# Chapter 12

# Structural Types in Oxide-Bridged Manganese Chemistry

# Toward a Model of the Photosynthetic Water Oxidation Center

### George Christou and John B. Vincent

## Department of Chemistry, Indiana University, Bloomington, IN 47405

A survey is presented of the structural types encountered during synthetic efforts in oxide-bridged manganese chemistry. These materials have resulted from efforts to model the Mn aggregate at the water oxidation center (WOC) of green plants. Complexes with Mn nuclearities in the range 2-12 are currently known, and their structural parameters are compared with those deduced by study of the WOC. The 'short' (ca 2.7Å) Mn...Mn separation of the latter has been seen to date only in synthetic species containing two oxide bridges between a Mn2 pair, whereas, the 'long' (ca 3.3Å) separation is compatible with at most only one oxide bridge. Particular emphasis is given to the dinuclear and tetranuclear complexes which most closely reproduce features observed or deduced in the WOC, and the potential correspondence of these complexes to the various  ${\rm S}_{\rm n}$  states of the latter is discussed.

It is now well established that manganese (Mn) is an essential component of the photosynthetic water oxidation center (WOC) (1). A variety of techniques have been applied to its study, and some pertinent conclusions can be briefly summarized: (i) the WOC contains between 2-4 Mn atoms (2,3); (ii) Mn...Mn separations of  $\underline{ca} 2.7\dot{A}$  and possibly  $\underline{ca} 3.3\dot{A}$  are present (3,4); (iii) the Mn atoms are bridged by  $0^2$  (or OH ) groups with Mn-O distances of  $\underline{ca} 1.75\dot{A}$ , and peripheral ligation is provided by O/N-based groups (from amino acid side chains) at distances of  $\underline{ca} 1.98\dot{A}$  (4); (iv) the Mn aggregate can adopt various oxidation levels (the S<sub>n</sub> states) involving combinations of Mn oxidation states of II, III, and/or IV (1); and (v) the S<sub>2</sub> level is EPR-active and displays a spectrum containing a Mn-hyperfine-structured ("multiline") signal at  $g\approx 2$  (2). Fuller details of the native manganese assembly can be found elsewhere in this volume.

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One consequence of the intense effort being concentrated on the WOC has been a greater level of exploration by inorganic chemists of the chemistry of higher oxidation state Mn. The objective is the synthesis of Mn/O complexes which possess the appropriate structural features, oxidation levels, and spectroscopic and physical properties to allow them to be considered synthetic models of the WOC in its various  $S_n$  states. Their attainment should result in a greater level of understanding of the structural changes and general mechanism of action of the native site during the water oxidation cycle, including mode of substrate (H<sub>2</sub>O) binding and conversion to O<sub>2</sub>.

The purpose of this chapter is to review the current status of this model approach and to describe the structural types of discrete oxide-bridged Mn aggregates which have been synthesized to date. For completeness, all known nuclearities will be described, in terms of increasing nuclearity. Space restrictions preclude a complete survey and we shall concentrate mainly on the structural features of these materials; the reader is referred to the original literature for more detail, such as variable-temperature magnetic susceptibility, electrochemical and EPR data.

### Dinuclear Complexes

The possibility of a dinuclear unit in the WOC has prompted much effort at this nuclearity and a variety of dinuclear oxidebridged complexes are now known, containing either one or two bridging O<sup>2</sup> groups. They have been made employing a variety of procedures, including direct assembly from appropriate mononuclear reagents and appropriate modification of preformed dinuclear materials. Examples of the latter approach include chemical oxidation of  $[Mn_2^{111}O(O_2CMe)_2(TACN)_2]^{2+}$  to the trication with  $S_2O_8^{2^-}$  (10), and its hydrolytically-induced oxidation to  $[Mn_2O_2(O_2CMe)(TACN)_2]^{2+}$  (13). Some representative structures are reproduced in Figures 1 and 2. As can be seen from Table I, three types of bridging arrangements have been encountered; linear Mn-O-Mn, bent Mn-O-Mn and Mn\_2( $\mu$ -O)<sub>2</sub>.

The complexes with linear oxide bridges contain no other bridging ligands and are characteristic of species with extensive Mn-0  $\pi$ -bonding. The linear arrangement necessitates a large Mn...Mn separation and observed distances are in the 3.42-3.54Å range. In contrast, complexes with a single bent oxide bridge invariably contain additional bridging ligands, and structurally-characterized materials possess the triply-bridged [Mn( $\mu$ -0)( $\mu$ -0<sub>2</sub>CMe)<sub>2</sub>Mn]<sup>2+,3+</sup> core. The TACN and Me<sub>3</sub>-TACN species display an electrochemically reversible one-electron couple relating the Mn<sub>2</sub>II/Mn<sup>III</sup>Mn<sup>IV</sup> levels, and examples of both have been isolated and structurally characterized. The [Mn<sub>2</sub>O(O<sub>2</sub>CMe)<sub>2</sub>]<sup>2+,3+</sup> species have a characteristic Mn...Mn separation in the range 3.08-3.23Å. Interestingly, the Mn<sup>III</sup>Mn<sup>IV</sup> complex has the longer rather than the shorter Mn...Mn separation that one might have expected.

The di- $\mu$ -oxide-bridged complexes have been observed in two types: (i) with no additional bridging ligands, and (ii) with an additional bridging MeCO<sub>2</sub> group. The former has been seen with both Mn<sup>III</sup>Mn<sup>IV</sup> and Mn<sup>2IV</sup> oxidation states, while the latter only

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Figure 1. The structure of  $[Mn_2O(O_2CMe)_2(Me_3-TACN)_2]^{3+}$ ; the other  $[Mn_2O(O_2CMe)_2]$  complexes in Table I differ structurally only in the identity of the terminal ligands. (Reproduced with permission from ref. 10. Copyright 1986 VCH Verlagsgesellschaft)



Figure 2. The structure of  $[Mn_2O_2(O_2CMe)(TACN)_2]^{2+}$ ; the dashed line indicates the imposed two-fold axis. (Reproduced with permission from ref. 13. Copyright 1987 Royal Society of Chemistry)

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for Mn<sup>III</sup>Mn<sup>IV</sup>. The latter also display slightly shorter Mn...Mn separations (2.59, 2.67Å) than the former (2.70-2.75Å). The  $[Mn_2O_2(phen)_4]^{3^+,4^+}$  pair allows a useful structural comparison of the effect of oxidation level on exactly isostructural species, and again the higher oxidation state yields the slightly longer Mn...Mn separation (2.75 vs. 2.70Å).

TABLE I. Structural Parameters (Å) of Dinuclear Complexes

Complex	MnMn	Mn-O	ref
Linear Oxide Bridges			
[Mn <sub>2</sub> <sup>III</sup> O(CN) <sub>10</sub> ] <sup>6<sup>-</sup></sup> [Mn <sub>2</sub> <sup>III</sup> O(phthal) <sub>2</sub> ]	3.446(4) 3.42(1)	1.723(4) 1.71(1)	5 6
[Mn <sub>2</sub> <sup>IV</sup> O(TPP) <sub>2</sub> ] <sup>2+</sup>	3.537(4)	1.743(4),1.794(4)	7
Bent Oxide Bridges			
[Mn <sub>2</sub> IIIO(O <sub>2</sub> CMe) <sub>2</sub> (TPB) <sub>2</sub> ] [Mn <sub>2</sub> IIIO(O <sub>2</sub> CMe) <sub>2</sub> (bipy) <sub>2</sub> Cl <sub>2</sub> ] [Mn <sub>2</sub> IIIO(O <sub>2</sub> CMe) <sub>2</sub> (TACN) <sub>2</sub> ] <sup>2+</sup> [Mn <sub>2</sub> III,IVO(O <sub>2</sub> CMe) <sub>2</sub> (Me <sub>3</sub> -TACN) <sub>2</sub> ] <sup>3+</sup>	3.159(1) 3.153(1) 3.084(3) 3.230(3)	1.773(2),1.787(2) 1.777(12),1.788(11 1.80(1) 1.826(6),1.814(6)	8 ) a 9 10
Di-µ-oxide Bridges			
[Mn <sub>2</sub> III,IV <sub>O2</sub> (bipy) <sub>4</sub> ] <sup>3+</sup> [Mn <sub>2</sub> III,IV <sub>O2</sub> (phen) <sub>4</sub> ] <sup>3+</sup> [Mn <sub>2</sub> III,IV <sub>O2</sub> (O <sub>2</sub> CMe)(TACN) <sub>2</sub> ] <sup>2+</sup> [Mn <sub>2</sub> III,IV <sub>O2</sub> (O <sub>2</sub> CMe)(bipy) <sub>2</sub> Cl <sub>2</sub> ] [Mn <sub>2</sub> IV,IV <sub>O2</sub> (phen) <sub>4</sub> ] <sup>4+</sup>	2.716(2) 2.700(1) 2.588(2) 2.667(2) 2.748(2)	1.784-1.856 1.808-1.820 1.817(5),1.808(4) 1.793-1.843 1.794-1.805	11 12 13 a 12
$[Mn_2^{IV,IV}O_2(pic)_4]$	2.747(2)	1.819(3)	a

a. unpublished

Should the WOC site prove to be dinuclear (or two separated dinuclear units), the question arises as to which known dinuclear complexes can be considered good models. As noted above, the Mn...Mn separations of Table I reflect the identity of the bridge and are not (seriously) dependent on the metal oxidation states. Thus, only the Mn<sub>2</sub>O<sub>2</sub>-containing complexes possess Mn...Mn separations in the ca 2.7Å range suggested by EXAFS data on the WOC. This can be taken as some evidence that a similar  $Mn_2O_2$  unit might be present in the latter. In accord with this, a striking similarity has been noted between the EXAFS spectrum of  $[{\rm Mn_2O_2(bipy)_4}]^{3^+}$  (and its phen analogue) and the EXAFS spectrum of the WOC (14). Strong correspondence was found between the number, type and distances of the ligand atoms in the first coordination sphere of the Mn from both sources. It would thus seem that it is the  $\rm Mn_2O_2$  complexes which represent structural models of the WOC. The  $\rm Mn^{III}Mn^{IV}$  complexes display a Mn-hyperfinestructured EPR signal in the g = 2 region for which 16 hyperfine lines are clearly resolvable (1, 13, 15). The latter bears

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similarity to the S<sub>2</sub> multiline signal suggesting that the  $Mn^{III}Mn^{IV}$  complexes represent models of the S<sub>2</sub> level and, therefore, that the  $Mn_2^{IV}$  complexes might correspond to S<sub>3</sub>; a reversible one-electron redox couple has been observed between these two oxidation levels in the synthetic complexes. Models for S<sub>0</sub> and S<sub>1</sub> would then presumably require  $Mn^{II}Mn^{III}$  and  $Mn_2^{III}$  dinuclear complexes, but no di- $\mu$ -oxide bridged species at these oxidation states are currently known and must represent objectives of future work. A complex with a  $Mn_2^{III}$  (OH)<sub>2</sub> core has been reported (Mn...Mn = 2.72Å) (16), but there is some debate as to whether this might really be a  $Mn_2^{IV}O_2$  species.

Should the longer (<u>ca</u> 3.3Å) Mn...Mn separation suggested by the EXAFS data on the WOC turn out to be real, this could either be interpreted as two of the above  $Mn_2O_2$  units separated by <u>ca</u> 3.3Å (no example currently known) or, alternatively, a single  $Mn_2O_2$  unit with one or two additional (and well separated) Mn atoms at <u>ca</u> 3.3Å from the central  $Mn_2O_2$  unit (*vide infra*). The important point, however, is that two distinctly different Mn...Mn separations would not be possible for two <u>isolated</u>  $Mn_2O_2$ units or a highly symmetrical trinuclear or tetranuclear species. Overall, the current status of dinuclear modelling studies suggests that  $Mn_2O_2$  complexes represent a good minimal representation of the WOC.

### Trinuclear Complexes

All reported trinuclear complexes possessing oxide bridges which have been characterized to date have been prepared from  $MnO_4$  in either aqueous or non-aqueous media, and possess the "basic carboxylate" structure viz. a  $\mu_3$ -oxide-centered  $Mn_3$  triangle. Both  $Mn^{II}Mn_2^{III}$  and  $Mn_3^{III}$  species are currently known, and their pertinent structural parameters are listed in Table II.

TABLE II. Structural Parameters (Å) of Trinuclear Complexes

Complex	MnMn	Mn-O	ref
$Mn_3O(O_2CMe)_6(py)_3^{a}$	3.363(1)	1.941(1)	17
$Mn_3O(O_2CMe)_6(py)_3^b$	3.351(1)	1.9364(18)	18
Mn <sub>3</sub> O(O <sub>2</sub> CMe) <sub>6</sub> (3-Cl-py) <sub>3</sub>	n.r.	1.863-2.034	19
$Mn_3O(O_2CPh)_6(py)_2(H_2O)$	3.214-3.418	1.798-2.154	18
$[Mn_3O(O_2CPh)_6(ImH)_3]^+$	3.259(1)-	1.888(4)-1.881(8)	С
	3.2/0(1)		

a. room temperature b. -50°C c. unpublished n.r. = not reported

A representative structure is shown in Figure 3. In all cases, Mn...Mn separations are 'long' (ca 3.3Å), similar to values found for the mono-oxide-bridged Mn<sub>2</sub> complexes described above. Even in the trapped-valence complex  $Mn_3O(O_2CPh)_6(py)_2(H_2O)$  (18) shown in Figure 3, where the Mn<sub>3</sub> unit is isosceles rather than equilateral, the Mn...Mn separations are not distinctly different, and no separation is found in the ca 2.7Å range. It could thus be concluded that an Mn<sub>3</sub>O-type unit cannot represent the complete

Mn aggregate found in the WOC; this conclusion is admittedly based only on the synthetic trinuclear complexes currently known.

### Tetranuclear Complexes

The possibility of a tetranuclear unit in the WOC has also prompted intense effort at this nuclearity. The first characterized tetranuclear Mn/O complex was  $[Mn_4O_6(TACN)_4]^{4+}$ , reported by Wieghardt and coworkers (20). This compound possesses a central Mn<sub>4</sub>O<sub>6</sub> core with an adamantane-like structure (shown in Figure 4) and all Mn centers in the +4 oxidation level. The Mn...Mn separations (Table III) are all in the <u>ca</u> 3.2Å range and are thus again too long to model the <u>ca</u> 2.7Å separation seen in the WOC. Note that each Mn...Mn edge of the central Mn<sub>4</sub> tetrahedron is bridged by only one  $\mu$ -O<sup>2+</sup> group; the observed Mn...Mn separation is thus consistent with those observed in dinuclear and trinuclear complexes possessing only one  $\mu$ -O<sup>2+</sup> group between a Mn<sub>2</sub> pair.

In 1987, tetranuclear oxide-bridged Mn complexes became available which possess two distinct types of Mn...Mn separations. Vincent *et al.* showed that the trinuclear complexes containing  $[Mn_3O]^{6^+,7^+}$  cores will react with 2,2'-bipyridine (bipy) to give complexes containing the  $[Mn_4O_2]^{6^+,7^+,8^+}$  core in high yield. With  $[Mn_3IIIO(O_2CMe)_6(py)_3]^+$ , the product was  $[Mn_4O_2(O_2CMe)_7(bipy)_2]^+$  shown in Figure 5 (21). All Mn are in the +3 oxidation level, and the  $Mn_4O_2$  core can be considered as a

TABLE III. Structural Parameters (Å) of Tetranuclear Complexes

Complex	MnMn (short)	MnMn (long)	Mn-O	ref
[Mn <sub>4</sub> O <sub>6</sub> (TACN) <sub>4</sub> ] <sup>4+</sup>		3.21(1) <sup>a</sup>	1.79(1) <sup>a</sup>	20
$[Mn_4O_2(O_2CMe)_7(bipy)_2]^+$	2.848(5)	3.299- 3.385	1.804-	21
$[Mn_4O_2(O_2CMe)_6(bipy)_2]$	2.7787(12)	3.288(1) 3.481(1)	1.8507(20) <sup>b</sup> 1.8560(21) <sup>b</sup> 2.1032(21) <sup>c</sup>	22
$[Mn_4O_3Cl_6(O_2CMe)_3(ImH)]^2$	2.806- 2.818	3.246- 3.323	1.797-2.002	23
[Mn <sub>4</sub> 0 <sub>3</sub> Cl <sub>4</sub> (0 <sub>2</sub> CMe) <sub>3</sub> (py) <sub>3</sub> ]	2.8145(15)	3.269(1)	1.865- 1.966	d

a. average distances, b. Mn(III)-O, c. Mn(II)-O, d. unpublished

"butterfly" with a  $\mu_3 - 0^2$  bridging each triangular face. An alternative way of viewing the structure emphasizes its Mn<sub>3</sub>O parenthood; the product can be considered as two triangular units sharing an edge. Extension of the bipy reaction to the mixed-valence trinuclear complexes leads to products whose oxidation level depends on the identity of the carboxylate group. Thus, Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(py)<sub>2</sub>(H<sub>2</sub>O) reacts with bipy to yield Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>7</sub>



Figure 3. The structure of  $Mn_3O(O_2CPh)_6(py)_2(H_2O)$  illustrating the unique terminal ligand asymmetry; Mn(3) is the  $Mn^{11}$  center possessing a terminal  $H_2O$  ligand. (Reproduced from ref. 8. Copyright 1987 American Chemical Society.)



Figure 4. The structure of  $[Mn_4O_6(TACN)_4]^{4+}$ ; only the nitrogen atoms of the TACN ligands are shown. (Reproduced with permission from ref. 20. Copyright 1983 VCH Verlagsgesellschaft.)

(bipy)<sub>2</sub> containing  $Mn^{II}Mn_3^{III}$  (21). However, use of  $Mn_2O(O_2CMe)_6$  (py)<sub>3</sub> leads instead to  $Mn_4O_2(O_2CMe)_6$  (bipy)<sub>2</sub> containing  $Mn_2^{II}Mn_2^{III}$  (22). The structure of this latter complex, shown in Figure 6, shows it to be similar to  $[Mn_4O_2(O_2CMe)_7(bipy)_2]^+$  except that the four Mn atoms are now planar and the unique carboxylate group bridging the central  $Mn_2$  pair is absent.

The pertinent structural parameters of  $[Mn_4O_2(O_2CMe)_7(bipy)_2]^+$  and  $Mn_4O_2(O_2CMe)_6(bipy)_2$  are included in Table III. The two-hinge Mn atoms in the former complex are separated by 2.848(5)Å, whereas the remaining Mn...Mn separations are much longer, in the range 3.299(5)-3.385(5)Å. Note that the short Mn...Mn separation possesses two  $\mu$ -oxide bridges, whereas the longer separations possess only one.  $Mn_4O_2(O_2CMe)_6(bipy)_2$  has a similar arrangement with the corresponding separations being 2.779(1) and 3.288(1)-3.481(1)Å. The central  $Mn_2O_2$  rhomb in these complexes is thus akin to those in the dinuclear systems containing two oxide bridges.

As for the dinuclear complexes, one might now ask how closely do the synthetic materials correspond overall to the native site should it contain an Mn<sub>4</sub> aggregate. There are indeed several features which again suggest that close approach to the native site may have been achieved: (i) four Mn atoms in two inequivalent pairs with two distinct Mn..Mn separations (24); (ii) bridging  $0^{2^-}$  atoms between the metal centers; (iii) peripheral ligation by carboxylate and bipy corresponding to the metal-binding functions of aspartic/glutamic acids and histidine (the pyridine ring is a conservative replacement for imidazole); and (iv) metal oxidation levels corresponding to those in the  $S_n$  states.

Point (iv) warrants further comment. The EPR-active  $S_2$  state is thought to contain  $Mn_3^{III}Mn^{IV}$  (2). (The alternative possibility is  $Mn^{III}Mn_3^{IV}$ ; the latter cannot be ruled out with certainty but the results of NMR solvent relaxation studies (25) and UV/vis difference spectroscopy (26,27) suggest the former to be the more likely.) Based on this and assuming the Mn aggregate in the WOC is indeed tetranuclear, the Mn oxidation states in the  $S_n$  levels can be defined:  $S_0, Mn^{II}, 3Mn^{III}; S_1, 4Mn^{III}; S_2, 3Mn^{III}, Mn^{IV}; S_3, 2Mn^{III}, 2Mn^{IV}$ . Additionally, the putative  $S_{-1}$  level (28-30), accessible under certain conditions but not participating in the water oxidation cycle, would contain  $2Mn^{II}$ ,  $2Mn^{III}$ . The synthetic  $Mn_4O_2$  complexes would therefore have the following oxidation state correspondence to the  $S_n$  states:

Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CMe)<sub>6</sub>(bipy)<sub>2</sub> Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>7</sub>(bipy)<sub>2</sub> [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CMe)<sub>7</sub>(bipy)<sub>2</sub>]<sup>+</sup>

S<sub>0</sub>

S -1

### S<sub>1</sub>

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That the  $Mn_4O_2$  is capable of adopting at least three isolable oxidation levels thus lends support, albeit circumstantial, to the possibility that it is to be found as the redox component in the WOC, if only at the lower  $S_n$  states. In support of this, the various oxidation levels of the synthetic materials have been found to be electrochemically interconvertible, and a  $[Mn_4O_2]^{g+1}$  level has been detected electrochemically (31).



Figure 5. The structure of  $[Mn_4O_2(O_2CMe)_7(bipy)_2]^+$ . (Reproduced with permission from ref. 21. Copyright 1987 Royal Society of Chemistry.)



Figure 6. The structure of  $Mn_4O_2(O_2CMe)_6(bipy)_2$ ; unlike the structure in Figure 5, the  $Mn_4$  core is exactly planar. (Reproduced with permission from ref. 22. Copyright 1987 Royal Society of Chemistry).

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More recent work has resulted in synthetic access to higher oxidation state tetranuclear complexes. Bashkin *et al.* have shown that treatment of "manganic acetate" with Me<sub>3</sub>SiCl and imidazole (HIm) leads to formation of  $[Mn_4O_3Cl_6(O_2CMe)_3(ImH)]^2$ <sup>-</sup> shown in Figure 7 (23). The structure is best described as a Mn<sub>4</sub> pyramid with a  $\mu_3$ -Cl<sup>-</sup> bridging the basal plane and three  $\mu_3$ -O<sup>2<sup>-</sup></sup> atoms bridging each remaining Mn<sub>3</sub> plane. Each vertical Mn<sub>2</sub> pair is thus bridged by two O<sup>2<sup>-</sup></sup> atoms, and, not surprisingly from the discussion above, the Mn...Mn separation is 'short' (<u>ca</u> 2.8Å). In contrast, the basal Mn<sub>2</sub> pairs are bridged by only one O<sup>2<sup>-</sup></sup> atom and have longer Mn...Mn separations (<u>ca</u> 3.3Å); the Mn- $\mu_3$ -Cl<sup>-</sup> bonds are quite long (<u>ca</u> 2.6Å) and do not serve to contract the Mn...Mn separation. The complex has a Mn<sub>3</sub>III MnIV oxidation state and the apical Mn is assigned as the Mn<sup>IV</sup> center by inspection of structural parameters. In addition, it displays an EPR spectrum showing a l6-line Mn-hyperfine-structured feature at g≈2; it has

The  $Mn_4O_2$  and  $Mn_4O_3$  complexes both have two distinct Mn...Mn separations and oxide bridges, and are also more structurally related than might be apparent at first glance. It can readily be seen that the  $Mn_4O_3$  core can be obtained from an  $Mn_4O_2$  butterfly unit by incorporation of a third  $\mu_3 - O^2^-$  to bridge the two "wing-tip" Mn and one of the "hinge" Mn atoms of the  $Mn_4O_2$  "butterfly". This leads to an interesting mechanistic proposal for water oxidation by the WOC (vide infra).

The Me<sub>3</sub>SiCl reaction system has since been extended to other starting materials. Treatment of  $[Mn_3O(O_2CMe)_6(py)_3]^+$  with Me<sub>3</sub>SiCl leads to the isolation of neutral Mn\_4O\_3Cl\_4(O\_2CMe)\_3(py)\_3 (31). The Mn\_4O\_3Cl core of this complex is essentially identical to that of the previous complex with respect to its structural parameters and also contains Mn\_3^{III}Mn^{IV}.

### Higher Nuclearity Complexes

To complete our survey of structurally-characterized oxidebridged Mn complexes, we describe species with nuclearities >4. Three distinct types have been reported; hexanuclear, nonanuclear and dodecanuclear. The hexanuclear complex  $Mn_6O_2(piv)_{10}(pivH)_4$ results from the treatment of  $MnCO_3$  with pivalic acid in refluxing toluene (32). Its structure is shown in Figure 8. The complex has an average Mn oxidation state of +2.33 (4Mn<sup>II</sup>, 2Mn<sup>III</sup>), and the two central Mn atoms have been assigned as the Mn<sup>III</sup> centers. The Mn...Mn separations were not reported. The complex can be structurally related to the  $Mn_4O_2$  core of  $Mn_4O_2(O_2CMe)_6(bipy)_2$  by noting that the two  $\mu_3 \cdot O^2^-$  atoms of the latter complex have become  $\mu_4$  by binding to two additional  $Mn^{II}$ centers to yield the  $Mn_6O_2$  core of the hexanuclear species.

The reaction of  $Mn_3O(O_2CPh)_6(py)_2(H_2O)$  with salicylic acid (salH<sub>2</sub>) leads to formation of the nonanuclear species  $Mn_9O_4(sal)_4(salH)_2(O_2CPh)_8(py)_4$ , with an average Mn oxidation state of +2.89 (8Mn<sup>III</sup>, Mn<sup>II</sup>) (33). The structure is shown in Figure 9. It can be conveniently described as two  $Mn_4O_2$  units held together by a central 'bridging' Mn<sup>II</sup> atom; the latter is eight-coordinate by being bound to both oxygens of four salicylate carboxylate groups. The  $Mn_4O_2$  units have the same "butterfly" arrangement as



Figure 7. The structure of  $[Mn_4O_3Cl_6(O_2CMe)_3(HIm)]^{2-}$ . (Reproduced from ref. 23. Copyright 1987 American Chemical Society.)



Figure 8. The structure of  $Mn_6O_2(piv)_{10}(pivH)_4$ ; only portions of the peripheral ligands are shown. (Reproduced with permission from ref. 32. Copyright 1986 Royal Society of Chemistry).



Figure 9. The structure of  $Mn_9O_4(O_2CPh)_8(salH)_2(sal)_4(py)_4$ . (Reproduced with permission from ref. 33. Copyright 1987 VCH Verlagsgesellschaft).

found in  $[Mn_4O_2(O_2CMe)_7(bipy)_2]^+$ , with 'short' and 'long' Mn...Mn separations of 2.817(6) and 3.406(6)-3.443(6)Å, respectively.

The largest oxide-bridged Mn aggregate known is  $Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4$  (R = Me, Ph) (34). The structure of the benzoate complex is shown in Figure 10 (31). This remarkable complex contains a central  $Mn_4O_4$  cubane enclosed within a nonplanar ring of eight Mn centers via the intermediacy of additional  $\mu_3$ - $O^2$  bridges. The complex is mixed-valence ( $8Mn^{III}$ ,  $4Mn^{IV}$ ), and structural parameters indicate the 'cubane' Mn atoms to be the  $Mn^{IV}$  centers. Again,  $Mn_2$  pairs bridged by two oxide groups have Mn...Mn separations noticeably shorter (2.8-3.0Å) than those bridged by only one oxide group (3.3-3.5Å).

As for the nonanuclear complex, the  $Mn_{12}O_{12}$  core can be structurally related to the  $Mn_4O_2$  complexes by noting that the former can be considered as four  $Mn_4O_2$  butterfly units fused together such that a  $Mn^{\rm IV}$  center occupies a 'hinge' position of each butterfly. Four additional  $\mu_3 \cdot O^2$  bridges then complete the central cubane yielding the complete  $Mn_{12}O_{12}$  core.

### Summary of Structural Results

The current status of synthetic efforts in  $Mn/0^2$  chemistry is summarized below, emphasizing some general observations and trends which have become apparent:

1. Synthetic procedures to  $Mn/0^2$  complexes with a variety of nuclearities (2,3,4,6,9,12) are now at hand. The larger complexes can be considered aggregates of the smaller nuclearity species.

2. Structurally-characterized materials contain average Mn oxidation levels from +2.33 - +4, encompassing the complete range thought to be occurring in the WOC in its various  $S_n$  states.

3. In most cases, peripheral ligation is by 0<sup>-</sup> and/or Nbased groups as believed to be present in the WOC and provided by amino-acid side chain functions.

4. The 'short' (<u>ca</u> 2.7Å) Mn...Mn separation of the WOC deduced by EXAFS would appear to be associated with the presence of <u>two</u> bridging  $0^2$  groups between a Mn<sub>2</sub> pair. Only when such an arrangement is present has a Mn...Mn separation in this range been seen to date.

5. The 'long' (<u>ca</u> 3.3Å) separation would appear to be consistent with <u>at most</u> only one bridging  $0^2$  group between a Mn<sub>2</sub> pair; we say at most because bridging carboxylate or phenoxide groups (and no  $0^2$ ) can also result in a lengthened Mn...Mn separation.

6. Two types of tetranuclear complexes, containing  $Mn_4O_2$ and  $Mn_4O_3$  cores, are known which possess both 'short' and 'long' Mn...Mn separations; together these complexes span the oxidation range believed to be possessed by the WOC in its  $S_{-1}$ -- $S_2$  states.

### Mechanistic Proposals for the Water Oxidation Cycle

Two proposals for the water oxidation cycle involving Mn/O assemblies established in synthetic complexes have been published to date. These have attempted to describe the structural rearrangements of the  $Mn_4$  core and concomitant substrate binding



Figure 10. The structure of  $Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4$ . The four  $H_2O$  molecules are bound to Mn atoms Mn(8) and Mn(12); only portions of the peripheral ligands are shown.



Figure 11. Proposed mechanistic scheme for water oxidation employing the  $\rm Mn_4O_2$  and  $\rm Mn_4O_3$  cores established in model complexes.

and transformation to  $O_2$  which may be occurring during the catalytic cycle.

The first published proposal involved an Mn<sub>4</sub>O<sub>4</sub> cubane at the lower S<sub>n</sub> states converting to a Mn<sub>4</sub>O<sub>6</sub> adamantane-like unit in the higher S<sub>n</sub> states on incorporation of the two H<sub>2</sub>O molecules (35). Subsequent formation and evolution of O<sub>2</sub> returns the unit to a Mn<sub>4</sub>O<sub>4</sub> core ready for recycling. The second proposal employs the Mn<sub>4</sub>O<sub>2</sub> butterfly unit at the lower S<sub>n</sub> states converting, on incorporation of the two H<sub>2</sub>O molecules, into a Mn<sub>4</sub>O<sub>4</sub> cubane at the higher S<sub>n</sub> states (36). Subsequent formation and evolution of O<sub>2</sub> converts the cubane back into a Mn<sub>4</sub>O<sub>2</sub> unit ready for recycling.

Since the second proposal was formulated, the synthesis of Mn403- containing complexes was achieved. The structural relationship of this unit to the Mn402 core (vide supra) has led to an alternative scheme which is presented for the first time in Figure 11. It differs from the published version only in the identity of S2. Essentially, incorporation of only one substrate molecule could convert the butterfly  $Mn_4O_2$  unit at  $S_1$  into a  $Mn_4O_3$  unit (shown as  $Mn_4O_2(OH)$ ) at  $S_2$ . Subsequent incorporation of the second  $H_2O$  molecule now completes the  $Mn_4O_4$  ( $Mn_4O_2(OH)_2$ ) core, followed by evolution of  $O_2$  and return to a  $Mn_4O_2$  unit at  $S_0$ . Whether the modified proposal is any more relevant to the actual mechanism of photosynthetic water oxidation is uncertain given our current knowledge of the latter, but it does have the attraction of incorporating more structurally-established structural units than the previous proposals. Indeed, only its proposed S3 structure has yet to be found in a discrete tetranuclear model complex.

In conclusion, it is apparent that considerable progress has been made in the synthesis and characterization of higher oxidation state Mn/O complexes. A sufficiently large pool of complexes is now available to aid in the inter-disciplinary investigation of this important biological center, and structural and mechanistic proposals can now be made with more confidence and precedence. More work in the model area obviously remains to be performed, but the required synthetic procedures and knowledge of Mn/O chemistry is now at hand to allow and guide this extension.

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### Abbreviations

phthal = phthalocyanine TPP = tetraphenylporphyrin TBP = hydrido-tris(pyrazolyl)borate TACN = 1,4,7-triazacyclononane piv = pivalate Me<sub>3</sub>-TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane bipy = 2,2'-bipyridine py = pyridine ImH = imidazole phen = 1,10-phenanthroline
pic = picolinate

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