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ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · MAY 1998

Impact Factor: 12.11 · DOI: 10.1021/ja9730573

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Modeling the Photosynthetic Water Oxidation Complex: Activation of Water by Controlled Deprotonation and Incorporation into a Tetranuclear Manganese Complex

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Received September 2, 1997

Elucidating the structure and mechanism of action of the predominantly carboxylate-ligated, oxide-bridged Mn_4 cluster at the water oxidation center (WOC) of plants and cyanobacteria is of great current interest.[1,2] This cluster binds, deprotonates, and oxidatively couples two H_2O molecules to yield O_2, but the precise details of this transformation are unclear. Recently, we have developed preparative methodology to the $Mn^{III}_3Mn^{IV}$ complexes $[Mn_4O_3X(O_2CMe)_3(dbm)_3]$ ($X^- = Cl^-$, Br^-, $PhCO_2^-$, $MeCO_2^-$; dbmH = dibenzoylmethane)[3] containing the $[Mn_4O_3]$ oxide-bridged trigonal pyramidal Mn_4 core that is one of the topologies consistent with recent EXAFS data on the native site,[4] which has both short (∼2.7 Å) and long (∼3.3 Å) Mn...Mn separations. A major objective is to employ these model complexes to obtain structural and mechanistic insights into the interaction of the native cluster with its cofactors (Cl^-, Br^-, NO_3^-, etc.), inhibitors (F^-, NH_3, RNH_2, ROH), and substrate (H_2O);[1] we have shown, for example, that $[Mn_4O_3(O_2CMe)_4(dbm)_3]$ (**1**) readily reacts with a F^- source to give $[Mn_4O_3F(O_2CMe)_3(dbm)_3]$.[3c] Understanding the means by which a Mn_4 cluster binds, deprotonates, and oxidizes H_2O molecules is the primary objective, and we are attempting to use model complexes to achieve this in a stepwise fashion that might allow intermediates to be identified and thus provide insights into how such a transformation might proceed. In the present work, we report that **1** will spontaneously react with H_2O under mild, nonforcing conditions leading to deprotonation of the latter and its incorporation into the core. This reaction represents a controlled activation of H_2O and is proposed as a model system for the crucial first steps along the path to O_2 evolution.

The reactivity of **1** with H_2O and MeOH was conveniently monitored by ^2H NMR spectroscopy using $[Mn_4O_3(O_2CCD_3)_4(dbm)_3]$ (**1a**); this avoids the complicating presence of dbm resonances and gives sharper resonances than ^1H NMR spectroscopy. In addition to the signal for $CHDCl_2$ impurity, the spectrum of **1a** at room temperature shows two signals at 36.8 and 66.1 ppm in a 3:1 integration ratio from the μ-O_2CCD_3 and unique μ_3-O_2CCD_3 groups, respectively (Figure 1, top). Addition of distilled MeOH causes a decrease in these two signals and

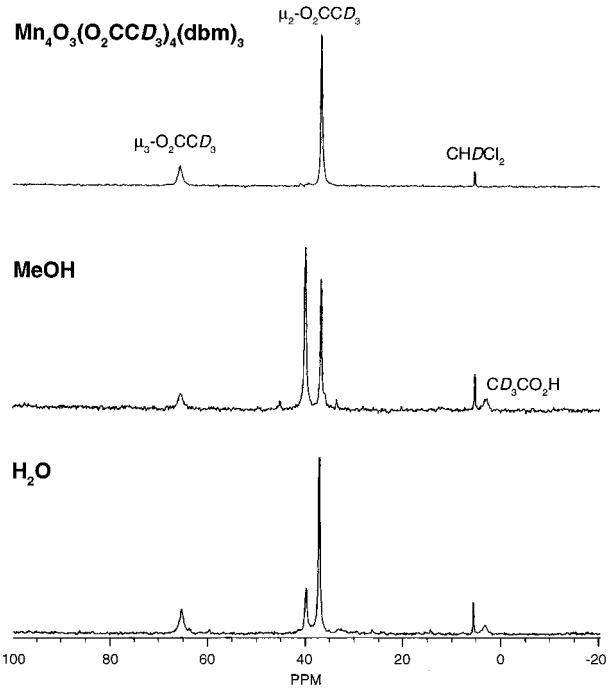

Figure 1. ^2H NMR spectrum at ∼23 °C of complex **1a** in CD_2Cl_2 (top); spectrum resulting from addition of 10 equiv of MeOH (middle); spectrum resulting from addition of an excess (immiscible) of H_2O (bottom).

appearance of free CD_3CO_2H at ∼3 ppm and a new resonance at 39.7 ppm (Figure 1, middle). Addition of more MeOH causes an increase in the latter two signals at the expense of the former two. These data suggest a site-specific ligand substitution of the unique acetate group to give $[Mn_4O_3(OMe)(O_2CCD_3)_3(dbm)_3]$ (**2a**). Similarly, addition of an excess of distilled H_2O (only sparingly miscible in CD_2Cl_2) causes analogous spectral changes with a new resonance appearing at 39.5 ppm (Figure 1, bottom), again suggesting displacement of the unique μ_3-$CD_3CO_2^-$ group and possible formation of $[Mn_4O_3(OH)(O_2CCD_3)_3(dbm)_3]$ (**3a**). Firm identification of these two products followed from their bulk isolation and structural characterization.

Complex **1** was dissolved in CH_2Cl_2 containing ∼300 equiv of MeOH, the solvent removed in vacuo, the cycle repeated, and the residue again dissolved in CH_2Cl_2/MeOH; the product was precipitated with Et_2O, filtered, and dried in vacuo to give $[Mn_4O_3(OMe)(O_2CMe)_3(dbm)_3]$ (**2**) in ∼50% yield (eq 1). With

$$[Mn_4O_3(O_2CMe)_4(dbm)_3] + MeOH \rightarrow [Mn_4O_3(OMe)(O_2CMe)_3(dbm)_3] + MeCO_2H \quad (1)$$

the identity of **2** established,[5,6] its reaction with H_2O was found to provide a more convenient route to **3**. Thus, **2** was twice treated to cycles of dissolution in CH_2Cl_2/MeCN (7:1) containing 30 equiv of H_2O, followed by precipitation of the solid with Et_2O. The final solid of $[Mn_4O_3(OH)(O_2CMe)_3(dbm)_3]$ (**3**) was obtained in 55−60% yield (eq 2).[7]

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(5) Dried solid analyzed as $2\cdot{}^1/_4CH_2Cl_2$. Anal. Calcd (found): C, 53.8 (53.8); H, 4.1 (4.0). Crystal data for $2\cdot 2CH_2Cl_2$: monoclinic, $P2_1/c$, a = 14.278(5) Å, b = 15.108(6) Å, c = 27.500(12) Å, β = 100.51(2)°, Z = 4, V = 5832 Å^3, d_{calc} = 1.498 g cm^{-3}, T = −171 °C; $R(F)$ = 9.82 and $R_w(F)$ = 8.77% using 5203 unique reflections with $F > 3\sigma(F)$.

(6) Pure **2a** was made in a similar fashion from **1a**. The ^2H NMR spectrum of **2a** exhibits only the 39.7 ppm resonance, confirming **2a** as the product of the methanolysis in Figure 1, middle.

(7) Pure **3a** was made in a similar fashion from **2a**. The ^2H NMR spectrum of **3a** exhibits only the 39.5 ppm resonance, confirming **3a** as the product of the hydrolysis in Figure 1, bottom.

S0002-7863(97)03057-6 CCC: $15.00
Published on Web 05/30/1998

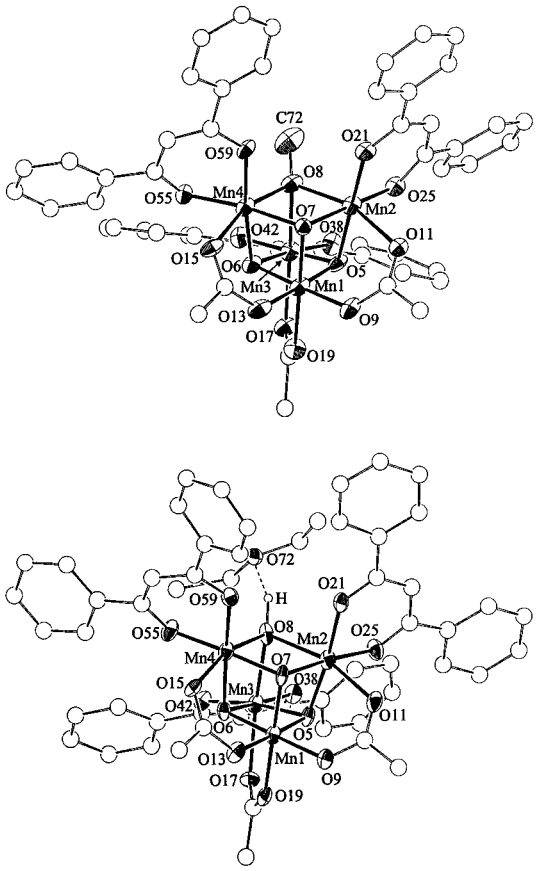

Figure 2. ORTEP representations of complexes **2** (top) and **3** (bottom) at the 50% probability level.

Table 1. Comparison of $[Mn_4O_3X]^{6+}$ Core Distances in Complexes **1**−**3**[a−c]

	1	**2**	**3**
$Mn^{III}...Mn^{IV}$	2.799(12)	2.798(6)	2.789(2)
$Mn^{III}...Mn^{III}$	3.201(12)	3.132(26)	3.122(17)
$Mn^{III}-O_X$	2.299(21)	2.182(23)	2.215(39)
$Mn^{III}-O_b$	1.933(21)	1.936(23)	1.930(25)
$Mn^{IV}-O_b$	1.867(9)	1.862(9)	1.862(12)

[a] Averaged using C_{3v} virtual symmetry. [b] Numbers in parentheses are the greatest deviations of single values from the mean. [c] Mn(1) is Mn^{IV}; Mn(2), Mn(3), and Mn(4) are Mn^{III}; O_X = O of μ_3-$MeCO_2^-$, MeO^-, or HO^-; O_b = μ_3-O^{2-} ions.

$$[Mn_4O_3(OMe)(O_2CMe)_3(dbm)_3] + H_2O \rightarrow [Mn_4O_3(OH)(O_2CMe)_3(dbm)_3] + MeOH \quad (2)$$

The structures of **2**[5] and **3**[8] (Figure 2) show great similarity to that of **1** except that the μ_3-O_2CMe^- is replaced by μ_3-OMe^- or OH^- groups: in each case there is a $Mn^{III}_3Mn^{IV}$ trigonal pyramid whose Mn^{III}_3 basal face is capped by a μ_3-X^- (X^- = O_2CMe^-, OMe^-, OH^-) group and its other faces by μ_3-O^{2-} to give a highly distorted cubane $[Mn_4O_3X]^{6+}$ core. Interatomic distances (Table 1) confirm retention of both "short" (∼2.8 Å) and "long" (3.1−3.2 Å) Mn...Mn separations in **2** and **3**; indeed, variation of X^- causes almost insignificant changes to the structure of the core. Note that the $[Mn_4O_3(OH)]^{6+}$ core of **3** is different from the more symmetric $[Mn_4O_4]^{6+}$ cubane core of $[Mn_4O_4(O_2PPh_2)_6]$ where all Mn...Mn separations are in the range 2.904−2.954 Å.[9] The presence of hydrogen bonding in **3** between the μ_3-OH^- and an Et_2O group (O...O = 2.951(16) Å) confirms the protonated nature of O(8). The X^- groups in **1**−**3** lie on the three Mn^{III} Jahn−Teller elongation axes, and the resulting enhanced lability undoubtedly facilitates the site-specific substitution at this position. The process described in eq 1 is driven by the large excess (∼300 equiv) of MeOH and the resulting shorter, stronger $Mn^{III}-O_X$ bonds (table) even though the acidity of MeOH (pK_a = 15.5) is much less than $MeCO_2H$ (4.8). The conversion in eq 2 is favored by the relative acidity of MeOH (pK_a = 15.5) versus H_2O (pK_a = 14) and such a large excess of H_2O is not necessary. We currently believe the substitutions occur via an intermediate whereby the μ_3-X^- (X^- = $MeCO_2^-$ or MeO^-) group becomes μ_2-X^- as the incoming group binds to one Mn^{III} site, followed by loss of XH as the new group is deprotonated and adopts a μ_3 mode.

Magnetic susceptibility data (2.00−300 K) on powdered samples of **2** and **3** were fit to the appropriate theoretical χ_m vs T expression for a C_{3v} symmetry $Mn^{III}_3Mn^{IV}$ unit,[3a,10] and the fitting parameters, in the format (J_{34}, J_{33}, g), were −31.8 cm^{-1}, +9.6 cm^{-1}, and 1.92 for **2** and −32.7 cm^{-1}, +11.9 cm^{-1}, and 2.02 for **3**. These values are very similar to those for **1** (−33.9 cm^{-1}, +5.4 cm^{-1}, and 1.94) and other $[Mn_4O_3X]$ (X^- = Cl^-, Br^-, F^-) complexes.[3,10] Complexes **1**−**3** thus all have $S = {}^9/_2$ ground states.

Complexes **1**−**3** display quasi-reversible one-electron reductions at 0.39, 0.16, and 0.16 V vs SCE, respectively, when examined by DPV and CV in CH_2Cl_2 and quasi-reversible oxidations at 1.55, 1.22, and 1.26V. These changes with X^- are consistent with the relative basicities of the latter as gauged by the above pK_a values and show that HO^- and MeO^- facilitate access to a higher oxidation state compared with $MeCO_2^-$. The conversion of free H_2O into a bound OH^- in **3** without change to the Mn_4O_3 core and via H^+ transfer to a $MeCO_2^-$ or MeO^- leaving group could parallel a similar transformation following (or accompanying) a S_n-to-S_{n+1} oxidation in the WOC, where according to recent theories both the electron and H^+ transfers are to the Y_z tyrosine radical.[11,12] The hydrogen-bonded Et_2O group may also be considered a model of how a second H_2O molecule could interact with the OH^- to give a $[H_2O\cdots HO^-]$ pair poised for subsequent multiple deprotonations and oxidative coupling to form O_2;[13] such a system would also be consistent with data showing both a slowly and rapidly exchanging substrate molecule at the native site.[14] Current studies thus include isolation of **1** (or related species) at the $4Mn^{III}$ oxidation level to study H_2O binding and concomitant oxidation/deprotonation steps and deprotonation of **3** either alone or as a consequence of an oxidation to the $2Mn^{III},2Mn^{IV}$ level.

Acknowledgment. This work was funded by NIH Grants GM 39083 (G.C.) and HL 13652 (D.N.H.).

Supporting Information Available: Data collection and refinement details and listings of atomic coordinates and thermal parameters for complexes **2** and **3** and fitting of $\chi_m T$ vs T data for **2** and **3** (46 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9730573

(8) Dried solid analyzed as **3**·Et_2O·1.7CH_2Cl_2. Anal. Calcd (found): C, 50.4 (50.4); H, 4.2 (4.2). Crystal data for **3**·0.9Et_2O.1.1CH_2Cl_2: monoclinic, $P2_1/c$, a = 14.478(5) Å, b = 14.910(5) Å, c = 26.644(8) Å, β = 101.00(2)°, Z = 4, V = 5646 Å^3, d_{calc} = 1.518 g cm^{-3}, T = −171 °C; $R(F)$ = 7.84 and $R_w(F)$ = 7.57% using 4836 unique reflections with $F > 3\sigma(F)$.

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(13) We have, in fact, been able to crystallize **3** with the OH^- hydrogen-bonded to *two* H_2O molecules instead of one Et_2O; however, the quality of the crystallographic data is currently very poor.

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