O_2 Evolution from the Manganese−Oxo Cubane Core $Mn_4O_4^{6+}$: A Molecular Mimic of the Photosynthetic Water Oxidation Enzyme?

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Abstract: Photosynthesis produces molecular oxygen from water catalyzed by an enzyme whose active site contains a tetramanganese−oxo core of incompletely established structure. The first functional mimic of this core has been synthesized containing a cubical $[Mn_4O_4]^{n+}$ core, surrounded by six facially bridging bidentate chelates to the manganese ions ($(dpp)_6Mn_4O_4$ (**1**); $dpp^- =$ diphenylphosphinate anion). Bond enthalpy data predict that the $Mn_4O_4^{6+}$ core is thermodynamically capable of releasing molecular O_2, but is kinetically prevented from doing so by an activation barrier. UV light absorption into a Mn−O charge-transfer excited state (but not excitation of a Mn ligand-field excited state) efficiently releases an O_2 molecule if performed in the gas phase and concomitantly releases a bridging dpp^- anion and the cationic species $(dpp)_5Mn_4O_2^+$ (presumed Mn_4O_2-butterfly core type). All species were identified by high resolution mass spectrometry. This reaction proceeds with high quantum efficiency (>50%) and is the only observable reaction channel. The O_2 product derived exclusively from the corner oxo's of the cube based on photochemistry of the ^{18}O-isotopomer, $((dpp)_6Mn_4(^{18}O)_4$. Neither O_2 release nor dpp^- dissociation are observed individually to occur in the excited state, indicating that O−O bond formation and O_2 release require dissociation of one of the six dpp^- chelates ("Jack-in-the-Box" mechanism for O_2 formation). By contrast, neither O_2 production nor chelate photodissociation are observed in condensed phases, presumably due to either quenching of the photoexcited state or rapid recombination of dpp^- and $(dpp)_5Mn_4O_4^+$ in the solvent cage. Previous results show that chemical reduction of (**1**) in solution using hydrogen atom donors produces the deoxygenated $(dpp)_6Mn_4O_2$ core and releases two water molecules as the only products. Thus the $[Mn_4O_4]^{n+}$ cubane core is an intrinsically reactive core topology that facilitates both the selective chemical reduction of two of the four oxygen atom bridges to water molecules and their photorearrangement to an O_2 molecule under the control of chelation of the manganese ions by dpp^-. These results may offer insight into the possible nature of the photosynthetic O_2-evolving mechanism.

Introduction

Chemists have long sought to prepare catalysts capable of oxidizing water to oxygen, eq 1, as it would provide a pure source of O_2 free of atmospheric N_2 that is needed for environmentally clean combustions.

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

However, despite considerable efforts there are few man-made catalysts of any kind available for this conversion and none have made an impact on industrial chemistry.[1,2] The difficulty of catalyzing this seemingly simple reaction has both thermodynamic and mechanistic origins. The catalyst must break four strong O−H bonds on two water molecules (enthalpy 119 kcal mol^{-1} $bond^{-1}$ for free water). In addition these water molecules need to be in very close proximity to enable the favorable enthalpy for O−O bond formation (33 kcal/mol for HO−OH) to contribute to driving the unfavorable bond breaking steps. Furthermore, the chemical intermediates formed are so reactive that autoxidation of the catalyst often leads to self-destruction.

Nature solved these problems approximately 3 billion years ago through evolution of a unique metalloenzyme required for oxygenic photosynthesis in all plants and cyanobacteria. This enzyme is called the Photosystem II water oxidizing complex, or WOC. Its active site is comprised of an oxo-bridged tetramanganese cluster, one Ca^{2+} ion, and one or more Cl^- ions, denoted $Mn_4O_xCa_1Cl_y$.[3−5] In association with a tyrosyl radical this core catalyzes reaction 1, using a chlorophyll cation radical as terminal electron acceptor generated in Photosystem II by light absorption.[6] Sequential removal of individual electrons by light absorption produces five metastable oxidation states of the WOC, designated S_0, S_1, ..., S_4, with S_4 decaying spontaneously to S_0 and releasing O_2 in the dark.

Although many useful manganese complexes have guided thoughts on the structure of the WOC,[7,8] only two functional models that are known to oxidize water have been reasonably well characterized to date. Neither is a structural model of the WOC.[9,10] A few incompletely characterized manganese heterogeneous systems have also been reviewed.[1] One of these, Mn_6−

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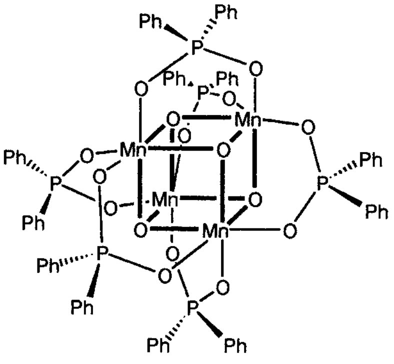
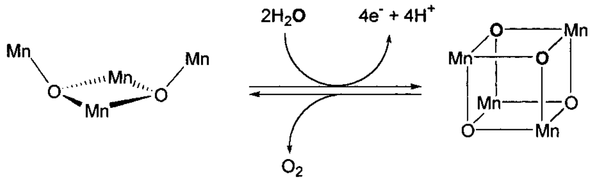
silesquioxane, works exclusively in two-phase aqueous suspensions with low activity and short-term stability.[9] The other is a covalently linked perfluorinated-dimangano−porphyrin complex that autoxidizes rapidly.[10] A few O_2 molecules can be produced from highly oxidized precursors such as hydrogen persulfate (H_2SO_5) or hypochlorite (ClO^-) catalyzed by a simple $[Mn_2O_2]^{3+}$ rhombohedral core complex, which was hypothesized to form a terminal oxo (Mn═O) as intermediate prior to catalyst destruction.[11] However, in none of these cases has the mechanism of O−O bond formation been conclusively established (i.e. coupling of terminal oxo, bridging oxo, water nucleophile, etc.).



$L_6Mn_4O_4$ **(1)**

We have previously reported the synthesis of the first example of an all-oxo $[Mn_4O_4]^{n+}$ cubane core in a molecular complex that has each face bridged by a diphenylphosphinate chelate, $L_6Mn_4O_4$ (L = diphenylphosphinate anion ($Ph_2PO_2^-$) = dpp^-).[13] Both X-ray diffraction studies of the solid and NMR spectroscopy of solutions of $L_6Mn_4O_4$ have established a symmetrical cubane core topology for this compound, with dpp^- chelates bridging all six faces of the cube between pairs of structurally similar Mn ions (tetrahedral core symmetry). The existence of a symmetrical core geometry for $L_6Mn_4O_4$ with only one environment for each of the four Mn ions, despite the formally inequivalent mixed-valence oxidation states of 2Mn(III) + 2Mn(IV), is a very rare observation in Mn−oxo compounds.[14] This contrasts with the deeply trapped Mn(III) and Mn(IV) ions found in all examples of the $[Mn_2O_2]^{3+}$ core compounds, where Mn−O bond differences typically range from 0.05 to 0.2 Å.[8] This electronic difference and the long O,O′ distance of the dpp^- ligand (0.25 Å longer than typical carboxylatos) combine to create considerably longer Mn−O(μ_3-oxo) bonds (1.95 Å) in the cubane than the Mn−O(μ_2-oxo) bonds in $[Mn_2O_2]^{3+}$ cores (1.8 Å) and $Mn_2O_2(O_2CR)^{2+}$ cores (1.8 Å). This also gives rise to correspondingly longer Mn−Mn separations (by 0.2−0.3 Å). These metrical differences lead to the prediction that intramolecular O−O bond coupling of the oxo bridges and release of O_2 might be possible starting from $L_6Mn_4O_4$ if one of the dpp^- chelates could be removed, thereby freeing two of the core oxos from the geometrical constraints imposed by the chelate.[23]

Scheme 1. Proposed Butterfly-Cubane Rearrangement for Photosynthetic Water Oxidation



An early proposal for the mechanism of photosynthetic water oxidation is given in Scheme 1.[12] This mechanism hypothesized that a $[Mn_4O_4]^{n+}$ cubane core forms transiently in the S_4 state, and undergoes internal charge transfer by oxidation of the oxide bridges and reduction of the Mn ions coupled to intramolecular O−O bond formation with formation of O_2 and a deoxygenated $[Mn_4O_2]^{n+}$ butterfly core. A catalytic cycle was imagined to be possible (but never demonstrated) by binding of two water molecules followed by four successive oxidation/deprotonation steps to complete the catalytic cycle. Direct tests of this proposal have not been possible until a synthetic method was developed to prepare the first example of the all-oxo $[Mn_4O_4]^{n+}$ cubane core in a molecular complex.[13] Herein we report experiments testing this proposal which establish the existence of an intramolecular pathway for O_2 formation from oxide bridges in the cubane core complex $L_6Mn_4O_4$.

Experimental Section

Synthesis of $L_6Mn_4O_4$ containing the cubane core was previously achieved by fusion of two $[(bpy)_4Mn_2O_2]^{3+}$ (bpy = 2,2′-bipyridine) rhombohedral cores by displacement of bpy (a neutral, bidentate, chelate) with dpp^-.[13] We have found the longer O,O′ distance of phosphinates ($RRPO_2^-$) vs carboxylates (RCO_2^-) along with the insolubility of the resulting neutral complex to be important for achieving high yields of $L_6Mn_4O_4$. The absorption spectrum of $L_6Mn_4O_4$ in dichloromethane exhibits a maximum at 498 nm (1400 M^{-1} cm^{-1}) and a shoulder at 300 nm (21000 M^{-1} cm^{-1}) with additional bands in both the far-UV and near-IR.[13,15] Synthesis of the $^{18}O_4$-isotopomer of $L_6Mn_4O_4$ was performed starting from $[Mn_2(^{18}O)_2(bpy)_4](ClO_4)_3$ achieved by acid-catalyzed exchange against 99% ^{18}O-enriched water. Laser resonance Raman spectroscopy confirmed incorporation of greater than 90% ^{18}O into the oxo bridges (courtesy of D. Ji and R. Czernuszewicz). Laser-desorption−ionization time-of-flight mass spectroscopy, LDI-TOF-MS, was conducted by vaporization and ionization of the solid compound using a pulsed N_2 laser (337 nm, 1 ns duration) to excite the UV absorption band. This method enables detection of either positive or negative ions by vaporization of the solid compound from an inert gold substrate. Positive ion detection was performed using the following conditions: laser power = 0.19−4.19 μJ, vacuum = the order of 10^{-7} Torr, ion optics = −28 kV, and detector = −4.75 kV. Negative ions were detected using the following conditions: laser power = 1.62 μJ, vacuum = 1.05 × 10^{-7} Torr, ion optics = +28 kV, and detector = +4.75 kV. A quadrupole mass spectrometer with electron impact ionization source was employed for O_2 detection. This spectrometer was interfaced with a Nd:YAG laser for excitation at 355 nm (pulse duration = 14 ns) of solid $L_6Mn_4O_4$ deposited on a gold substrate. Repetitive sweeps were acquired in the mass range 15 to 40 amu with the laser excitation synchronized at the start of the sweep.

Results

Figure 1A shows the positive-ion laser-desorption−ionization time-of-flight mass spectrum of $L_6Mn_4O_4$. This method detects two dominant peaks in the mass range of >50 to 2000 amu

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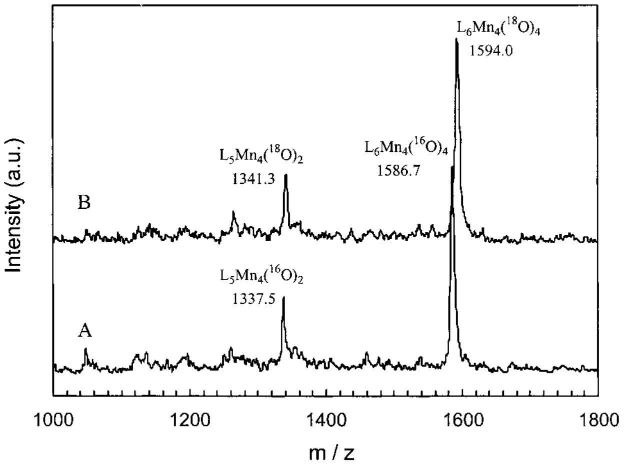

Figure 1. Laser desorption ionization-time-of-flight mass spectrometry (LDI-TOF-MS; positive ion detection) of $L_6Mn_4O_4$ using nitrogen laser excitation (337 nm): (A) natural abundance $^{16}O_4$-isotopomer ($L_6Mn_4(^{16}O)_4$) and (B) $^{18}O_4$-isotopomer ($L_6Mn_4(^{18}O)_4$) with four core oxo's replaced by ^{18}O (>90%, incorporation confirmed by resonance Raman spectroscopy).

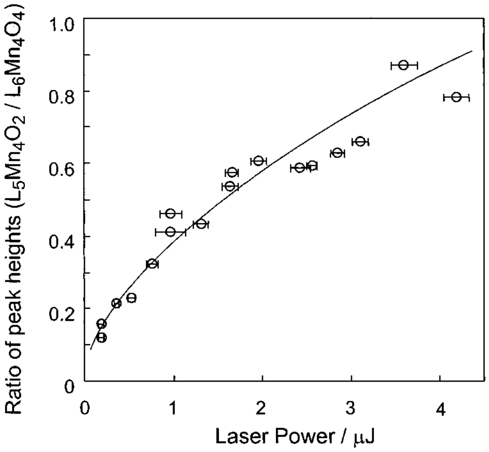

Figure 2. Dependence of the ratio of peak heights for masses of $L_5Mn_4O_2^+$ (*m/z* 1337)/$L_6Mn_4O_4^+$ (*m/z* 1586) on the laser power in the LDI-TOF-MS experiment of Figure 1.

and these were the dominant fragments at all laser powers investigated. The most intense peak corresponds to the parent cation, $L_6Mn_4O_4^+$ (*m/z* 1586.7 ± 3.8), while the other major product is a fragment species, $L_5Mn_4O_2^+$ (*m/z* 1337 ± 2.1), corresponding to the loss of one dpp⁻ ligand (*m/z* 217.2**)** and two O atoms (*m/z* 32.0):

$$[L_6Mn_4O_4]^* \rightarrow [L_5Mn_4O_2]^+ + L^- + 2O \text{ (or } O_2) \qquad (2)$$

Importantly, no peaks were found for loss of one dpp⁻ without concomitant loss of two oxygen atoms, nor loss of only 2 oxygen atoms without loss of one dpp⁻. This fragmentation pattern indicates that two of the corner oxos can be released, but only if one of the facially bridging chelates is also released.

As expected, the amplitudes of both the parent and photofragment mass peaks increase with laser power used to vaporize the solid. Figure 2 shows that as the laser power is increased by 20-fold the ratio of intensities for the fragment/parent mass peaks (*m/z* 1337/1586) increases by 8-fold and approaches a relative quantum yield of nearly 50% at the highest power used. The absence of saturation in yield suggests that an even greater quantum yield should be possible at higher laser powers. These data also indicate that the $L_5Mn_4O_2$ photofragment is produced from $L_6Mn_4O_4$ by an activated process involving either direct photolysis or possibly subsequent thermal reaction following light absorption. The requirement for input of activation energy for release of dpp⁻ and two O atoms is denoted in eq 2 by the asterisk. By contrast, the unexcited parent cation, $[L_6Mn_4O_4]^+$, exists as a stable species that has been isolated and structurally characterized.[16]

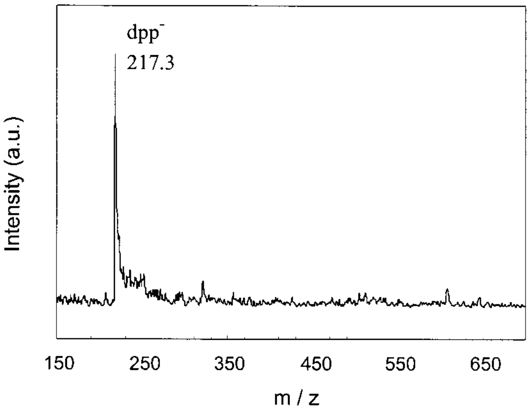

Figure 3. Laser desorption ionization-time-of-flight mass spectrometry (LDI-TOF-MS; negative ion detection) of $L_6Mn_4O_4$ using nitrogen laser excitation (337 nm) under the following conditions: laser power = 1.62 μJ, vacuum = 1.05 × 10^{-7} Torr, and ion optics = 28 kV.

Investigation of the source of these fragments was examined by comparison to the ^{18}O-isotopomer, $L_6Mn_4(^{18}O)_4$, in which the corner oxygen atoms were replaced with ^{18}O. The LDI-TOF mass spectrum of $L_6Mn_4(^{18}O)_4$ in Figure 1B shows a parent ion peak at *m/z* 1594.0 ± 3.0 amu, or 7−8 amu greater than the $^{16}O_4$-isotopomer, indicating labeling of 3−4 oxo's on average. Again only a single dominant photofragment was observed, in this case at *m/z* 1341.3 ± 2.4 amu vs 1337.5 for the ^{16}O-isotopomer. These mass changes corroborate the assignment of the photofragment as having lost two oxygen atoms from the core and one dpp⁻ ligand, but they do not distinguish whether the O atoms are released as two O atoms, as molecular O_2, or, alternatively, by insertion into the ejected phosphinate chelate to form oxidation products such as the diphenyl phosphate diester, $(PhO)_2PO_2^-$.

Therefore, to identify the anionic products induced by the photochemistry of **1** we performed a search for negative ions by LDI-TOF-MS in the anion detection mode. This method was restricted to masses above *m/z* 150. Figure 3 presents the data in the range *m/z* 150−700 using a laser power of approximately 1.62 μJ, where oxidized dpp⁻ would be detectable if it forms. A single major photoinduced peak is observed at *m/z* 217.3 based on calibration standards including diphenylphosphinic acid (dpp⁻; *m/z* 217.2). There is no evidence for formation of the mono- or dioxygenated chelates at 233 or 249 amu, respectively. The observed peak at 217.3 was not changed if **1** was replaced by its ^{18}O-isotopomer, $(dpp)_6Mn_4(^{18}O)_4$ (data not shown). Thus, we may conclude that the photochemically induced fragment corresponds to the dpp⁻ anion exclusively, as summarized by eq 2. [25]

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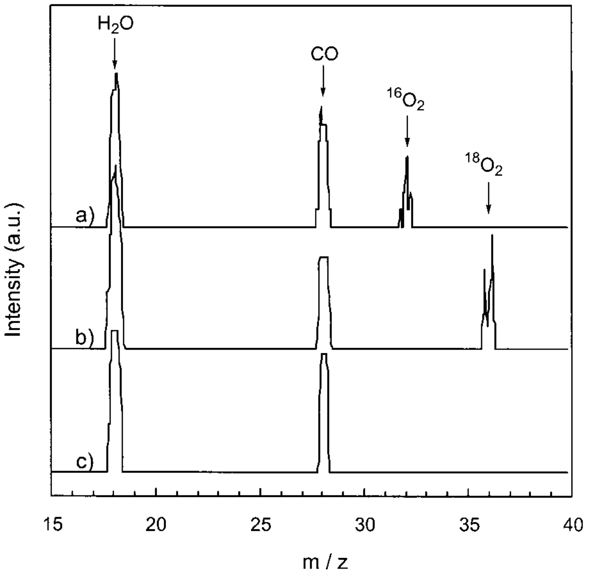

Figure 4. Detection of photoproduced O_2 from $L_6Mn_4O_4$ by quadrupole-mass spectrometry synchronized to a laser flash (355 nm, 14 ns pulse duration, Nd:YAG laser) using (a) $L_6Mn_4(^{16}O)_4$, (b) $L_6Mn_4(^{18}O)_4$, or (c) no complex. Internal standard peaks at *m/z* 18 and 28 are due to H_2O and CO as constant background. Intensity was normalized based on the peak area of CO (*m/z* 28). Background pressure 10^{-9} Torr.

To search for smaller mass products, including dioxygen, we employed a quadrupole mass spectrometer interfaced to a Nd:YAG laser for excitation at 355 nm (pulse duration = 14 ns). Figure 4 shows the data for both the natural abundance cubane and the $L_6Mn_4(^{18}O)_4$ isotopomer. Comparison to the control, corresponding to laser excitation of the blank gold substrate, shows that UV excitation of $L_6Mn_4O_4$ produces a single species in the range 15−40 amu having mass 32 amu corresponding to photoproduction of O_2.[17] Confirmation of this assignment and proof that it originates from the corner oxo atoms of the cubane was obtained by repeating the experiment with the $^{18}O_4$-isotopomer of $L_6Mn_4O_4$. This experiment, shown in Figure 4, also yielded a single peak at *m/z* 36, corresponding to formation of $^{18}O_2$. Less than 10% of $^{16,18}O_2$ was detected which is consistent with the >90% isotopic enrichment of the sample. No evidence was observed for photoproduction of free O atoms or OH radicals,[26,27] nor are these products expected based on predictions of a large energetic barrier.[28] We may conclude that the photoreaction given in eq 2 releases O_2 molecules, not O atoms, and that these molecules originate exclusively from the corner oxygen atoms of the cubane by intramolecular bond formation. We refer to this photochemical controlled pathway as the “Jack-in-the-Box” mechanism for O_2 formation.

The above experiment was repeated on $L_6Mn_4O_4$ using the 532 nm line of the Nd:YAG laser. Despite the higher power available at this wavelength (× 6−7-fold greater power than at 355 nm) there was no evidence for production of O_2 or other low mass photoproducts (<40 amu) in the gas phase. There is significant absorption at this wavelength by $L_6Mn_4O_4$. The molar absorptivity at this wavelength is 1300 M^{-1} cm^{-1} in CH_2Cl_2 solvent. Preliminary evidence suggests that this band may correspond to a Mn(III) or Mn(IV) ligand field band. The absence of O_2 formation at 532 nm even though more laser energy was used than in the UV experiments suggests that the photoreaction is photolytic rather than thermal in origin.

The absolute yield of O_2 could not be obtained from the MS data in Figure 4 using the present experimental system. We did observe that the yield of O_2 does increase approximately in proportion to the laser power, although absolute calibration versus the yield of the photofragment species ($L_5Mn_4O_2$) in Figure 2 could not be made since the experimental setups are completely different. However, based on the absence of any other detectable photochemical reaction than eq 2, the maximum relative yield of O_2 should be equal to that for the photofragment species ($L_5Mn_4O_2$), i.e., 50% or greater.

Photolysis experiments were also conducted in CH_2Cl_2 solutions using a closed quartz cell and a water-filtered tungsten halogen source for illumination in the UV−vis region. The headspace above the solution was sent to an isotope-ratio mass spectrometer after passage through a cold trap at −75 °C to remove solvent. Both the parent cubane and the $L_6Mn_4(^{18}O)_4$ isotopomer where investigated.[29] The mass spectrometry results showed no evidence for production of O_2 in the gas phase, corresponding to less than 0.01% yield. The absorption spectrum of the solution was also monitored after photolysis of the solutions and revealed no evidence for loss of the starting material ($L_6Mn_4O_4$) in solution.

Discussion

The requirement for loss of one phosphinate ligand during the photolytic release of O_2 in the gas phase confirms our hypothesis that the symmetrical bridging dpp^- ligands may contribute at least a portion and possibly most of the activation barrier against O−O bond formation in the cubane core of $L_6Mn_4O_4$. The distance between the oxide bridges in $L_6Mn_4O_4$ is 2.53−2.60 Å, a distance that is considerably longer than the O−O distance in either O_2 (1.21 Å) or hydrogen peroxide, H_2O_2 (1.50 Å), and slightly shorter than the van der Waals radius (2.8 Å) of O atom. Therefore, very little of the O−O bond enthalpy can be available for promoting O_2 formation in $L_6Mn_4O_4$ without great distortion to reduce the O···O distance.

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(25) In the negative ion detection mode of LDI-TOF-MS electrochemical reduction of **1** to form the parent anion $\mathbf{1}^-$ at *m/z* 1586.7 (1594.0 for the $L_6Mn_4(^{18}O)_4$ isotopomer) can also occur during drift down the TOF detector (held at −4.75 kV). This reduction leads to chemical fragmentation, in addition to the photochemical ejection of the dpp^- chelate from the excited neutral parent **1*** by eq 2. Chemical fragmentation of $\mathbf{1}^-$ produces additional peaks at *m/z* 1193.3, 1095.5, 706.3, and 120.2, which correspond to $L_5Mn_2^-$, $L_4Mn_3O_4^-$, L_3Mn^-, and MnO_4^-, respectively. This chemical fragmentation in the gas phase is consistent with previous results showing the instability of $\mathbf{1}^-$ generated in solution by chemical reduction using cobaltocene, leading to formation of monomeric Mn(II) species.

(26) Although atmospheric water in the mass spectrometer produces a constant background signal, photoproduced water species can be distinguished by a “spike” appearance in the mass scan. This arises due to the short laser pulse which produces transient mass changes on a much shorter time scale than the slower sweep rates of the mass analyzer.

(27) The bimolecular rate that two O atoms which are photoreleased from different cubanes would encounter one another and combine to produce O_2 at the pressure of the chamber (10^{-9} Torr) is vanishingly small.

(28) In ref 15, the calculated Δ*H* for the reaction of $L_6Mn_4O_4 \rightarrow L_6Mn_4O_2 + 2[O]$ (O atom) has a sign error and should read +442 kcal/mol. Accordingly, the Δ*H* for the reaction of $L_6Mn_4O_4 \rightarrow L_6Mn_4O_2 + O_2$ should read −6.2 kcal/mol.

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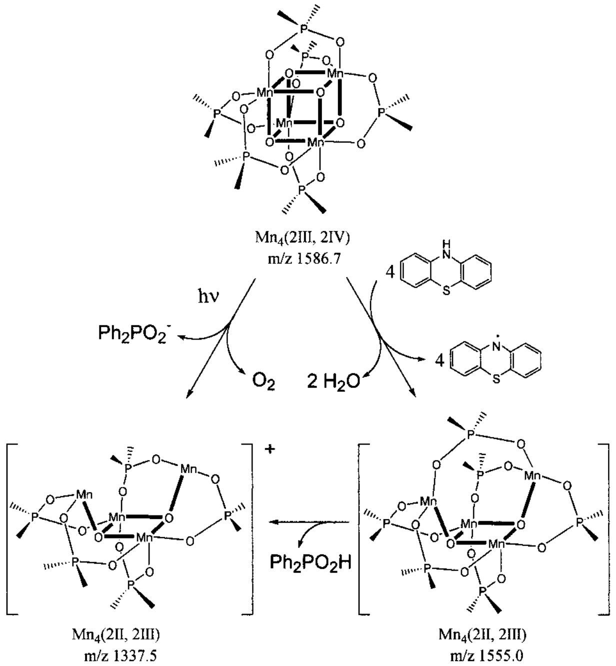
Scheme 2. Reactions of the Manganese−Oxo Cubane, $Mn_4O_4L_6$, L = $Ph_2PO_2^-$, in the Gas Phase (left) and as a Solute in Acetonitrile/Methylene Chloride Solvent (right)



NMR studies of $L_6Mn_4O_4$ in solution reveal no evidence for free dpp$^-$ ligands, which is consistent with the stability of the core against spontaneous O_2 release. This conclusion is also supported by the data showing no evidence for O_2 release or photodecomposition of $L_6Mn_4O_4$ in fluid solution or solid-state phase under UV−vis illumination. This result could indicate either photochemical quenching of the excited state or rapid geminate recombination of dpp$^-$ and $L_5Mn_4O_4^+$ in the solvent cage.

We recently showed that two of the corner oxygens of the cubane can also be converted into two labile water molecules by treatment with various chemical reductants in solution, thus establishing the critical link between the corner oxo bridges and the formation of water molecules, as required for a functional model of the WOC[15,20] (right side of Scheme 2). On the basis of these data a thermodynamic cycle for O_2 evolution from $L_6Mn_4O_4$ was constructed using the known bond enthalpies of the reductant (phenothiazine H−N bond, 82 kcal/mol) and the O_2 bond. This cycle showed that the cubane core has a favorable enthalpic driving force toward spontaneous release of O_2 (<-6.2 kcal/mol),[28] but must be prevented from doing so by a large activation barrier.

A kinetic barrier also blocks the release of O_2 from the permanganate anion (MnO_4^-) in its stable ground state, but can be overcome by photochemical excitation into an O → Mn(VII) charge-transfer band.[18] In this case, the reorganization barrier that is overcome in the excited state which allows O_2 release involves weakening of the Mn−O bonds by two-electron intramolecular reduction of Mn(VII) to form a Mn(V)(O_2^{2-}) "peroxyl" intermediate. Like permanganate, the $Mn_4O_4^{6+}$ core of the cubane also has tetrahedral symmetry in its ground electronic state. Therefore, we speculate that intramolecular two-electron charge transfer from oxide bridges forming a peroxyl core intermediate, $[Mn_4O_2(O_2^{2-})]^{6+}$, may be the photochemical intermediate that precedes O_2 formation by eq 2. In support of this proposal, O−O bond formation by reversible, solvent-induced, oxide/peroxide conversion between $Cu_2(O^{2-})_2$ and $Cu_2(O_2^{2-})$ cores also occurs in the ground state of some copper complexes, although these do not further react to release O_2.[19]

Preliminary tests also indicate that mild thermal excitation of $L_6Mn_4O_4$ also can overcome the activation barrier to O_2 production, possibly triggered by rearrangement of a dpp$^-$ chelate[20] (Carrell & Dismukes, unpublished results). The existence of a low-energy thermal pathway for release of O_2 from $L_6Mn_4O_4$ supports the original hypothesis by Vincent and Christou that a cubane-butterfly rearrangement could provide a viable ground-state pathway for formation of O_2 from a Mn_4O_4 cubane core in the photosynthetic process.

The reactions of the cubane to form both water and O_2, as summarized in Scheme 2, suggest some interesting possibilities for the corresponding photosynthetic reaction pathway. The conversions between the S_0 to S_4 states could involve the binding of two water molecules to an incomplete cubane core (Mn_4O_2) or by substrate-induced displacement of one or two chloride ions within a distorted cubane core ($Mn_4O_2X_2$), followed by or in parallel with stepwise removal of four-electrons and four-protons. The transient S_4 state might contain a reactive $[Mn_4O_4]^{7+}$ core with compensation of charges from the protein and ligands. The location of calcium juxtaposed to one face of the Mn_4 core[4,22] might then enable it to control both substrate water binding and also lower the activation barrier to O−O bond coupling by stabilization of a peroxide intermediate, $Ca(O_2^{2-})$-Mn_4O_2.[23] Other proposed mechanistic features for the photosynthetic process, including the possibility of H atom transfer to tyrosyl radical, are neither precluded nor necessarily supported by this mechanism.[6,24]

The low symmetry of the Mn_4O_x core of the photosynthetic WOC, inferred from Mn EXAFS studies, has been taken as evidence against the presence of a symmetrical cubane core.[5] However, there are no data for the transient S_4 state to make such a claim, and moreover, EPR data for the S_2 state are consistent with the presence of distorted cubane or incomplete cubane core types for the WOC.[23] Hence, the cubane-butterfly rearrangement hypothesis cannot be excluded merely on the basis of the available structural data at the present time. Resolution of the debate over the structure of the WOC will undoubtedly achieve consensus in the future as more tools are brought to bear on the problem. Irrespective of the outcome of this debate, the present data show that the manganese−oxo cubane core topology does indeed represent a highly reactive molecular scaffolding for the conversion of water to oxide bridges and to form molecular oxygen. The $L_6Mn_4O_4$ molecules offer a bioinspired structural topology that holds great promise for the design of future catalysts capable of oxidizing water and delivering oxygen atoms, OH radicals, H_2O_2, or O_2.

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