

# Chloride-Induced Conversion of $[\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{py})_2(\text{dbm})_2]$ to $[\text{Mn}_4\text{O}_3\text{Cl}(\text{OAc})_3(\text{dbm})_3]$ : Potential Relevance to Photosynthetic Water Oxidation\*\*

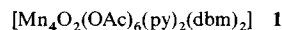
By Sheyi Wang, Kirsten Folting, William E. Streib, Edward A. Schmitt, James K. McCusker, David N. Hendrickson,\* and George Christou\*\*

We are currently seeking models for the various oxidation levels ( $S_n$  states;  $n = -1$  through 4) of the photosynthetic water oxidation center (WOC), to assist in the elucidation of its nature and mode of action.<sup>[1]</sup> The WOC requires four Mn atoms for activity, and these are oxo-bridged and ligated by O- and perhaps N-based groups, primarily of aspartate and glutamate carboxylates in the protein matrix; recent reports suggest<sup>[2]</sup> the nitrogen ligation to be minimal, at the level of  $1 \pm 1$  per four Mn centers. The WOC also requires  $\text{Cl}^\ominus$  for activity, and it has been suggested, for example, that the  $\text{Cl}^\ominus$  is a ligand of the Mn atoms, or that it is involved in acid/base chemistry at the polypeptides.<sup>[11–31]</sup> The  $\text{Cl}^\ominus$  is an essential cofactor for the WOC; in the absence of  $\text{Cl}^\ominus$ , an abnormal  $S_2$  state is formed and advancement to  $S_3$  is blocked.<sup>[36, 41]</sup> Whatever its precise role,  $\text{Cl}^\ominus$  thus seems to be important at the higher  $S_n$  states.

We recently described the preparation of various Mn complexes that were proposed as potential models of certain  $S_n$  states.<sup>[15, 61]</sup> The complexes  $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CR})_6(\text{bpy})_2]$  and  $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CR})_7(\text{bpy})_2]^{10, \oplus}$  ( $\text{bpy} = 2,2'$ -bipyridine), whose  $[\text{Mn}_4\text{O}_2]^{2\oplus}$  core contains a  $\text{Mn}_4$  unit that is either planar or nonplanar (“butterfly” structure), were proposed as models for  $S_{-1}$ ,  $S_0$  and  $S_1$ .<sup>[15, 71]</sup> In addition, the complexes  $[\text{Mn}_4\text{O}_3\text{Cl}_6(\text{OAc})_3(\text{HIm})]^{2\oplus}$  ( $\text{HIm} = \text{imidazole}$ ) and  $[\text{Mn}_4\text{O}_3\text{Cl}_4(\text{OAc})_3(\text{py})_3]$ , which contain three  $\text{Mn}^{\text{III}}$  and one  $\text{Mn}^{\text{IV}}$  in a distorted  $\text{Mn}_4\text{O}_3\text{Cl}$  cubane core, were proposed as

$S_2$  models.<sup>[6, 71]</sup> Obviously, the coordination spheres of the  $\text{Mn}_4\text{O}_2$  and  $\text{Mn}_4\text{O}_3\text{Cl}$  complexes are not equivalent. Furthermore, the  $\text{bpy}$  and terminal  $\text{Cl}^\ominus$  ligands are inconsistent with current WOC data,<sup>[81]</sup> and we were unable to convert  $\text{Mn}_4\text{O}_2$ - into  $\text{Mn}_4\text{O}_3\text{Cl}$ -containing species, which must be possible for potential  $S_1$  and  $S_2$  models. We report herein that all of the above shortcomings have now been redressed and, in addition, that a remarkable influence of  $\text{Cl}^\ominus$  has been observed that may be of significant biological relevance.

Treatment of  $[\text{Mn}_3\text{O}(\text{OAc})_6(\text{py})_3(\text{ClO}_4)]$  in MeCN with ca. 1.5 equiv. of dibenzoylmethane slowly gives red microcrystals that can be recrystallized from hot MeCN to give red-black crystals in 45–55% overall yield. The product, the  $\text{Mn}_4^{\text{III}}$  complex **1**,<sup>[91]</sup> has crystallographically imposed  $C_i$  symmetry (Fig. 1) with chelating dbm ligands occupying the bpy positions of the previous complexes, and with six bridging  $\text{AcO}^\ominus$  and two terminal py ligands.



Complex **1** displays remarkable reactivity with  $\text{Cl}^\ominus$ . If 1 equiv of  $n\text{Bu}_4\text{NCl}$  is added to the hot MeCN recrystallization medium, **1** is not recovered; the product on cooling is instead the  $\text{Mn}_3^{\text{III}}\text{Mn}^{\text{IV}}$  complex **2** in 20–25% nonoptimized yield. Based on the precedence of other systems,<sup>[5, 61]</sup> we



believe that **2** is formed from **1** by disproportionation and ligand redistribution. The structure<sup>[110]</sup> of **2** (Fig. 2) consists of a  $[\text{Mn}_4\text{O}_3\text{Cl}]^{6\oplus}$  core with three bridging  $\text{AcO}^\ominus$  and three chelating dbm groups. To emphasize the change that has occurred during the transformation of **1** into **2**, their central

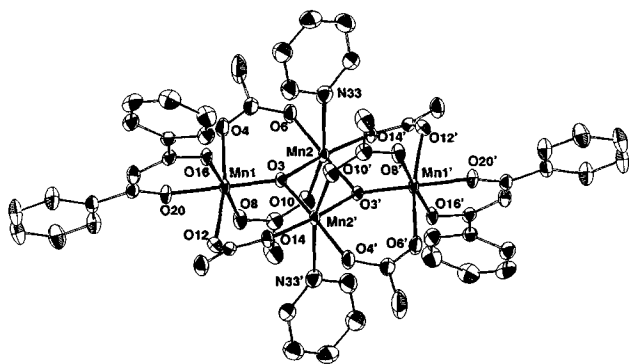


Figure 1. ORTEP representation of complex **1** at the 50% probability level. Selected bond distances (Å) and angles (°):  $\text{Mn2} \cdots \text{Mn2}'$ , 2.8749(11);  $\text{Mn2} \cdots \text{Mn1}$ , 3.308(1);  $\text{Mn2} \cdots \text{Mn1}'$ , 3.398(1);  $\text{Mn1-O3}$ , 1.877(2);  $\text{Mn1-O4}$ , 2.136(2);  $\text{Mn1-O8}$ , 1.928(2);  $\text{Mn1-O12}$ , 2.206(2);  $\text{Mn1-O16}$ , 1.931(2);  $\text{Mn1-O20}$ , 1.925(2);  $\text{Mn2-O3}$ , 1.885(2);  $\text{Mn2-O3'}$ , 1.894(2);  $\text{Mn2-O6}$ , 1.957(2);  $\text{Mn2-O10}$ , 2.187(2);  $\text{Mn2-O14}$ , 1.953(2);  $\text{Mn2-N33}$ , 2.410(3);  $\text{Mn1-O3-Mn2}$ , 123.17(10);  $\text{Mn1-O3-Mn2'}$ , 128.61(10);  $\text{Mn2-O3-Mn2'}$ , 99.07(9). Primed and unprimed atoms are related by the inversion center.

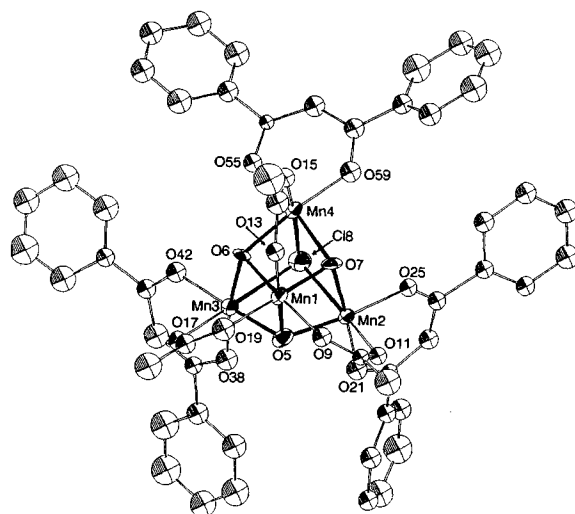


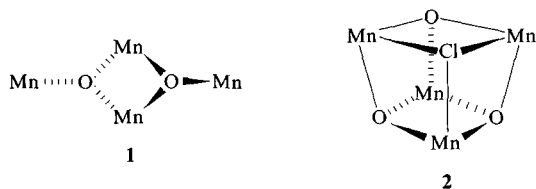
Figure 2. ORTEP representation of complex **2** at the 50% probability level. Selected bond distances (Å) and angles (°):  $\text{Mn1} \cdots \text{Mn2}$ , 2.797(5);  $\text{Mn1} \cdots \text{Mn3}$ , 2.797(4);  $\text{Mn1} \cdots \text{Mn4}$ , 2.792(5);  $\text{Mn2} \cdots \text{Mn3}$ , 3.252(5);  $\text{Mn3} \cdots \text{Mn4}$ , 3.264(5);  $\text{Mn2} \cdots \text{Mn4}$ , 3.237(5);  $\text{Mn2-Cl8}$ , 2.641(7);  $\text{Mn-Cl8}$ , 2.656(7);  $\text{Mn4-Cl8}$ , 2.654(7);  $\text{O5-Mn}(1,2,3)$ , 1.883(15), 1.926(14), 1.922(15), respectively;  $\text{O6-Mn}(1,3,4)$ , 1.867(14), 1.945(13), 1.920(13), respectively;  $\text{O7-Mn}(1,2,4)$ , 1.842(13), 1.945(14), 1.939(14), respectively;  $\text{Mn2-Cl8-Mn3}$ , 75.74(19);  $\text{Mn2-Cl8-Mn4}$ , 75.37(19);  $\text{Mn3-Cl8-Mn4}$ , 75.85(19);  $\text{Mn1-O5-Mn2}$ , 94.5(7);  $\text{Mn1-O5-Mn3}$ , 94.6(6);  $\text{Mn2-O5-Mn3}$ , 115.4(7);  $\text{Mn1-O6-Mn3}$ , 94.4(6);  $\text{Mn1-O6-Mn4}$ , 95.0(6);  $\text{Mn3-O6-Mn4}$ , 115.2(7);  $\text{Mn1-O7-Mn2}$ , 95.2(6);  $\text{Mn1-O7-Mn4}$ , 95.2(6);  $\text{Mn2-O7-Mn4}$ , 112.9(6).

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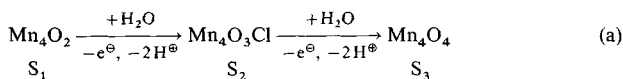
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portions are shown below in diagrammatic form. The  $Mn_4O_3Cl$  core of **2** is essentially superimposable on those of other  $Mn_4O_3Cl$  complexes, showing that the complete exchange of oxygen-ligating ligands (dbm) for the previously present peripheral ligands (py, HIm,  $Cl^\ominus$ ) has little structural effect. It does, however, have a small effect on the magnetic exchange interactions within **2**. The effective magnetic moment,  $\mu_{\text{eff}}/Mn_4$ , steadily rises from  $8.49 \mu_B$  at 381.5 K to  $10.42 \mu_B$  at 10.0 K. Fitting of the data to the theoretical susceptibility equation derived previously<sup>[6b]</sup> gave  $J_1 (Mn^{III}-Mn^{IV}) = -33.4 \text{ cm}^{-1}$  and  $J_2 (Mn^{III}-Mn^{III}) = +5.1 \text{ cm}^{-1}$ ; these values are similar to those for  $[Mn_4O_3Cl_4(OAc)_3(py)_3]$  for which  $J_1 = -26.8 \text{ cm}^{-1}$  and  $J_2 = +12.1 \text{ cm}^{-1}$ .<sup>[6b]</sup> For complex **1**, the exchange interactions are similar in sign and magnitude to those in  $[Mn_4O_2(OAc)_7(bpy)_2]^\ominus$ , even though the latter has a butterfly rather than a planar disposition of the four Mn ions.<sup>[5b]</sup>



The described results represent important progress in our WOC modeling efforts. The predominantly oxygen ligation in **1** is now much more consistent with WOC data,<sup>[8]</sup> and not only does the  $S_2$  model complex **2** have equivalent ligation, but also an  $Mn_4O_2$  ( $S_1$  model) complex has been directly converted into an  $Mn_4O_3Cl$  ( $S_2$  model) complex for the first time, paralleling the native  $S_1 \rightarrow S_2$  conversion. In addition, the  $Cl^\ominus$ -dependent nature of the model conversion perhaps sheds light on the  $Cl^\ominus$ -dependence of water oxidation and on why an abnormal  $S_2$  state is formed in the absence of  $Cl^\ominus$ . Finally, we have previously hypothesized,<sup>[17]</sup> based merely on the structures of  $Mn_4O_2$  and  $Mn_4O_3Cl$  materials, that substrate ( $H_2O$ ) incorporation into the WOC  $Mn_4$  aggregate may occur stepwise as bridging oxides during the  $S_1 \rightarrow S_2 \rightarrow S_3$  transitions, and that this may be how  $H_2O$  is activated to oxidation to  $O_2$  (eq. a). The conversion of **1** to **2**, while mechanistically unclear, does involve an increase in the number of



oxide bridges, as in eq. (a), emphasizing the feasibility of this suggestion. We are currently investigating whether the  $Mn_4O_3Cl$  to  $Mn_4O_4$  conversion can be accomplished. Of course, in the absence of X-ray structural data on the WOC, it is uncertain to what extent these model complexes reproduce the actual structure and transformations of the WOC Mn site. Nevertheless, we believe that the chemistry observed with synthetic complexes may parallel that of the native site and, therefore, at the very least, provide insights into the functioning of the WOC.

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- [9] The dried solid is hygroscopic; correct elemental analyses (C,H,N,Mn); crystal data:  $C_{52}H_{50}N_2O_{18}Mn_4$ , triclinic,  $P\bar{1}$ ,  $T = -131^\circ C$ ,  $a = 10.868(3)$ ,  $b = 13.864(3)$ ,  $c = 10.625(3) \text{ \AA}$ ,  $\alpha = 108.62(1)$ ,  $\beta = 118.98(1)$ ,  $\gamma = 89.34(2)^\circ$ ,  $V = 1307.24 \text{ \AA}^3$ ,  $Z = 1$ ,  $6^\circ \leq 2\theta \leq 45^\circ$ , 3432 unique, 3141 observed reflections,  $F > 3.0\sigma(F)$ . All non-hydrogen atoms were refined anisotropically; final  $R(R_w) = 3.24 (3.70)\%$ .
- [10] Correct elemental analyses for **2** (C,H,Cl,Mn); crystal data:  $C_{51}H_{42}O_{17}ClMn_4$ , monoclinic,  $P2_1/n$ ,  $T = -155^\circ C$ ,  $a = 13.900(3)$ ,  $b = 22.038(5)$ ,  $c = 16.518(5) \text{ \AA}$ ,  $\beta = 107.80(1)^\circ$ ,  $V = 4817.63 \text{ \AA}^3$ ,  $Z = 4$ ,  $6^\circ \leq 2\theta \leq 45^\circ$ , 6317 unique, 2267 observed reflections,  $F > 2.33\sigma(F)$ . Only the  $Mn_4O_3Cl$  core atoms were refined anisotropically; final  $R(R_w) = 7.85 (7.38)\%$ . Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW (UK), on quoting the complete journal citation.

## 1,3-(C → O) Silyl Shift in $\alpha$ -Diazo $\alpha$ -Silyl Ketones: Cycloaddition Reactions and Kinetic Proof for the $\beta$ -Siloxydiazoalkene Intermediate\*\*

By Rainer Munschauer and Gerhard Maas\*

The thermal treatment of  $\alpha$ -diazo  $\alpha$ -silyl ketones **1** at temperatures up to  $80^\circ C$  leads by nitrogen elimination to products which are derived from alkylidenecarbenes (**3**).<sup>[1]</sup> We have suggested that the carbenes **3** are formed from diazoalkenes (**2**) which in turn result from a 1,3-(C → O) silyl migration in **1**. Diazoalkenes have as yet not been isolated. Recently the first low-temperature matrix isolation of a diazoethene derivative was reported;<sup>[2]</sup> furthermore, there are indications that diazoalkenes are formed in solution as reactive intermediates, which spontaneously eliminate  $N_2$  to yield unsaturated carbenes.<sup>[3]</sup> In spite of these experimentally documented (and for the parent compound, diazoethene, even calculated<sup>[4]</sup>) high thermal lability, there are results which can be interpreted as trapping of intermediate diazoalkenes.<sup>[5–8]</sup>

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