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Towards a synthetic model of the photosynthetic water oxidizing complex: $[Mn_3O_4(O_2CMe)_4(bpy)_2]$ containing the $[Mn^{IV}{}_3(\mu\text{-}O)_4]^{4+}$ core

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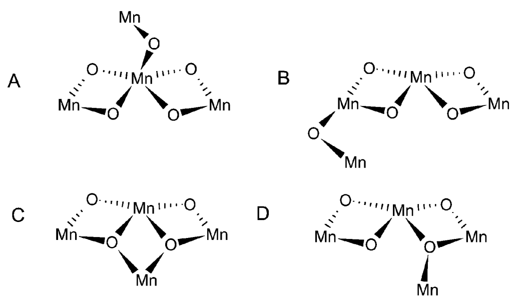
The 3 Mn^{IV} title compound has been prepared and characterized by X-ray crystallography and magnetochemistry; the complex contains a $[Mn(\mu\text{-}O)_2Mn(\mu\text{-}O)_2Mn]^{4+}$ core and possesses an $S = 3/2$ ground state.

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.[1–3] 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

$$2\,H_2O - 4\,e^- \rightarrow O_2 + 4\,H^+ \qquad (1)$$

for oxidizing equivalents generated by the photoinduced electron transfer at the Photosystem II reaction centre, as well as acting as the site of binding, deprotonation and oxidative coupling of the substrate water molecules. The WOC comprises a tetranuclear, oxide-bridged Mn cluster whose precise structure is still unclear, even with preliminary crystallographic results available.[5] 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 $[Mn(\mu\text{-}O)_2Mn(\mu\text{-}O)_2Mn]$ 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 a breakthrough in this regard with the synthesis of the $[Mn_3O_4]$ unit common to the above structures in the complex $[Mn_3O_4(O_2CMe)_4(bpy)_2]$ that also contains multiple sites suitable for attachment of a fourth Mn ion.

The reaction of 8.35 equivalents of 2,2-bipyridine (bpy) with $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ (**1**)[8] in $MeCN/CH_2Cl_2/MeCO_2H$ (25:2:1.5 v/v) gave a dark brown solution. After 15 min, this was filtered and the filtrate maintained for 2 days at room temperature to give X-ray quality, black crystals of $[Mn_3O_4(O_2CMe)_4(bpy)_2]\cdot MeCO_2H\cdot xH_2O$ (**2**) in 10% yield. The structure[9,10] of **2** (Fig. 1) contains a $[Mn^{IV}(\mu\text{-}O)_2Mn^{IV}(\mu\text{-}O)_2Mn^{IV}]^{4+}$ core that is the fusion at central Mn(2) of two familiar $[Mn_2(\mu\text{-}O)_2]$ rhombs, each of which also has a bridging *syn,syn*-$MeCO_2^-$ group. Octahedral coordination at each terminal Mn(1) and Mn(3) centre is completed by a chelating bpy and a monodentate $MeCO_2^-$ group. The $MeCO_2H$ molecule of crystallization is hydrogen-bonded to the $MeCO_2^-$ ligand on Mn(1) (O(14)···O(4), 2.569(4) Å). The Mn···Mn distances and Mn–O–Mn angles (average 2.663Å and 94.37°) are smaller than normally seen in planar $[Mn_2(\mu\text{-}O)_2]^{4+}$ species, which usually have values of > 2.7Å and $> 97°$, 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 $[Mn_2(\mu\text{-}O)_2(\mu\text{-}O_2CR)]$ 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 magnetochemical 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 $[Mn_3O_4]$ core is given by eqn. 2,

$$H = -2J[\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3] - 2J'\hat{S}_1\hat{S}_3 \qquad (2)$$

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 $\hat{S}_A = \hat{S}_1 + \hat{S}_3$, $\hat{S}_T = \hat{S}_A + \hat{S}_2$,

$$E(S_T,S_A) = -J[S_T(S_T + 1) - S_A(S_A + 1)] - J'[S_A(S_A + 1)] \qquad (3)$$

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 equation yields a theoretical χ_M *vs.* T expression for **2**, which was used to fit the experimental χ_M data collected at 5 kG (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}. The

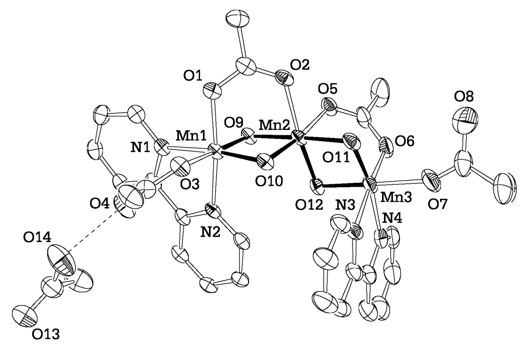


Fig. 1 ORTEP representation at the 50% probability level of **2**. Selected distances (Å): Mn(1)..Mn(2) 2.660(1), Mn(2)..Mn(3) 2.667(1), Mn(1)–O(9) 1.782(2), Mn(1)–O(10) 1.785(2), Mn(2)–O(9) 1.863(2), Mn(2)–O(10) 1.828(2), Mn(2)–O(11) 1.876(2), Mn(2)–O(12) 1.813(2), Mn(3)–O(11) 1.774(3), Mn(3)–O(12) 1.803(2).

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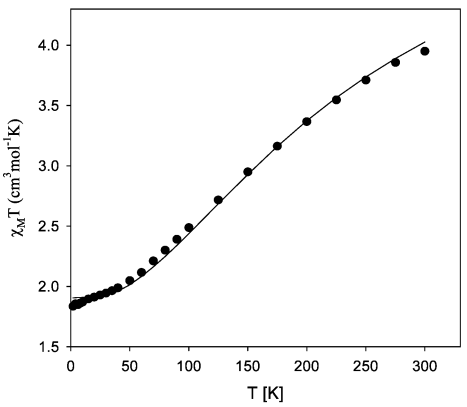

Fig. 2 Plot of $\chi_M T$ *vs.* T for **2**. The solid line is the fit of the data to the theoretical equation.

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 $S_T = 3/2$ ground state (the $|S_T, S_A> = |3/2, 3>$ state) with a $S_T = 1/2$ ($|1/2, 2>$) and $S_T = 5/2$ ($|5/2, 3>$) degenerate first excited state at 123 cm^{-1} above the ground state. In order to independently confirm the $S_T = 3/2$ 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_z^2). The data are plotted as $M/N\mu_B$ *vs.* H/T in Fig. 3 (N is Avogadro's number and μ_B is the Bohr magneton), and the fit (solid line) gave $S_T = 3/2$, $D = 0.56(5)$ cm^{-1} and $g = 1.88$. An equally good fit was obtained with $D = -0.50(5)$ cm^{-1}. Complex **2** clearly has an $S_T = 3/2$ ground state.

The J value of -24.6 cm^{-1} value would be unusual for complexes with a planar $[Mn^{IV}_2(\mu\text{-}O)_2]^{4+}$ unit for which J is normally -78 to -200 cm^{-1}.[12] A magnetostructural correlation has been observed between J and the Mn–O–Mn angle in planar $[Mn^{IV}_2(\mu\text{-}O)_2]^{4+}$ complexes where there are no additional bridging ligands,[12] but not for complexes with a triply-bridged $[Mn^{IV}_2(\mu\text{-}O)_2(\mu\text{-}O_2CR)]^{4+}$ core as in **2**, which contain a non-planar $[Mn^{IV}_2(\mu\text{-}O)_2]^{4+}$ rhomb. Indeed, these latter $[Mn_2O_2(O_2CR)]^{4+}$ complexes, whose Mn_2O_2 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 $[Mn_2O_2(O_2CMe)(bpy)_2(H_2O)_2]^{3+}$.[15] The even weaker value for the $[Mn_2O_2(O_2CR)]$ 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.

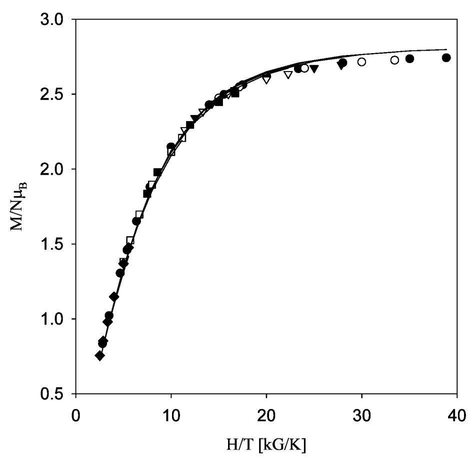

Fig. 3 Plot of $M/N\mu_B$ *vs.* H/T for **2** in the range 1.75 to 10.0 K in fields of 2(□), 3(■), 4(▽), 5(▼), 6(○) and 7(●) Tesla. The solid lines are the fit.

Various reactions of **2** are currently being explored, including those with mononuclear Mn^{III} and Mn^{IV} species to introduce a fourth Mn into the complex and identify synthetically attainable Mn_4 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 Mn^{III},$3Mn^{IV}$ S_2 state, $S = 1/2$, 5/2 and $\geq 5/2$ ground states have been reported.[1,2,16,17] Attachment of a Mn^{III} ion to one or more μ-O^{2-} ions of **2** (*e.g.*, to give C, D, or similar) would introduce new antiferromagnetic $Mn^{III}\cdots Mn^{IV}$ (J_{34}, J_{34}') 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, J_{34} and J_{34}', and capable of giving a ground state of $S = 1/2$, 3/2, 5/2 or higher. Such spin frustration in tetranuclear Mn complexes was originally identified many years ago.[18] For example, $[Mn_4O_2(O_2CMe)_7(bpy)_2]^+$ has a $S = 3$ ground state even though all interactions are antiferromagnetic, and $[Mn_4O_2(O_2CR)_7(bpy)_2]$ 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 Mn^{IV}_2 interactions, protonation of O^{2-} ions bridging Mn^{IV} ions, or similar. The isolation and magnetic properties of **2** may thus represent an important step in understanding this important biological site, and tetranuclear derivatives are thus very actively being pursued.

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Notes and references

1 R. D. Britt, in *Oxygenic Photosynthesis: The Light Reactions*: ed. D. Ort and C. F. Yocum, Kluwer Academic, Dordrecht, The Netherlands, 1996, pp. 137.
2 R. J. Debus, *Biochim. Biophys. Acta*, 1992, **1102**, 269.
3 V. K. Yachandra, K. Sauer and M. P. Klein, *Chem. Rev.*, 1996, 2927.
4 B. Kok, B. Forbrush and M. McGloin, *Photochem. Photobiol.*, 1970, **11**, 457.
5 A. Zouni, H.-T. Witt, J. Kern, P. Fromme, N. Krauss, W. Saenger and P. Orth, *Nature*, 2001, **409**, 739.
6 J. M. Peloquin, K. A. Campbell, D. W. Randall, M. A. Evanchik, V. L. Pecoraro, W. H. Armstrong and R. D. Britt, *J. Am. Chem. Soc.*, 2000, **122**, 10926.
7 P. E. M. Siegbahn, *Inorg. Chem.*, 2000, **39**, 2923.
8 T. Lis, *Acta Crystallogr., Sect. B*, 1980, **36**, 2042.
9 *Crystal data* for **2**·$MeCO_2H\cdot xH_2O$: $C_{30}H_{32}Mn_3N_4O_{14}$ (excl. water), 837.42 g mol^{-1}, monoclinic, $P2_1/c$, $a = 16.059(5)$, $b = 15.377(4)$, $c = 14.872(3)$ Å, $\beta = 101.648(16)°$, $Z = 4$, $V = 3597.1(17)$ Å^3, $D_{calc} = 1.546$ g cm^{-3}, $T = 110$ K. The structure was solved using SIR-923 and refined on F^2 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 13.39%, respectively. CCDC 189067. See http://www.rsc.org/suppdata/cc/b2/b26302f/ for crystallographic data in CIF or other electronic format.
10 Another $[Mn_3O_4]^{4+}$ complex is known but is unpublished. G. C. Dismukes, personal communication.
11 L. Que and A. E. True, *Prog. Inorg. Chem.*, 1990, **38**, 97.
12 N. A. Law, J. W. Kampf and V. L. Pecoraro, *Inorg. Chim. Acta*, 2000, **297**, 252.
13 H. J. Mok, J. A. Davis, S. Pal, S. K. Mandal and W. H. Armstrong, *Inorg. Chim. Acta*, 1997, **263**, 385.
14 Note that fitting of the data for **2** to models where $J' = 0$, or a Curie–Weiss constant is introduced, or only data above 20 K or above 50 K were employed, all gave J values in the -22 to -27 cm^{-1} range. We feel confident in the quoted value and uncertainty of J.
15 K. R. Reddy, M. V. Rajaseharan, S. Padhye, F. Dahan and J.-P. Tuchagues, *Inorg. Chem.*, 1994, **33**, 428.
16 A. Boussac, S. Un, O. Horner and A. W. Rutherford, *Biochemistry*, 1998, **37**, 4001.
17 O. Horner, E. Rivière, G. Blondin, S. Un, A. W. Rutherford, J.-J. Girerd and A. Boussac, *J. Am. Chem. Soc.*, 1998, **120**, 7924.
18 E. Libby, J. K. McCusker, E. A. Schmitt, K. Folting, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1991, **30**, 3486.
19 B. Albela, M. S. El Fallah, J. Ribas, K. Folting, G. Christou and D. N. Hendrickson, *Inorg. Chem.*, 2001, **40**, 1037, and references therein.