authors stated that they prefer a “dimer-of-dimers” topology, but in principle any of the 10 possibilities could be present in the WOC.

As part of our program to obtain synthetic analogues of the WOC, we have developed procedures to a number of tetra-nuclear, oxide-bridged Mn carboxylate clusters.⁶,⁷,⁸,⁹,¹⁰,¹¹,¹² One type

References:

(2) Yocum, C. F. in ref 2, Chapter 4, pp 71–84 and references cited therein.
and solvents as received. CH₂Cl₂ and MeCN for spectroscopic and electrochemical studies were distilled from CaH₂. The complexes [Mn₄O₂(py)(ClO₄)₂] and Mn₂O₂(py)(ClO₄)₂ were available from previous work.

[Mn₄O₂Cl₂(pypr)][(dbm)₄](2). (a) Method 1. Solid Bu₄NCl (0.070 g, 0.25 mmol) was added to a stirred dark brown solution of complex 1 (0.30 g, 0.25 mmol) in CH₂Cl₂ (15 mL). The resultant solution was filtered and the filtrate layered with Et₂O (20 mL) and MeCN (10 mL). After several days, well-formed black crystals were collected by filtration, washed with Et₂O and dried in air; yield was 5–8% based on available dbm. These crystals were suitable for X-ray diffraction studies. Anal. Calcd (Found) for C₅₁H₄₃O₁₅Cl₂·Mn₄: C, 53.5 (53.2); H, 3.7 (3.7); Cl, 19.1 (18.8). Electronic spectrum in CH₂Cl₂: ξ₅₅₀ nm (ε₅₅₀ L mol⁻¹ cm⁻¹): 372 (65 000), 450 (7600), 488 (5470). Selected IR data (Nujol mull): (b) Method 2. To a hot, filtered solution of complex 1 (0.30 g, 0.25 mmol) in MeCN (35 mL) was added solid Bu₄NCl (0.070 g, 0.25 mmol). The resultant solution was stirred for a few minutes and then allowed to cool undisturbed to room temperature. The red-brown crystalline solid that precipitated was collected by filtration, washed with MeCN, and dried in air; the yield was 35–43% based on dbm. The IR spectrum was identical to that for material from method 1. Anal. Calcd (Found) for C₅₁H₄₁O₁₅Cl₂·Mn₄: C, 53.3 (53.6); H, 3.7 (3.7); Cl, 19.1 (18.7). (c) Method 3. To a stirred dark brown solution of complex 1 (0.60 g, 0.50 mmol) in CH₂Cl₂ (25 mL) was added Me₃SiCl (0.10 mL, 0.78 mmol) dropwise to give a dark red-brown solution, and this produced dark brown crystals and a small amount of colorless material. The solids were collected by filtration, washed with absolute EtOH, and the black crystals were washed with Et₂O several days later, black crystals and some white solid had appeared. After several days, well-formed black crystals were collected by filtration, washed with Et₂O and dried in air. The yield was 38% based on dbm. The IR spectrum was identical to that for material from method 1. Anal. Calcd (Found) for C₅₁H₄₁O₁₅Cl₂·Mn₄: C, 53.3 (53.6); H, 3.7 (3.7); Cl, 19.1 (18.7). The sample lost weight during weighing prior to analysis. 

[Mn₄O₂Br₂(OAc)₂(dbm)₄](3). To a stirred dark brown solution of complex 1 (0.60 g, 0.50 mmol) in CH₂Br₂ (20 mL) was added Me₂SiBr (0.10 mL, 0.78 mmol) dropwise to give a dark red-brown solution. This was stirred for a further few minutes and some white precipitate was removed by filtration. The filtrate was layered with Et₂O (40 mL) after several days, black crystals and some white powder had precipitated and were collected by filtration. The white solid was readily removed by washing with a little EtOH; the crystals were further washed with Et₂O and dried in air. The yield was ~88% based on dbm. The IR spectrum was identical to that for material from method 1. Anal. Calcd (Found) for C₅₁H₄₁O₁₅Cl₂·Mn₄: C, 53.3 (53.6); H, 3.7 (3.7); Cl, 19.1 (18.7). (The sample lost weight during weighing prior to analysis.)

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates on a Nicolet Model 510 spectrophotometer; solution UV/visible spectra were obtained using a Hewlett-Packard Model 8452A spectrophotometer. Cyclic voltammograms and differential pulse voltammograms were recorded on an IBM EC225.
but the addition of 1 equiv of NBu₃Cl resulted from a carboxylate abstraction with Me₃SiCl. Thus, treatment of 1 with just 1 equiv of MeCO₂Cl and formation of a higher oxidation state product. Analogous reactions with Br⁻ sources were explored as potential routes to 3. It should be pointed out that there are very few known examples of stable MnIII−Br bonds owing to redox instability, and none with Br⁻ in a system containing MnIV. It was thus uncertain whether 3 would be capable of existence. Treatment of 1 with 1 equiv of NBu₃Br in hot MeCN led to precipitation of a microcrystalline solid whose IR spectrum was almost identical to that of 2 and which therefore appeared to be 3. However, elemental analysis gave a low Br content and a significant Cl content, the latter presumably a contaminant of the NBu₃Br. Rather than seek to purify the latter, we resorted to the reaction of 1 with Me₃SiCl in CH₂Cl₂; this also led to a nicely crystalline product but emphasizes the redox changes is given in eq 2. When MnO₂(C₂H₅O₂)₃(py)₃(dbm)₃ and MnO₂(C₂H₅O₂)(THF)₃(dbm)₃ instead of 1 were treated with 1.5 equiv of Me₃SiCl in CH₂Cl₂, MnO₂(C₂H₅O₂)(THF)₃(dbm)₃ was not obtained; only starting material was recovered. This suggests that the basicity of the carboxylate is yet another factor important to this reaction, with the more basic AcO⁻ appearing to favor the disproportionation and formation of a higher oxidation state product.


data. Variable-temperature magnetic susceptibility data were obtained with a Series 800 VTS-50 SQUID susceptometer (S.H.E. Corp.) operating at an applied magnetic field strength of 10 kG. Diamagnetic corrections were estimated from Pascal’s constants and subtracted from the experimental data to give the molar paramagnetic susceptibilities. The program GENSPIN was used to analyze variable-field magnetization data; the spin of the ground state is set at some quantized value and then the spin Hamiltonian matrix is diagonalized at each magnetic field to least-squares fit the experimental data.

**Results**

**Syntheses.** Previous examples of [Mn₄O₃Cl]⁶⁺-containing complexes (3MnIII-MnIV) were obtained by disproportionation reactions of [MnIII₄O₇]⁻⁻-containing starting materials triggered by carboxylate abstraction with Me₃SiCl. Thus, treatment of [Mn₃(OAc)₃(py)₃]ClO₄ with Me₃SiCl leads to formation of Mn₄O₃Cl₄(OAc)₃(py)₃ (6) in >80% yield based on available MeCO₂Cl. A similar disproportionation reaction but with I provided one route to 2 (vide infra); the latter was first obtained, however, from a reaction of 1 in CH₂Cl₂ with just 1 equiv of NBu₃Cl. This led to slow crystallization of small amounts (<10% yield based on dbm) of pure 2 in a form suitable for crystallography. Complex 1 is stable in CH₂Cl₂ in the absence of Cl⁻. Interestingly, previous work had shown that treatment of 1 in CH₂Cl₂ with NEt₃Cl followed by addition of Et₂O leads to good yields (55−60%) of (NEt₃)[Mn₄O₄(OAc)₁₀(dbm)₁₀]Cl, emphasizing the complexity of the reaction of 1 with Cl⁻ and rationalizing the low yield of 2 in the present work.

With complex 2 identified, higher yield routes were sought. Complex 1 is stable in hot MeCN (its recrystallization medium) but the addition of 1 equiv of NBu₃Cl leads on cooling to improved yields (35−43%) of 2. Even higher yields were obtained when Me₃SiCl was used in place of NBu₃Cl; a ratio dependence study showed that an optimum yield of ~88% resulted from a 1:Me₃SiCl ratio of 1:1.5; the yield dropped to 52% for a 1:0.8 ratio, and to 83% (1:3), 73 (1:4), 52 (1:5), and 41% (1:6) as more Me₃SiCl was used. Repetition of the 1.4 reaction with added dbmH did not improve the yield. The formation of 2 via a disproportionation reaction is supported by the coprecipitation of an off-white byproduct which, on the basis of analyses of such solids in analogous past reactions, is the Mn⁴⁺ product of the disproportionation; the latter is readily removed by washing with EtOH.

Using the above observations, eq 1 can be presented as a summary of the reaction; a simplified form of eq 1 that emphasizes the redox changes is given in eq 2. When MnO₂(C₂H₅O₂)₃(py)₃(dbm)₃ and MnO₂(C₂H₅O₂)(THF)₃(dbm)₃ instead of 1 were treated with 1.5 equiv of Me₃SiCl in CH₂Cl₂, MnO₂(C₂H₅O₂)(THF)₃(dbm)₃ was not obtained; only starting material was recovered. This suggests that the basicity of the carboxylate is yet another factor important to this reaction, with the more basic AcO⁻ appearing to favor the disproportionation and formation of a higher oxidation state product.

Analogous reactions with Br⁻ sources were explored as potential routes to 3. It should be pointed out that there are very few known examples of stable MnIII−Br bonds owing to redox instability, and none with Br⁻ in a system containing MnIV. It was thus uncertain whether 3 would be capable of existence. Treatment of 1 with 1 equiv of NBu₃Br in hot MeCN led to precipitation of a microcrystalline solid whose IR spectrum was almost identical to that of 2 and which therefore appeared to be 3. However, elemental analysis gave a low Br content and a significant Cl content, the latter presumably a contaminant of the NBu₃Br. Rather than seek to purify the latter, we resorted to the reaction of 1 with Me₃SiBr in CH₂Cl₂; this also led to a nicely crystalline product but


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**Table 1. Crystallographic Data for Mn₄O₃X(OAc)₃(dbm)₃ (X = Cl (2) or Br (3)) and (pyH)₃[Mn₄O₃Cl₄(OAc)₃]·2MeCN (4)**

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(a) Schmitt, E. A.; Hendrickson, D. N., unpublished results.
elemental analysis again indicated the presence of both Br and Cl. Finally, the reaction of 1 with Me3SiBr in CH3Br gave highly crystalline complex 3 with the expected IR spectrum, a correct Br analysis, and no Cl content. These observations suggest that the Mn4O3 unit has a much greater affinity for Cl− than for Br−, even to the point that Cl abstraction from CH2Cl2 occurs. On the other hand, the successful attainment of 3 confirms that this desired complex can indeed exist and be stable under normal conditions. Attempts to isolate F−-containing products from reactions of 1 with NBu4F proved unsuccessful; reactions with Me3SiF have not been attempted owing to the strong Si−F bond.

It should be emphasized that eqs 1 and 2 are similar to those previously developed to describe the formation of Mn4O3Cl2-(OAc)3(py)3 (6) from the treatment of [Mn4O6(OAc)6(py)3]ClO4 with Me3SiCl (eq 3).10 This previous work convinced us that the yield of 6 was now acetate/oxide-limited, as implied in eq 3. We subsequently wondered whether addition of H2O and acetic acid to the reaction mixture after [Mn4O6(OAc)6(py)3]ClO4 had been treated with Me3SiCl to trigger disproportionation (and generation of 6) but before crystals of product complex 6 had begun to form might increase the yield of 6 by providing O2− and AcO− sources. Interestingly, this procedure did indeed increase the yield of product, but the latter was 4, not complex 6, i.e., the py groups had been protonated and were present as cations rather than bound to MnIII ions as in 6. Nevertheless, the added H2O and acetic acid undoubtedly increase the yield of [Mn4O6Cl]4+ product by providing O2− and AcO−, and on this basis the obtained yield of 4 is 75% calculated on available Mn and the disproportionation reaction of eq 4, which indicates

\[ 3[Mn(OAc)]^2+ + Cl− → [Mn4O3Cl]6^+ + 4Mn^{3+} + 2Mn^{2+} \]  

(3)

a maximum yield of 4 of 80% based on available Mn; i.e., the yield of 4 is essentially quantitative (∼94%). It is paradoxical to note that this high-yield formation of 4 involves adding a water-sensitive carboxylate-abstraction reagent (Me3SiCl) to [Mn4O6(OAc)6(py)3]ClO4, followed by addition of carboxylate and water back into the reaction mixture.

It should be noted that a number of other tetranuclear Mn complexes with a cubane or distorted-cubane geometry are known, with the vast majority of these being at the MnI4 or MnII4 oxidation levels and containing Mn4X4 (X = Cl, Br, I). Finally, the reaction of 1 with Me3SiF has not been attempted owing to the generation of highly crystalline complex 5.

\[ 5\text{Mn}^{III} \rightarrow 3[\text{Mn}^{II} \text{Mn}^{IV}] + 3\text{Mn}^{III} \]  

(4)

and X(8). The structure consists of a trigonal pyramid of Mn atoms with the μ-O2− ion bridging each of the vertical faces and a μ-X− ion bridging the basal face to give a tetra-face-capped trigonal pyramid that may be described for convenience as a highly distorted [Mn4O3X]6+ cubane unit. Peripheral ligation is provided by three chelating dbm− and three sym-syn-bridging AcO− groups. Charge considerations indicate a 3MnII6MnIV metal oxidation-state description, and metric parameters indicate that apical Mn(4) is the MnIV center. The 3MnII atoms, Mn(2)−Mn(4), are Jahn−Teller (JT) distorted (elongated) as expected for a high-spin d4 ion in near-octahedral geometry, and the JT axes are the ones that include the MnIII−X bonds. The structures of the cores of 2 and 3 are thus similar to those previously reported for other [Mn4O3Cl]6+-containing complexes.10,11 The disposition of the three dbm− groups in 2 and 3 places their six Ph rings in a skirtlike fashion around the basal MnIII face of the trigonal pyramid, and this gives a concave cavity inside which is situated the μ-X− ion. This is shown for 2 as a space-filling stereoview in Figure 3, viewed approximately along the virtual C3 axis.

The structural parameters for 2 and 3 are listed in Tables 2 and 3 in a manner that allows ready comparison. Examination of these tables emphasizes that the two structures are essentially congruent except for the halide region of the molecules. Thus, almost all interatomic distances and angles are within the 6σ criterion except the following: the Mn−Cl distances in 2 (2.641(7)−2.656(7) Å) are significantly shorter than the Mn−Br distances in 3 (2.799(3)−2.807(3) Å); the difference (0.15−0.16 Å) is comparable with the difference in ionic radii (0.12 Å) for six-coordinate X− ions;20b (ii) the Mn−Cl−Mn angles (75.37(19)−75.85(19)°) are larger than Mn−Br−Mn angles (71.43(9)−71.83(9)°), consistent with the longer Mn−Br bonds; and (iii) MnIII−MnIV separations increase very slightly in going from 2 to 3 (3.237(5)−3.264(4) Å vs 3.274(3)−3.286(4) Å), individual changes being at the borderline of statistical significance but appearing to be real. Note, in contrast, that the MnIII−MnIV distances are identical in the two structures.

Complex 4 contains a [Mn(μ3-O)(μ2-Cl)]6+ core essentially identical to that in 2, and with μ-AcO− groups bridging each MnIII−MnIV pair (Figure 4). However, the other peripheral ligands on the MnIII atoms are now all terminally coordinated Cl− ions giving a [Mn4O3Cl4(OAc)3]3− trianion. As for 2 and 3, there is no crystallographically imposed symmetry in 4, but the anion has virtual C3v symmetry. The cations are three pyridinium (pyH+) groups whose protonated nature is clearly evidenced by their participation in hydrogen-bonding interac-


| Table 2. Comparison of Selected Interatomic Distances (Å) for Mn4O3X(OAc)3(dbm)2 (X = Cl (2) or Br (3)) |
|----|----|----|
| 2  | 3  | 3  |
| Mn1–Mn2 2.797(5) 2.804(4) | Mn1–Mn3 2.797(4) 2.786(3) | Mn1–Mn4 2.792(5) 2.793(4) |
| Mn1–Mn4 2.792(5) 2.793(4) | Mn2–Mn3 3.252(4) 3.274(3) | Mn2–Mn4 3.237(5) 3.286(4) |

References:

tions with the anion (Figure 4). Interestingly, the pyH⁺ groups interact with the anion in two different ways: the pyH⁺ group containing N(27) has its N–H vector pointing approximately to the midpoint between Cl(7) and Cl(8), with resultant N–H…Cl distances of 3.401 and 3.344 Å, respectively, indicating a N–H…Cl three-center hydrogen-bonding situation; the pyH⁺ group containing N(33) is similar (although a little more asymmetric), with N(33)…Cl(9) and N(33)…Cl(10) distances of 3.687 and 3.150 Å, respectively. In contrast, the third pyH⁺ group containing N(39) is oriented differently to the other two and has its N–H vector pointing approximately to the midpoint of the Cl(6), Cl(11), and O(14) face, with distances of N(39) from these three atoms of 3.453, 3.522, and 2.855 Å, respectively. In fact, the N(27)…O(12) and N(33)…O(13) distances are 2.866 and 2.970 Å, respectively, and although the N–H–O angles would be rather acute, it is likely that weak N–H…O interactions are present at these two pyH⁺ groups also, rationalizing why all three pyH⁺ groups are so compactly organized about the [Mn₄O₃Cl] core rather than projecting outward or above the plane of six terminal Cl⁻ ions.

**Magnetic Susceptibility Studies.** Variable-temperature, solid-state magnetic susceptibility studies were performed on powdered samples of complexes 2–4 in an applied magnetic field of 10.0 kG and in the temperature ranges of 5.01–300.0 and 5.01–320.0 K, respectively. Plots of effective magnetic moment (μ<sub>eff</sub>) per molecule vs temperature are presented in Figures 5–7, and they can be seen to be similar for the three complexes. For 2, μ<sub>eff</sub> steadily increases from 8.95 μ<sub>B</sub> at 300 K to a plateau value of 9.88 μ<sub>B</sub> at 30.0 K and then decreases sharply below ~12 K to 9.36 μ<sub>B</sub> at 5.01 K. For 3, μ<sub>eff</sub> increases from 9.06 μ<sub>B</sub> at 320 K to 10.13 μ<sub>B</sub> at 30.0 K and then decreases sharply below ~12 K to 9.54 μ<sub>B</sub> at 5.01 K. For 4, μ<sub>eff</sub> increases from 8.87 μ<sub>B</sub> at 320.0 K to 9.95 μ<sub>B</sub> at 11.0 K, whereupon there is a decrease to 9.61 μ<sub>B</sub> at 5.01 K. These data are plotted in Figure 7.

If there were no exchange interactions between the metal ions in a Mn<sup>III</sup>₃∕Mn<sup>IV</sup> complex, the spin-only (g = 2) μ<sub>eff</sub> value would be 9.33 μ<sub>B</sub> and it would be temperature independent. The metal ions are thus clearly involved in magnetic exchange interactions, and the data were therefore fit to the theoretical expression derived previously<sup>10</sup> for the χ<sub>M</sub> vs T behavior of a Mn<sup>III</sup>₃∕Mn<sup>IV</sup> trigonal pyramid of C₃v symmetry. This expression was derived from the spin Hamiltonian of eq 5, where J = J(Mn<sup>III</sup>…Mn<sup>IV</sup>),

\[
\hat{H} = -2J(S_1S_2 + S_1S_3 + S_2S_3) - 2J'(S_2S_3 + S_2S_4 + S_3S_4) \tag{5}
\]

\[
J' = J(Mn<sup>III</sup>…Mn<sup>III</sup>), S₁ = S₂(Mn<sup>IV</sup>) = 3/2 and S₂ = S₃ = S₄ = S(Mn<sup>III</sup>) = 2, by employing an equivalent operator approach based on the Kambe vector coupling method.<sup>20</sup> As described in detail elsewhere,<sup>10</sup> this leads to the eigenvalue expression of eq 6, which gives the energy, E(S₅), of each of the possible total spin states, S₅, of the Mn<sup>III</sup>₃∕Mn<sup>IV</sup> complex, where \( \hat{S}_5 = S_2 + \hat{S}_1 \) and \( \hat{S}_T = S_1 + \hat{S}_A \).

\[
E(S₅) = -J[S₅(S₅ + 1) - S₅(S₅ + 1)] - J'[S₅(S₅ + 1)] \tag{6}
\]

The fits of the experimental χ<sub>M</sub> vs T data to the theoretical expression are shown as solid lines in Figures 5–7: the fitting parameters for 2 are \( J = -28.4 \) cm<sup>-1</sup>, \( J' = +8.3 \) cm<sup>-1</sup>, and \( g = 1.98 \); those for 3 are \( J = -30.1 \) cm<sup>-1</sup>, \( J' = +7.4 \) cm<sup>-1</sup>, and \( g = 2.03 \); and those for 4 are \( J = -29.1 \) cm<sup>-1</sup>, \( J' = +10.2 \) cm<sup>-1</sup>, and \( g = 1.97 \). These values yield an \( S = 3/2 \) ground
state for all three complexes, with $S = \frac{7}{2}$ and $S = \frac{11}{2}$ first and second excited states, respectively. Only data for temperatures $\geq 30$ K were employed in the fits because below this temperature the effects of zero-field splitting (ZFS) become significant and result in the rapid decrease in $\mu_{\text{eff}}$ values.

In order to confirm the spin of the ground state and to determine the magnitude of the ZFS parameter $D$, magnetization ($M$) vs magnetic field ($H$) studies were performed on complexes 2 and 3 at 5.0 (2–4 K), 10.0 (2–30 K), 20.0 (2–4 K), 30.0 (2–4 K), 40.0 (2–4 K) and 50.0 kG (2–30 K). The data are plotted in Figures 8 and 9 as reduced magnetization ($\Delta MH/\Delta T$) vs $H/T$. In the absence of ZFS and at temperatures where only the ground state is populated, the $\Delta MH/\Delta T$ vs $H/T$ plots would follow the Brillouin function, which has a maximum value of $\Delta MH/\Delta T$ of $gS^2$ (i.e., a value of 9 for $S = \frac{7}{2}$ and $g = 2$) at low temperatures and high fields, and the various isofield lines would be superimposed. As can be seen in Figures 8 and 9, the maximum $\Delta MH/\Delta T$ values for 2 and 3 are 8.56 for 2 and 8.51 for 3, values consistent with an $S_T = \frac{7}{2}$ ground state, and the six isofield lines do not superimpose; the latter deviations from the Brillouin function result from ZFS within the $S_T = \frac{7}{2}$ ground state.

The $\Delta MH/\Delta T$ vs $H/T$ data for 2 and 3 were least-squares fit. For each setting of the parameters $g$ and $D$, the spin Hamiltonian matrix was diagonalized. For both complexes, the best fit of the data was found by assuming an isolated ground state with
In the case of 2, the data could be fit with $D = 0.55$ cm$^{-1}$ and $g = 2.03$; the solid lines in Figure 8 show that this fit is good. An equally good fit could be obtained with $D < 0$ with the values $D = -0.40$ cm$^{-1}$ and $g = 2.00$. For complex 3, the data were fit to give $D = 0.55$ cm$^{-1}$ and $g = 2.02$ (solid lines in Figure 9); these data were equally accommodated by $D = -0.35$ cm$^{-1}$ and $g = 1.99$. It is well-known that in fitting variable-field magnetization data for a polycrystalline sample, minima can be found for both $D > 0$ and $D < 0$. In the present case, $D < 0$ is likely the true situation, since $D$ values for mononuclear, octahedral, JT elongated Mn$^{III}$ ions are negative, the three Mn$^{III}$ ions in the [Mn$_4$O$_3$X]$^{6+}$ core are all JT elongated, and the $D$ value for the ground state of the tetranuclear complexes is a vectorial coupling of the $D$ values for the three Mn$^{III}$ ions. A $D < 0$ situation for the [Mn$_4$O$_3$X]$^{6+}$ core is also suggested by the results of AC susceptibility studies.

The values of $J$, $J'$, $g$, and $D$ obtained for 2 and 3 from the above studies may be compared with those obtained for previous examples of [Mn$_4$O$_3$Cl]$^{6+}$-containing complexes with pyridine (or imidazole) and Cl$^-$ as terminal ligands in place of the dbm$^-$ groups. These data are collected in Table 5, which also provides information on the first and second excited states. As can be seen, all [Mn$_4$O$_3$X]$^{6+}$-containing complexes prepared

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*S = 9/2.* In the case of 2, the data could be fit with $D = +0.55$ cm$^{-1}$ and $g = 2.03$; the solid lines in Figure 8 show that this fit is good. An equally good fit could be obtained with $D < 0$ with the values $D = -0.40$ cm$^{-1}$ and $g = 2.00$. For complex 3, the data were fit to give $D = 0.55$ cm$^{-1}$ and $g = 2.02$ (solid lines in Figure 9); these data were equally accommodated by $D = -0.35$ cm$^{-1}$ and $g = 1.99$. It is well-known that in fitting variable-field magnetization data for a polycrystalline sample, minima can be found for both $D > 0$ and $D < 0$. In the present case, $D < 0$ is likely the true situation, since $D$ values for mononuclear, octahedral, JT elongated Mn$^{III}$ ions are negative, the three Mn$^{III}$ ions in the [Mn$_4$O$_3$X]$^{6+}$ core are all JT elongated, and the $D$ value for the ground state of the tetranuclear complexes is a vectorial coupling of the $D$ values for the three Mn$^{III}$ ions. A $D < 0$ situation for the [Mn$_4$O$_3$X]$^{6+}$ core is also suggested by the results of AC susceptibility studies.

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The differences observed between these various complexes are relatively small with the various $J$, $J'$, and $D$ values being of comparable magnitude. In all cases, the exchange interactions gauged by $J$ and $J'$ are antiferromagnetic and ferromagnetic, respectively, with the former being of greater strength by a factor of 2–4.

1H NMR Spectroscopy. Proton NMR studies on complexes 2 and 3 have been carried out to probe their identity and stability in solution. Owing to the limited solubility of these complexes except in chlorinated hydrocarbons, these studies were performed in CDCl$_3$ solution. The two complexes give essentially superimposable spectra, and only the spectrum for complex 3 is shown in Figure 10; the number of resonances is consistent with effective $C_3v$ symmetry in solution and, therefore, retention of the solid-state structure on dissolution in this solvent. The chemical shifts are listed in Table 6. The MeCO$_2^-$ resonance at $\delta \approx 42$ ppm is diagnostic for this group attached to the $[\text{Mn}_4\text{O}_3\text{Cl}]^{6+}$ core. The dbm signals were assigned by consideration of relative broadnesses and integration ratios; the dbm methine proton is dramatically broadened and paramagnetically shifted downfield to $\delta \approx 79$ ppm, consistent with its close proximity to the metal centers. Integration of the two signals at $\delta = 5.1$ and $\delta = -1.7$ ppm gave a 2:1 ratio.
and it is thus obscured by the solvent impurity peaks at 39.0 ppm. The chemical shifts in ppm referenced to TMS using the solvent CHCl₃ are centered at δ ≈ 2 ppm. In the 1H NMR spectra of the complexes measured in CDCl₃, the δ values are essentially identical to those for the parent complexes with py/Cl⁺⁺⁻⁻. Complexes such as [Mn₄O₂X(OAc)₃(dbm)₃]⁺⁺⁺⁺ are thus members of the electron-transfer series defined by eq 7, which includes the potentials for 2. On the electrochemical time scale at least, the [Mn₄O₂X]⁺⁺⁺⁺ core is stable in three oxidation levels spanning 4MnIII to 2MnIII,2MnIV. Controlled-potential electrolyses experiments on these and a variety of other Mn₄ species are currently in progress in an attempt to isolate oxidized and reduced species and assess the level of structural similarity or difference with the parent compound.

Processes, the i/i² ratios are ~1 and plots of i/i² vs ν² are linear in the scan rate (ν) range of 20–200 mV/s, indicating diffusion-controlled processes. The peak separations for the reversible oxidation (200 mV) and reduction (180 mV) in Figure 12 may seem large but they are comparable with the ferrocene/ferrocenium one-electron couple under the same conditions (190 mV). Complex 4 shows only irreversible processes.

Complexes 2 and 3 are thus members of the electron-transfer series defined by eq 7, which includes the potentials for 2. On the electrochemical time scale at least, the [Mn₄O₂X]⁺⁺⁺⁺ core is stable in three oxidation levels spanning 4MnIII to 2MnIII,2MnIV. Controlled-potential electrolyses experiments on these and a variety of other Mn₄ species are currently in progress in an attempt to isolate oxidized and reduced species and assess the level of structural similarity or difference with the parent compound.

It is interesting to note that the potential of the 4MnIII/3MnIII,2MnIV couple (−0.25 V for 2) is significantly more negative than for the same process in the [Mn₄O₂X]⁺⁺⁺⁺-containing complexes such as 1 (+0.61 V in CH₂Cl₂), (NBu₄)[Mn₄O₂(O₃CPh)₇] (±0.48 V in MeCN), and (NBu₄)[Mn₄O₂(O₃CPh)₈] (±0.33 V in CH₂Cl₂), which also contain dbm. These data demonstrate the dramatic stabilization (by ≥ 570 mV) of a higher oxidation state Mn₄ complex by inclusion.

References:

Table 6. ¹H NMR Data* for Complexes 2–4

<table>
<thead>
<tr>
<th>Proton</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>para H</td>
<td>−1.52</td>
<td>−1.65</td>
<td></td>
</tr>
<tr>
<td>meta H</td>
<td>5.08</td>
<td>5.09</td>
<td></td>
</tr>
<tr>
<td>ortho H</td>
<td>no</td>
<td>no</td>
<td>1.94</td>
</tr>
<tr>
<td>MeCO₂⁻</td>
<td>42.4</td>
<td>42.3</td>
<td>39.0</td>
</tr>
<tr>
<td>CH</td>
<td>78.1</td>
<td>79.3</td>
<td></td>
</tr>
</tbody>
</table>

In CDCl₃ (2, 3) or CD₂CN (4) solution at −23 °C; quoted numbers are chemical shifts in ppm referenced to TMS using the solvent CHCl₃ (δ = 7.26 ppm) or CHD₂CN (δ = 1.94 ppm) signal as an internal standard. * no, not observed (obscured by impurities).

Figure 11. X-band EPR spectrum of 2 in a CH₂Cl₂/toluene (1:1) glass at 5 K.

Figure 12. Cyclic voltammogram at 100 mV/s for 2 (1.0 mM) in CH₂Cl₂. The bottom scan emphasizes the reversibility of the first reduction. Potentials are vs ferrocene/ferrocenium.

The Photosynthetic Water Oxidation Center

of a third O$_2^-$ bridge and an X$^-$ ion, i.e., the [Mn$_4$O$_3$Cl] vs [Mn$_4$O$_2$] cores.

**Discussion**

The reactions of the 4Mn$^{III}$ complex 1 with Cl$^-$ in hot MeCN or Me$_3$SiCl in CH$_2$Cl$_2$ provide convenient synthetic access to the new complex 2 via a disproportionation reaction. The yields are good, and the purity of the product is high. Use of Me$_3$SiBr in CH$_2$Br$_2$ provides an equally convenient route to the Br$^-$ analogue 3. The mechanisms of these reactions are undoubtedly complex, probably involving a variety of species in equilibrium in solution, and the successful isolation of 2 and 3 in satisfactory purity is likely due to their low solubility, which causes them to crystallize out from the reaction solution. Complex 4, formed by a slightly modified version of the procedure that originally gave Mn$_4$O$_3$(OAc)$_3$(py)$_3$,10 is a very rare example of a charged [Mn$_3$O$_3$(Cl)]$^{5+}$ complex. We had hoped that it might have increased solubility, allowing more detailed studies in solution, but this was not the case, probably due to the extensive hydrogen bonding between the anion and the pyH$^+$ cations and the consequent tight ion pairing.

The preparation of complexes 2 and 3 provides the first examples of the [Mn$_4$O$_3$X]$^{6+}$ (X = Cl$^-$, Br$^-$) in a totally O-based ligation environment. In this regard, the ligation is now more biologically relevant to that about the WOC of PSII O$_2$-based ligation environment. In this regard, the ligation is now more biologically relevant to that about the WOC of PSII O$_2$-based ligation environment.

The consequential tight ion pairing.

The electronic structure of these complexes is dominated by the electronic structure of the core. This further suggests that the α-superexchange pathway involving the X$^-$ ions and the singly-occupied Mn$^{III}$ d$_z^2$ magnetic orbitals (taking the Mn$_{III}$...X directions as the z axes) is not the dominant pathway controlling the Mn$_{III}$...Mn$_{III}$ exchange interactions, presumably because the X$^-$ ions lie on JT elongation axes that decrease overlap between α- (and γ-) symmetry orbitals on the Mn$^{III}$ and X$^-$ atoms. Thus, superexchange pathways involving the oxide bridges would appear to control the Mn$^{III}$...Mn$^{III}$ (and Mn$^{III}$...Mn$^{IV}$) exchange interactions. The incorporation of only terminal Cl$^-$ ions at the Mn$^{III}$ ions (complex 4) again causes only minor changes to the properties of the complex.

The characterization of 2, 3, and 4 brings to an end one aspect of our study of the magnetic properties of [Mn$_4$O$_3$(X$_2$O$_2$)(Cl)$_3$] complexes with the distorted-cubane core of C$_{3v}$ symmetry; we have now varied X (Cl, Br), R (Me, Et, Ph, substituted Ph), and L (three Cl/3 py, five Cl/HIm, six Cl, three dbm, where HIm is imidazole).10,11 The structure of the cores of these various complexes are approximately invariant, as are the magnetic properties, which are dominated by the oxide bridges. As a result, all these complexes have well-isolated S = 9/2 ground states, with the small changes to $J_{33}$ and $J_{44}$ as a function of X, R, and L affecting only the precise energy separations to the excited states. What are dramatically affected, however, are the redox properties of the complexes, which are sensitive to the peripheral L ligands: 2 and 3 are the only ones to support reversible redox properties, emphasizing the importance of the peripheral ligation to the ability of Mn$_4$/O/RCO$_2^-$ clusters to adopt multiple oxidation states; this is clearly of importance to the continuing attempts to understand the WOC, a multielectron redox system, and to devise and synthesize an accurate structural and functional model. Complexes 2 and 3 also provide a clear demonstration that Br$^-$ can substitute for Cl$^-$ in a tetranuclear Mn$_4$/O/RCO$_2$ aggregate without affecting structural properties or redox potentials, and this is of interest when compared with the recognized ability1,2 of Br$^-$ to support O$_2$ evolution by the WOC in place of Cl$^-$. Presumably, the structure and the redox capability of the WOC are two of the most important parameters affecting the activity of this multielectron, biological redox catalyst. The present work provides a precedent for believing that Br$^-$ can both structurally substitute for Cl$^-$ (i.e., allow maintenance of the same architecture of the WOC as obtains with Cl$^-$) and support the same redox changes at essentially equivalent potentials that are necessary for oxygen evolution.

The $S = 9/2$ ground state possessed by the [Mn$_4$O$_3$(X)$_2$]$^{6+}$ complexes contrasts with the $S = 1/2$ or $5/2$ EPR signals exhibited by the WOC in its $S_2$ oxidation level.12,26–28 Our systematic variation of peripheral bridging RCO$_2^-$ and terminal L groups, as well as bridging ion X, has now demonstrated that perturbations to the C$_{3v}$ symmetry [Mn$_4$O$_3$] subcore are required before a change in ground state $S$ value might prove possible. The precise structure of the WOC is currently uncertain, and our present and previous work demonstrates that if the [Mn$_4$O$_3$(X)] complexes are structurally related to the Mn$_4$ aggregate of the WOC, then the latter must have a [Mn$_4$O$_3$] core that is more distorted by environmental effects than is observed in our high-symmetry model complexes. Such distortions to the [Mn$_4$O$_3$] core (which need not be large in an absolute sense) that involve changes to the Mn$_{III}$...Mn$_{III}$ angles could significantly affect the various exchange parameters that determine the ground-state, and provide a feasible means by which the ground state $S$ value could conceivably change.10,11 A more detailed consideration of how ground state $S$ might vary in such lower-symmetry Mn$_4$ units (i.e., severely distorted versions of the [Mn$_4$O$_3$(X)] unit) will be provided in the next paper in this series involving the properties of a new family of [Mn$_4$O$_3$]$^{1+}$ complexes.22a,b


Of course, the face-capped trigonal-pyramidal [Mn₄O₃] unit is only one of the topological possibilities suggested by DeRose et al. as being consistent with EXAFS data. Indeed, the topology favored by EXAFS authors is a “dimer-of-dimers” structure involving a more “open” or extended arrangement of two [Mn₂(µ-O)₂] units. While it may be favored on EXAFS grounds, the dimer-of-dimers model also suffers from a difficulty in rationalizing the \( S = \frac{5}{2} \) state \((g = 4.1\) EPR signal) of the WOC at the \( S_2 \) level. Solomon, Armstrong, and co-workers, in their report of the magnetic properties of [Mn₂O₂(tpphn)]³⁺, have warned of the difficulty in explaining how such a dimer-of-dimers arrangement could yield the \( S = \frac{5}{2} \) \( S_2 \) state of the WOC that is responsible for the \( g = 4.1 \) EPR signal. Similarly, Girerd and co-workers, in their analysis of the complex [Mn₃O₆(bpy)₆]⁴⁺ with an extended [MnO₂MnO₂MnO₂Mn] conformation, have concluded that the only way to achieve a \( S = \frac{5}{2} \) ground state would be to have (i) (unprecedented) ferromagnetic couplings within a [Mn₂(µ-O)₂]⁴⁺ unit or (ii) (also unprecedented) strong ferromagnetic interactions between the two outermost Mn ions of the extended Mn₄ unit. These authors warned that it is not clear how ferromagnetic interactions could arise in a [Mn(µ-O)₂Mn]⁴⁺ unit. The other topological possibilities consistent with EXAFS data are not known in model complexes in discrete form at the biologically relevant oxidation levels (≥III), and their magnetic properties cannot therefore be assessed at the present time.

In summary, it appears fair to say that at the present time there is no theoretical structure or known synthetic complex that can be thought of as an exact model of the WOC, i.e., that is consistent with all the combined EXAFS, magnetic, EPR, and other known properties of this complicated biological metallosite. The [Mn₄O₆X] aggregates are one of the only very few tetranuclear complexes reasonably consistent with EXAFS data that have been prepared, and as such we believe their continued study to be warranted, including their use to investigate the sensitivity of electronic structure and other properties of Mn₄ clusters to changes in environmental influences and core symmetry (distortion).

Future work is directed toward more significant perturbations of the [Mn₄O₆X]⁴⁺ core, including its isolation at other oxidation levels or with a more distorted core, and preparing versions where X is F (an inhibitor of the WOC), other small anions, or absent altogether. Preliminary results along these directions have recently been communicated.

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Supporting Information Available: Complete listings of crystallographic data, fully labeled figures, bond lengths and angles, and thermal parameters for complexes 2–4 (48 pages). Ordering information is given on any current masthead page.