

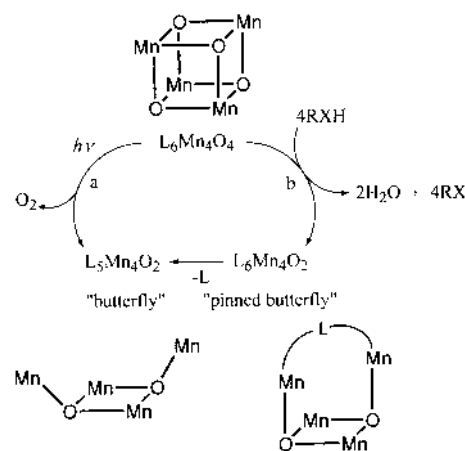
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Selective Photoproduction of O₂ from the Mn₄O₄ Cubane Core: A Structural and Functional Model for the Photosynthetic Water-Oxidizing Complex*

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Dedicated to Dr. Peter Gabriel

Both the announcement last year by the German Federal Government to eliminate the use of nuclear power generators by 2021^[1] and the recent shortage of electric power in California USA place renewed emphasis on development of socially acceptable energy sources such as solar^[2] and fuel cells.^[3] The latter cells rely on energy generated by the combination of H₂ (or hydrocarbons) with O₂. Both of these molecules are expected to be produced by solar-based water-splitting catalysts (H₂O → ½O₂ + H₂), hence, the efforts to understand Nature's photosynthetic process of O₂ generation by water oxidation in plants,^[4] and to functionally mimic the catalytic center,^[5,6] take on a pressing schedule. Key advances have occurred recently on both fronts with the first X-ray crystal structure at 3.8 Å resolution of the water-oxidizing complex (WOC) and its associated photochemical reaction center (photosystem II) from a cyanobacterium^[7] and the first report of intramolecular O₂ photoproduction from the bridging oxygen atoms of a manganese–oxo cluster of cubane-type geometry, L₆Mn₄O₄ (**1**; L = diphenylphosphinate; Ph₂PO₂⁻)



Scheme 1. Reactions of L₆Mn₄O₄ cubane complexes **1** and **1'**: a) UV photochemical reaction in the gas phase and b) reductive dehydration reaction in solution. RXH = organoamine, phenol, etc. Bridging phosphinates omitted for clarity.

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(Scheme 1 path a).^[8] O₂ release may proceed via a bridging peroxy transition state. This core type appears to be structurally similar to the WOC in its highest oxidation state.^[9, 10] Complex **1** can also be reduced by weak reductants (including organoamines and phenols) that transfer hydrogen atoms to form L₆Mn₄O₂ and two water molecules derived from the core oxygen atoms (Scheme 1 path b).^[11] Taken together these two reactions indicate a pathway for oxidizing water to O₂ that has the potential to be catalytic if the cycle can be closed.^[5, 6]

Only two other manganese complexes have provided evidence for O₂ production from water. A covalently linked perfluorinated dimanganese–porphyrin complex was reported to electrochemically oxidize water via O–O bond coupling within an unobserved (Mn^V=O)₂ intermediate, prior to oxidative destruction.^[12] Also, [(terpy)(H₂O)Mn(μ-O)₂Mn(terpy)(H₂O)]³⁺ (terpy = 2,2':6',2''-terpyridine) was reported to produce O₂ from oxidized precursors, such as hydrogen persulfate (H₂SO₅) or hypochlorite (ClO⁻), by nucleophilic addition to an unobserved Mn^V=O intermediate, prior to catalyst destruction.^[13, 14] However, in neither of these examples has the mechanism of O–O bond formation been conclusively established, nor are they likely to be a close model for the WOC.

Herein, we compare the photochemistry of manganese–oxo complexes having Mn₂O, Mn₂O₂, and Mn₃O₄ core types to that of the Mn₄O₄ cubane core. We find that the cubane core is unique in its ability to form O₂, and does so by selective rearrangement (without decomposition) to a complex with an Mn₄O₂ butterfly core.

For this study we have synthesized a new derivative of the cubane complex, L₆Mn₄O₄ (**1'**), containing the facially bridging bis(tolyl)phosphinate ligand, (MePh)₂PO₂⁻.^[15] Importantly, **1'** is 100 times more soluble than **1** in nonpolar solvents, which permits concentrations up to ~40 mM in CH₂Cl₂. For mass spectrometric studies all the complexes were dissolved in a volatile organic solvent (CH₂Cl₂, CH₃OH) and deposited on a gold substrate prior to evaporation to dryness. Laser desorption/ionization mass spectrometry (LDI-MS) (excitation at 337 nm, 1 ns duration, power = 1.2–7.9 μJ) and quadrupole mass spectrometry (Q-MS) (excitation at 355 nm, 14 ns duration, power = 500 μJ; excitation at 532 nm, power = 3.3 mJ) were performed as previously described for mass detection of ions (*m/z* 150–2000 amu) and neutrals (<40 amu), respectively.^[8]

The positive-ion LDI-MS spectrum of **1'** produces only two peaks above *m/z* 150 (Figure 1a) at *m/z* 1754.6 and 1477.4. The first peak corresponds to the parent cation **1'**⁺ (exact *m/z* 1755.2), while the latter peak is assigned to L₅Mn₄O₂⁺ (*m/z* 1477.9) arising from loss of one (MePh)₂PO₂⁻ ligand (mass 245.2) and two O atoms from **1'**. These assignments are corroborated by the LDI-MS spectrum of the L₆Mn₄(¹⁸O)₄ isotopomer (Figure 1b), in which the Mn₄O₄ core oxo units were replaced by ¹⁸O atoms.^[16] Only these two peaks were detected at all laser energies available (<4 μJ pulse⁻¹). The peak height of the fragment peak (*m/z* 1447.9) increases, while the parent ion peak (*m/z* 1755.2) decreases with laser pulse energy. Data supporting this correlation were previously published for the diphenyl derivative **1**.^[8] This trend was

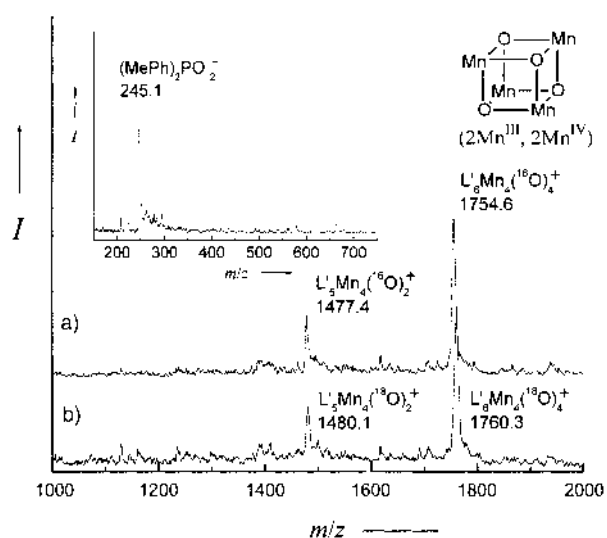
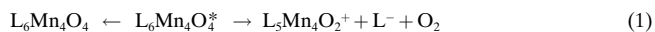


Figure 1. LDI-MS (positive ions) of a) L₆Mn₄O₄ and b) L₆Mn₄(¹⁸O)₄ with 75% labeling of core oxo groups by ¹⁸O. Excitation by N₂ laser at 337 nm; power = 2.9 μJ and 4.3 μJ for (a) and (b), respectively). Inset shows LDI-MS (negative-ions) of L₆Mn₄O₄. The ordinate axis is intensity (*I*: arbitrary units).

attributed to the competition between decay of the excited state **1*** to the ground state **1** and the photochemical reaction given in [Eq. (1)].



Consistent with the fragmentation pattern in Figure 1, the negative-ion LDI-MS of **1'** revealed only a single major peak at *m/z* 245.1 in the range *m/z* 150–750, corresponding to the (MePh)₂PO₂⁻ ligand (inset Figure 1). This photofragmentation pattern is identical to that observed for **1** prepared using Ph₂PO₂⁻ as bridging ligand.^[8] The Q-MS of **1'** (Figure 2a) reveals that the photoreaction releases an O₂ molecule^[17] and there is no evidence for any other oxygen-derived products (O, OH, OH₂).^[18] Thermodynamic estimates indicate that the O–O bond enthalpy should contribute greatly

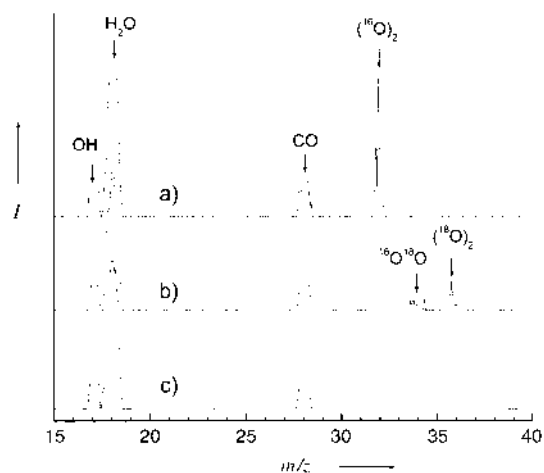


Figure 2. Q-MS of a) L₆Mn₄O₄, b) L₆Mn₄(¹⁸O)₄ with 75% labeling of the core oxo groups by ¹⁸O, and c) background (no complex). Internal standard peaks at *m/z* 17, 18, and 28 are from OH, H₂O, and CO. Excitation by Nd-YAG laser at 355 nm. The ordinate axis is intensity (*I*: arbitrary units).

(119 kcal mol⁻¹) to lowering the barrier to O₂ release.^[8, 11] The data for the L₆Mn₄(¹⁸O)₄ isotopomer (Figure 2b) reveals that the product O₂ is derived exclusively from the intramolecular combination of core oxo units; none of the oxygen atoms of (MePh)₂PO₂⁻ appear in the product O₂. These results explicitly show that laser UV excitation initiates a photochemical reaction in the gas phase (Scheme 1 path a). The relative quantum yield for O₂ production from **1'** increases with laser pulse energy and reaches 60% (not shown) at the maximum laser energy (7.9 μJ) available in our spectrometer (Table 1). These results extend the generality of the photochemistry previously observed with the first cubane complex **1** and summarized in Scheme 1 path a.

To determine if analogous photochemistry is observed with other manganese–oxo clusters the same experiments were carried out using the series of di- and trimanganese–oxo complexes^[19] listed in Table 1. This includes complexes having different bridging groups: di(*μ*-oxo), di(*μ*-oxo)-mono(*μ*-carboxylato), and mono(*μ*-oxo)-di(*μ*-carboxylato) and different formal oxidation states of the Mn ions: (III, III), (III, IV) and (IV, IV). Although all complexes absorb intensely at both UV excitation wavelengths (355 nm, and 337 nm), none of them produce molecular O₂ in significant yield when compared to the cubanes **1** and **1'**. LDI-MS reveals that these complexes do undergo laser-induced desorption and photoreactions at these wavelengths, leading to multiple fragments in the gas phase which vary with the laser power (not shown). However, the photo-products correspond to nonselective destruction of the complexes into multiple fragments. This is illustrated by the positive-ion LDI-MS spectrum of [(bpy)₂Mn(*μ*-O)₂Mn(bpy)₂](ClO₄)₃ (**2**; bpy = 2,2'-bipyridine) shown in Figure 3. One observes five photo-induced intense peaks in the range of *m/z* 100–2000. These correlate with the fragments derived from the decomposition of the core and ligands (Table 2). Neither a peak for the parent ion peak (*m/z* 255.5), nor for the intact core Mn₂O₂ fragment is detected. Rather, the preferred fragmentation leads to oxygen atoms which are detected exclusively in the two peaks assigned to [(bpy)_{*n*}MnO₂]⁺

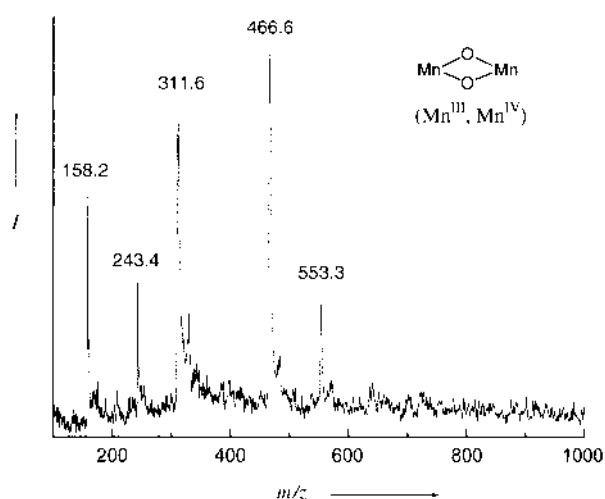


Figure 3. LDS-MS (positive-ions) of [(bpy)₂Mn(*μ*-O)₂Mn(bpy)₂](ClO₄)₃. The ordinate axis is intensity (*I*: arbitrary units).

Table 2. Proposed assignments of LDI mass fragment peaks for [(bpy)₂Mn(*μ*-O)₂Mn(bpy)₂](ClO₄)₃.

<i>m/z</i> ^[a]	Fragment	predicted <i>m/z</i>
158.2 ± 2.0	bpyH ⁺	157.2
243.4 ± 1.3	[MnO ₂ (bpy)] ⁺	243.1
311.6 ± 12.7	[2bpy – H] ⁺	311.4
466.6 ± 10.7	[3bpy – 2H] ⁺	466.5
553.3 ± 2.5	[MnO ₂ (3bpy – 2H)] ⁺	552.5

[a] *m/z* range denotes the full width at half height.

(*n* = 1, 3). Thus, the dimeric [Mn₂O₂]³⁺ core complex does not photorearrange to release O₂ despite having the same Mn oxidation state (Mn^{III}, Mn^{IV}) as **1'**; nor do any of the other core topologies shown in Table 1 containing the [Mn(*μ*-O)Mn]⁴⁺, [Mn(*μ*-O)₂Mn]³⁺, or [Mn(*μ*-O)₂Mn(*μ*-O)₂Mn]⁴⁺ cores.

Laser excitation in the visible absorption band at 532 nm (14 ns duration, power = 3.3 mJ) failed to produce O₂ from any of the complexes given in Table 1, including **1** and **1'**, even at a six-fold higher pulse energy than at 355 nm (no Q-MS

Table 1. Structures of Mn complexes used, photochemical O₂ yield and asymmetric vibration energies of the Mn-O-Mn core.

Complex ^[a]	Oxidation state	Core geometry	Excitation wavelength [nm]	O ₂ quantum relative yield[%] ^[b]	Mn-O-Mn ν_{as} [cm ⁻¹]
1 L ₆ Mn ₄ O ₄	(2Mn ^{III} , 2Mn ^{IV})		355	60 ^[c]	633
			532	0	
1' L' ₆ Mn ₄ O ₄	(2Mn ^{III} , 2Mn ^{IV})		355	60 ^[c]	633
			532	0	
2 [(bpy) ₂ Mn(<i>μ</i> -O) ₂ Mn(bpy) ₂](ClO ₄) ₃	(Mn ^{III} , Mn ^{IV})		355	0	690
			532	0	
3 [(HBPz ₃)Mn(<i>μ</i> -O)(<i>μ</i> -RCO ₂) ₂ Mn(HBPz ₃)]	(2Mn ^{III})		355 ^[d]	0	716 ^[d]
			532 ^[d]	0	
			355 ^[e]	0	
			532 ^[e]	0	
4 [(HBPz ₃)Mn(<i>μ</i> -O) ₂ (<i>μ</i> -RCO ₂)Mn(<i>μ</i> -O) ₂ (<i>μ</i> -RCO ₂)Mn(HBPz ₃)]	(3Mn ^{IV})		355 ^[d]	0	702 ^[d]
			532 ^[d]	0	

L = Ph₂PO₂⁻, L' = (MePh)₂PO₂⁻, bpy = 2,2'-bipyridine, HBPz₃⁻ = hydrotris(1-pyrazolyl)borate; [a] The number of moles the complex used in each experiment is constant. [b] The zero quantum yield indicates values less than the detection limit for O₂ based on the sensitivity for O₂ detection from **1'** (< 3.7%). [c] The yield was taken as the ratio of LDI-MS peak heights (L₅Mn₄O₂/L₆Mn₄O₄). [d] R = CH₃, [e] R = C₂H₅.

peaks at all!). Hence, the UV photoproduction of O₂ occurs exclusively for the Mn₄O₄ cubane core type upon excitation of the O → Mn charge-transfer absorption at 300 nm ($\epsilon = 2.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), but not the visible band at 498 nm ($\epsilon = 1.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).^[8] We may conclude that of the complexes listed in Table 1 only the Mn₄O₄ cubane core topology provides a favorable geometry for efficient and selective photorearrangement to produce O₂ by charge-transfer excitation. The L₅Mn₄O₂ photoproduct of **1'** (see below) is presumed to have a “butterfly” core geometry (Scheme 1). The gas-phase structure is unknown, and is only suggested based on comparison to the deoxygenated product, L₆Mn₄O₂, produced in solution by chemical reduction.^[11]

Importantly, no mass spectral evidence is found for the photochemical O₂ release from excited **1'** without the loss of one (MePh)₂PO₂⁻ ligand, nor of ligand release without the loss of O₂. The release of O₂ to form the pinned butterfly structure L₆Mn₄O₂ is thermodynamically favored by $-6.2 \text{ kcal mol}^{-1}$ in the ground state, but is not observed because of a kinetic barrier that the present data show to be imposed by the phosphinate bridges.^[8] The origin of the selective O₂ release observed for the photo-excited Mn₄O₄ cubane core appears to correlate with the considerably weaker Mn–O (core) bonds, as found by both X-ray diffraction (mean bond length 1.95 Å for **1** versus 1.8 Å for the Mn₂(III, IV) complex **2**, both in their ground states) and by their much lower-energy Mn–O–Mn core vibrations ($\tilde{\nu}_s = 516 \text{ cm}^{-1}$, $\tilde{\nu}_{as} = 633 \text{ cm}^{-1}$ for the symmetric and asymmetric modes stretches in the ground state) versus the model complexes in Table 1. The inter-oxygen separation in the core of **1** and **1'** is 2.53–2.60 Å which is much longer than the O–O bond in hydrogen peroxide (1.50 Å) and O₂ (1.21 Å). Thus, it is clear that an O–O bond of appreciable stability can not be formed in the ground-state cubanes without large-scale distortion. The experimental data points to the release of a phosphinate bridge and further weakening of the O–Mn bonds in the photo-excited state as the trigger that enables the distortion of the core bonds to occur. The resulting distortion might then permit the oxygen atoms to move sufficiently close together to allow the large intermolecular O–O bond enthalpy ($-36 \text{ kcal mol}^{-1}$ in HO–OH) to contribute to lowering the activation barrier for O₂ formation. By contrast, the much stronger and shorter Mn–O bonds within the planar Mn₂O₂ rhombohedra of the dimer and trimer complexes in Table 1 may be why these core types photodecompose to MnO₂X fragments without Mn–O bond cleavage or O₂ formation.

EPR spectroscopy indicates that cubanes **1** and **1'** have the same oxidation state as the so-called S₃ state of the WOC, or one-electron below the S₄ state that is the precursor to thermal O₂ release.^[9, 10] This assignment is debatable particularly in light of data from X-ray absorption near-edge spectroscopy.^[10] It will be interesting to see if the one-electron oxidized cubanes **1**⁺ and **1'**⁺, which have been isolated,^[20] will also prove to be selective precursors to photolytic and/or thermal evolution of O₂. Based on EPR and X-ray absorption

spectroscopic evidence distorted Mn₄O₄ cubane or Mn₄O₂X₂ pseudo-cubane cores have been implicated as possible core types for the S₃ and S₄ states of the WOC.^[10] The present study indicates a molecular basis for why the cubane core topology appears to be uniquely suited for O₂ evolution.

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- [15] **1'** was synthesized according to the earlier reported synthesis of **1**^[21] by replacing Ph₂PO₂H with (MePh)₂PO₂H (65% yield). (MePh)₂PO₂H was prepared by the Grignard reaction of MePhMgBr with Et₂N-POCl₂ according to the literature.^[22] The ¹H NMR, MS, FT-IR, and electronic spectra indicate a symmetrical cubane core very similar to **1**^[21]
- [16] Synthesis of L₆Mn₄(¹⁸O)₄ was performed starting from [Mn₂(¹⁸O)₂(bpy)₄](ClO₄)₃ achieved by acid catalyzed exchange against 99% ¹⁸O-enriched water. The incorporation of av. 75% ¹⁸O was confirmed by FT-IR and LDI-MS analysis.
- [17] Upon photoexcitation of **1'** only a single peak was observed at *m/z* 32 corresponding to (¹⁶O)₂. For L₆Mn₄(¹⁸O)₄ (av. 75% isotopic enrichment) two peaks at *m/z* 34 and 36 were observed, corresponding to ¹⁶O¹⁸O and (¹⁸O)₂, respectively.
- [18] Atmospheric H₂O and CO₂ in the mass spectrometer produce a constant background signal (Figure 2c), while photoproducted species can be distinguished by a “spike” appearance in the mass scan. The spikes arise as a result of the short laser pulse, which produces transient mass changes on a much shorter time scale than the slower sweep rates of the mass analyzer.
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