Towards a synthetic model of the photosynthetic water oxidizing complex: [Mn$_3$O$_4$(O$_2$CMe)$_4$(bpy)$_2$] containing the [Mn$^{IV}$$_3$(μ-O)$_4$]$^{4+}$ core

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The reaction at the water oxidizing complex (WOC) of green plants and cyanobacteria represents the terminal electron donor to photosynthesis, and is the source of essentially all the O$_2$ gas in this planet’s biosphere.$^1$ Water oxidation to O$_2$ is a four-electron process (eqn. 1), and the WOC in its various oxidation levels (the so-called S$^n$-states, n = 0 to 4$^+$$^4$) thus acts as a storage site for oxidizing equivalents generated by the photoinduced coupling of the substrate water molecules. The WOC comprises a tetranuclear, oxo-bridged Mn cluster whose precise structure is still unclear, even with preliminary crystallographic results available.$^2$ However, EXAFS studies have narrowed down the Mn$_4$ topological possibilities,$^3$ and detailed EPR/ENDOR$^6$ and DFT computational$^7$ studies have narrowed these further to the currently favoured combination of a [Mn(μ-O)$_2$]Mn(μ-O)$_2$Mn$^{IV}$ unit and a fourth, more-loosely connected (‘dangler’) Mn ion. Some obvious possibilities are shown.

Clearly, the synthesis and study of such currently unknown species would be invaluable to allow comparison of their data with those of the WOC. This would also allow reactivity of relevance to the native system to be explored. We herein report with those of the WOC. This would also allow reactivity of species would be invaluable to allow comparison of their data in this planet characterized by X-ray crystallography and magnetochemistry.

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Clearly, the synthesis and study of such currently unknown species would be invaluable to allow comparison of their data with those of the WOC. This would also allow reactivity of relevance to the native system to be explored. We herein report a breakthrough in this regard with the synthesis of the Mn$_3$O$_4$(O$_2$CMe)$_4$(bpy)$_2$ complex, which usually have values of > 2.7 Å and > 95°, respectively.$^{11,12}$ However, Mn$^{−}$Mn distances of 2.58–2.64 Å and Mn$^{−}$O$^{−}$Mn angles of < 95° are typical of dinuclear complexes with triply-bridged, non-planar [Mn$_2$(μ-O)$_2$(μ-O$^2$CR)$_2$] cores,$^13$ as also found in 2. The bridging O$^2$− ions display a significant trans influence, and at Mn(2) two Mn–O$^2$− bonds are trans to each other and their resulting lengths (av. 1.869 Å) are noticeably longer than the other Mn(2)–O$^2$− bonds (av. 1.820 Å). Finally, complex 2 crystallizes as dimers formed by strong π-stacking interactions between the bpy group on Mn(1) and the analogous bpy on the adjacent molecule (bpy⋯bpy separation = 3.4 Å).

The magnetochromical properties of 2 were investigated on powdered samples by dc magnetic susceptibility studies in the 1.7–300 K range in fields up to 7 Tesla. The Heisenberg spin Hamiltonian for the exchange-coupled [Mn$_4$O$_4$] core is given by eqn. 2.

$$H = -2J[S_1S_2 + S_3S_4] - 2S_1S_3$$

using the numbering scheme of Fig. 1, where $S_1 = S_2 = S_3 = 3/2$, and it is assumed that $J_{12} = J_{23} = J$. The eigenvalues of eqn. 2 are given in eqn. 3, where $S_T = S_1 + S_3$, $S_T = S_1 + S_2 + S_3$, and $S_T = S_3 + S_4$.

$$E(S_T, S_T) = -J[S_T(S_T + 1) - S_3(S_3 + 1) - J][S_T(S_T + 1)]$$

and $S_T$ is the total spin of complex 2. There are twelve $S_T$ states ranging in value from $S_T = 1/2$ to 9/2. Use of eqn. 3 and the van Vleck expression yields a theoretical $X_M$ vs. T expression for 2, which was used to fit the experimental $X_M$ data collected at 5 K (Fig. 2), giving $J = -24.6$ cm$^{-1}$, $J = 8.2$ cm$^{-1}$, $g = 1.98$ and $p = 0.027$, with a temperature independent paramagnetism held constant at 600 × 10$^{-6}$ cm$^3$ K mol$^{-1}$; $p$ is the fraction of paramagnetic impurity, assumed to be mononuclear Mn$^{II}$.

![Fig. 1 ORTEP representation at the 50% probability level of 2. Selected distances (Å); Mn(1), Mn(2), Mn(3), Mn(4), O(1), O(2), O(3), O(4), O(5), O(6), O(7), O(8), O(9), O(10), O(11), O(12).](image-url)
fitting model takes no account of the dimerization of 2, and an uncertainty of ±10% is consequently estimated in J and J'. 14 The obtained values indicate that 2 has a well-isolated S = 3/2 ground state (the S = 3/2, 1/2 state) with a S = 1/2 (|1/2, 2 > and S = 5/2, |5/2, 3 >) degenerate first excited state at 123 cm⁻¹ above the ground state. In order to independently confirm the S = 3/2 ground state, magnetization vs. field and temperature data were collected and fit by a matrix diagonalization method that assumes only the ground state is populated and also includes axial zero-field splitting (DS). The data are plotted as M/Ni₂⁺ vs. H/T in Fig. 3 (N is Avogadro’s number and µΩ is the Bohr magneton), and the fit (solid line) gave S = 3/2, D = 0.56(5) cm⁻¹ and g = 1.88. An equally good fit was obtained with D = −0.50(5) cm⁻¹. Complex 2 clearly has an S = 3/2 ground state.

The J value of −24.6 cm⁻¹ would be unusual for complexes with a planar [MnIV₂(μ-O)₂]⁴⁺ unit for which J is normally −78 to −200 cm⁻¹. 12 A magnetostuctural correlation has been observed between J and the Mn–O–Mn angle in planar [MnV₂(μ-O)₂]⁴⁺ complexes where there are no additional bridging ligands, 12 but not for complexes with a triply-bridged [MnIV₂(μ-O)(μ-O₂CR)]⁻ core as in 2, which contain a non-planar [MnIV₂(μ-O₂CR)]⁻ rhomb. Indeed, these latter [MnO₂(O₂CR)]⁻ complexes, whose MnO₂ units are non-planar due to a folding along the O–O vector caused by the carboxylate bridge, have much weaker J values; for example, J = −43.7 cm⁻¹ for [MnO₂(C₂O₄)(bpy)₂(H₂O)]₃⁺. 15 The even weaker value for the [MnO₂(O₂CR)]⁻ units in 2 can reasonably be attributed to their fused nature, and the resulting Mn–O bond lengthening by the trans influence noted above decreasing the superexchange interaction via the bridging oxide ions.

Various reactions of 2 are currently being explored, including those with mononuclear MnIII and MnIV species to introduce a fourth Mn into the complex and identify synthetically attainable Mn₄ topologies and their properties. The weak J value determined for 2 might also be relevant to the question of how the WOC can readily exist with various ground state spin values; for example, in the MnIII₃MnV S = 1/2, 5/2 and 5/2 ground states have been reported. 16, 17 Attachment of a MnII ion to one or more μ-O²⁻ ions of 2 (e.g. to give C, D, or similar) would introduce new antiferromagnetic MnIII···MnIV (J₄a, J₄b) exchange interactions likely comparable in magnitude to J. This sets up a triangular, spin-frustrated system where the ground state becomes very sensitive to the relative strengths of the competing antiferromagnetic exchange interactions J, J₄a and J₄b, and capable of giving a ground state of S = 1/2, 3/2, 5/2 or higher. Such spin frustration in tetravalent Mn complexes was originally identified many years ago. 18 For example, [MnIII₂O₂(C₂O₄)(bpy)₂]⁺ has a S = 3 ground state even though all interactions are antiferromagnetic, and [MnIV₂O₂(C₂O₄)(bpy)₂] complexes have S = 5/2 or 7/2 ground states depending on the R group and the relative strengths of the antiferromagnetic exchange parameters. 19 Thus, any observed S = 2 state could be similarly obtained, without having to invoke ferromagnetic MnIV interactions, protonation of O²⁻ ions bridging MnV ions, or similar. The isolation and magnetic properties of 2 may thus represent an important step in understanding this important biological site, and tetravalent derivatives are thus very actively being pursued.

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Notes and references

9. Crystal data for 2. MeCO₂H: C₁₂H₁₄Mn₃N₄O₁₄ (excl. water), 83.47 g mol⁻¹, monoclinic, P2₁/c, a = 16.059(5), b = 15.377(2), c = 14.872(3) Å, β = 101.648(16), V = 3597.1(17) Å³, Dcalc = 1.546 g cm⁻³, T = 110 K. The structure was solved using SHELX-92 and refined on F with SHELXL-97 using all data. Hydrogen atoms were included in fixed, calculated positions and refined using a riding model with isotropic thermal parameters. The final refinement parameters R₁ and wR₂ were 4.91 and 13.89, respectively.
10. Other Mn₄O₆⁺ complex is known but is unpublished. G. C. Dismukes, personal communication.