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Modeling the Oxygen-Evolving Center of Photosystem II: Synthesis and Characterization of a Tetranuclear Manganese Carboxylate Complex

Sir:

The role of manganese in photosynthetic oxygen evolution[1] has been extensively studied in recent years. The pioneering work of Kok and co-workers[2] demonstrated the existence of five discrete oxidation levels of the O_2-evolving complex (OEC), S_0–S_4. Since then, the proposal that a manganese center is responsible for the storage of redox equivalents and the actual site of water oxidation has become fairly well accepted. Recent temperature-dependent EPR studies[3] of the native enzyme show the magnetic properties of the S_2 state to be consistent with a $Mn^{III}Mn^{IV}_3$ tetramer, comprising two antiferromagnetically exchange-coupled dimers which are mutually ferromagnetically exchange coupled. On the basis of these results, we have proposed a model[4] for the active site of the oxygen-evolving enzyme, in which the manganese tetramer exists as a Mn_4O_4 cubane-like array in the S_0–S_2 states and as a Mn_4O_6 adamantane-like array in the S_3 and S_4 states, both of which structural types have literature precedent.[5] In order to test our model, we sought to synthesize and characterize manganese tetramers, in the hope of obtaining a cubane or adamantane-like complex. We believe that comparison of the chemical and spectroscopic properties of such model compounds will aid in the elucidation of the structure of the OEC in the natural system. The structures of several manganese tetramers have been reported by Christou, Hendrickson, et al.[6] We report here the synthesis and crystal structure of a mixed-valence manganese tetramer that we propose as a model for a superreduced form of the manganese tetramer in the OEC.

Evidence discussed in a recent review[7] supports exclusive or at least predominant oxygen ligation to manganese in the OEC, and we have therefore avoided nitrogen-donor ligands entirely. Our initial synthetic efforts have focused upon the application of carboxylate ligands because carboxylic acid residues are the most likely O-donor ligands for a higher valent manganese tetramer. We thought that bulky carboxylates would preclude formation of the known trimeric $[Mn_3O(O_2CR)_6L_3]$ complexes[8] on steric grounds and thus chose triphenylacetate.

Oxidation of a dichloromethane suspension of manganese(II) trifluoromethanesulfonate and triphenylacetic acid by tetra-*n*-butylammonium permanganate produces a brown solution, from which crystals of **1** can be isolated in modest yield (44%).[9] Analytical and redox titration data[10] support the formulation of **1** as $[Mn^{II}_2Mn^{III}_2O_2(O_2CCPh_3)_6(H_2O)_2]$. The infrared spectrum of **1** is consistent with the presence of bridging carboxylates[11] only ($\nu(CO_2)$ = 1577, 1447 cm^{-1}). In order to elucidate fully the structure of **1**, an X-ray crystallographic study was performed.

The crystal structure[12] (Figure 1, including pertinent bond distances and angles) shows a tetrameric $Mn_4(\mu_3\text{-}O)_2$ core. The

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(9) (a) Experimental procedure for **1**: To a suspension of manganese(II) trifluoromethanesulfonate (0.50 g, 1.4 mmol, synthesized by the neutralization of $MnCO_3$ with 2 equiv of CF_3SO_3H) and triphenylacetic acid (1.02 g, 3.54 mmol, Aldrich Chemical Co.) in dichloromethane (20 mL) was added a solution of tetra-*n*-butylammonium permanganate (0.341 g, 0.94 mmol, synthesized by the method of Sargent[9b]) in dichloromethane (20 mL) dropwise over 30 min. The resulting dark brown suspension was stirred overnight at room temperature and evaporated in vacuo, the residue was extracted with toluene (30 mL), and the extracts were filtered and evaporated in vacuo. The resulting dark brown residue was dissolved in dichloromethane (5 mL) and the product precipitated by addition of pentane (45 mL). The copper-brown powder was collected on a fritted disk, washed with pentane, and dried in vacuo; yield 0.52 g (44%). Diffraction-quality crystals were grown by vapor diffusion of diethyl ether into a dichloromethane solution of **1** at 5 °C. (b) Sala, T.; Sargent, M. V. *J. Chem. Soc., Chem. Commun.* **1978**, 253.

(10) Anal (Desert Analytics, Tucson, AZ). Calcd for $C_{120}H_{94}Mn_4O_{16}$: C, 71.64; H, 4.90. Found: C, 71.28; H, 5.12. Redox titrimetry (excess acidic KI followed by $Na_2S_2O_3$ titration): equivalent weight, 980 ± 123 g/equiv; calcd equivalent weight, 1006 g/equiv.

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(12) X-ray crystal structure data: The structure of **1** was determined by X-ray crystallography by using a crystal that measured 0.50 × 0.37 × 0.37 mm. The crystal was sealed in a capillary bathed in mother liquor, which consisted of a mixture of dichloromethane and diethyl ether. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Preliminary indications of the unit cell based on 25 randomly selected reflections revealed monoclinic symmetry with the following lattice parameters: a = 16.121 (4) Å, b = 16.814 (7) Å, and c = 22.139 (8) Å with β = 96.76°. The space group, on the basis of the observed systematic extinctions, was assigned as $P2_1/n$ (No. 1014); Z = 4 with one molecule of composition $C_{64}H_{55}O_8Mn_2$ forming the asymmetric unit. The volume was 5959 Å^3, and the calculated density was 1.12 g/cm^3. There were 9339 reflections collected with $2\theta \leq 48°$; of those reflections 3656 (39%) with $I \geq 3\sigma(I)$ were judged observed. The structure was solved by locating the positions of the two manganese atoms by using MULTAN 80 and the WFOUR option in DIRDIF. Iterations of least-squares refinement and calculation of difference Fourier maps revealed the entire non-hydrogen structure. Inclusion of the hydrogens in their calculated positions and a full-matrix refinement of the non-hydrogen atoms resulted in convergence to an unweighted residual of 0.068 and a weighted residual of 0.083. All intramolecular bond distances and angles are within normal ranges.

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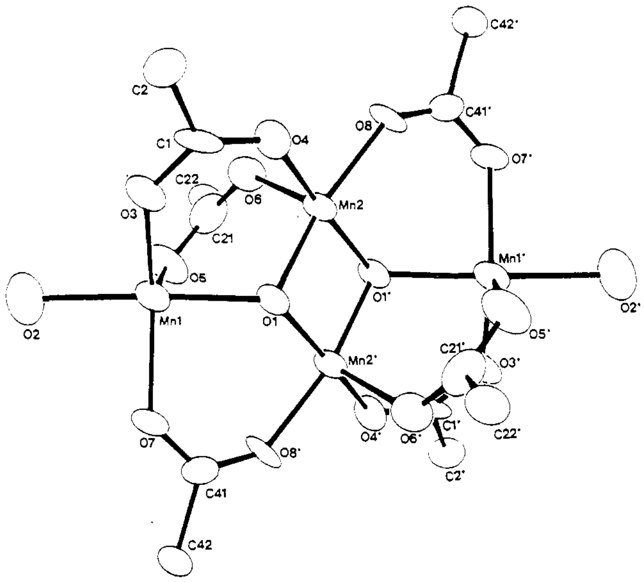

Figure 1. ORTEP diagram of 1, $[Mn_4(\mu_3\text{-}O)_2(O_2CCPh_3)_6(OEt_2)_2]$ (phenyl rings and ethyl groups omitted for clarity). Pertinent bond distances (Å) and angles (deg): Mn1–O1 = 2.077 (8), Mn1–O2 = 2.22 (1), Mn1–O3 = 2.084 (8), Mn1–O5 = 2.070 (9), Mn1–O7 = 2.114 (8), Mn1–Mn2 = 3.265, Mn2–Mn2* = 2.770 (4), Mn2–O1 = 1.828 (7), Mn2–O1* = 1.852 (7), Mn2–O4 = 1.952 (8), Mn2–O6 = 2.085 (8), Mn2–O8 = 1.936 (8); Mn1–O1–Mn2 = 113.3 (4), Mn1–O1–Mn2* = 119.7 (4), Mn2–O1–Mn2* = 97.6 (3); O1–Mn2–O1* = 82.4 (3), O1–Mn1–O2 = 171.8 (4), O3–Mn1–O7 = 135.5 (4), O3–Mn1–O5 = 111.3 (4), O5–Mn1–O7 = 113.2 (4), O1–Mn2–O4 = 93.7 (3), O4–Mn2–O8 = 85.3 (3), O8–Mn2–O1* = 95.2 (3), O1–Mn2–O6 = 100.3 (3), O4–Mn2–O6 = 96.7 (3).

two central manganese ions (Mn2, Mn2*) are bridged by two μ_3-oxygen atoms, with Mn–(μ-O) and Mn–O(carboxylate) distances (Mn2–O1 = 1.828 (7) Å, Mn2–O(carboxylate) = 1.936 (8)–2.086 (8) Å) similar to those previously observed for Mn(III).[13] The coordination geometry at Mn2 is distorted five-coordinate square pyramidal, a rather unusual geometry for Mn(III).[14a] The two outer manganese ions, bridged to the central Mn(III) ion via a μ_3-oxygen atom and three triphenylacetate ligands, have Mn–O distances (Mn1–O1 = 2.077 (8) Å, Mn1–O(carboxylate) = 2.070 (9)–2.114 (8) Å) consistent with Mn(II).[13] The coordination geometry at Mn1 is distorted trigonal bipyramidal, also unusual for Mn(II),[14b] with three carboxylate oxygen atoms occupying the equatorial sites. The molecule contains a center of inversion. A very unusual aspect of the structure is the presence of a coordinated diethyl ether ligand (Mn1–O2 = 2.22 (1) Å) in an axial position trans to the triply bridging oxygen atom, presumably arising from the displacement of water in the crystallization process. We are unaware of any other crystallographically characterized examples of diethyl ether acting as a ligand toward a transition metal. The most intriguing aspect of the structure of 1 is the Mn···Mn distances of Mn1···Mn2 = 3.265 Å and Mn2···Mn2* = 2.770 (4) Å. Recent EXAFS studies[15] have demonstrated a Mn···Mn distance of 2.7 Å and strongly suggest a second Mn···Mn distance of 3.3 Å. These distances are in excellent accord with the two Mn···Mn distances observed in 1 and support complex 1 as a model for the manganese site in the OEC.

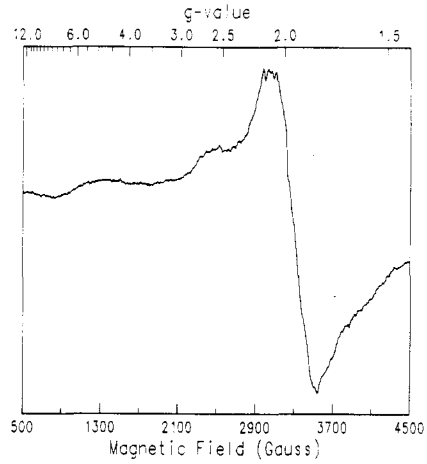

Figure 2. EPR spectrum of 1. Conditions: temperature, 5 K; microwave frequency, 9.1 GHz; magnetic field modulation frequency, 100 kHz; magnetic field modulation amplitude, 5 G; microwave power, 0.05 mW. Sample: 1 mM frozen solution in CH_2Cl_2.

The spin-only magnetic moment of 1 is 9.1 μ_B at ambient temperature, as determined by the Evans method.[16] This value is significantly lower than the expected uncoupled-ion limit of 10.86 μ_B and is thus indicative of moderate antiferromagnetic coupling. The low-temperature EPR spectrum of a frozen solution of 1 in dichloromethane (Figure 2) is characteristic of an integral-spin system with low-lying paramagnetic levels that give rise to the EPR signals. The dissimilarity between the spectrum of 1 and the spectra previously observed for mixed-valent manganese dimers,[17] as well as the absence of signals attributable to Mn(II), strongly suggest that the observed spectrum arises from a tetranuclear complex and not from decomposition products. We are currently investigating the variable-temperature EPR properties of 1.

Although the structure of 1 is not that of a cubane or adamantane as proposed for the S_0–S_2 and S_3 states of the OEC, respectively, we believe that the observed open structure may result from the relatively low oxidation state of $Mn^{II}_2Mn^{III}_2$. Since the oxidation state of the OEC is generally believed to be higher[4] (i.e. $Mn^{III}Mn^{IV}_3$ in the S_2 state), 1 may be a model for a superreduced state of the manganese in the OEC. Upon oxidation, a Mn_4O_2 array such as 1, other examples of which have recently been reported,[6] may close up to a more compact structure, such as a cubane. The relatively low oxidation state of 1 may be due in part to the poor oxidative stability of the triphenylacetate; $Ph_3C^{\bullet}$ and free Mn^{II} are observed by EPR in the room-temperature solution decomposition products of 1. We are currently investigating the properties of other manganese carboxylate tetramers,[18] which we hope will be stable in higher oxidation states.

In conclusion, we have synthesized the first mixed-valence manganese tetramer containing only oxygen-donor ligands and thus advance it as a model for the ligation in the OEC of photosystem II. The uniqueness of complex 1 lies in its all-oxygen coordination sphere, which may be biologically relevant, and in its coordinative unsaturation, which will allow the investigation of ligand-binding[19] and substitution reactions. We believe that

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the chemical and spectroscopic properties of complex 1 and related tetrameric complexes will prove to be fruitful in elucidating the structure and mechanism of the water-oxidizing complex in green plants.

Acknowledgment. We gratefully acknowledge the assistance of Professor J. W. Faller with the solution of the crystal structure. G.W.B. acknowledges receipt of a Camille and Henry Dreyfus Teacher-Scholar award and an A. P. Sloan research fellowship.

Supplementary Material Available: Summary of crystallographic data and tables of positional parameters and B(eq) values, intramolecular bond distances and angles, torsion angles, and U values (13 pages); a listing of F_o vs F_c values (24 pages). Ordering information is given on any current masthead page.

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Articles

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Photobehavior of Copper(I) Compounds. 4.[1a] Role of the Triplet State of (Arylphosphine)copper(I) Complexes in the Photosensitized Isomerization of Dienes

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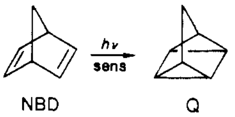
Received October 30, 1987

Photoisomerization of *cis*- and *trans*-piperylene can be sensitized with high quantum efficiency by Cu(diphos)BH_4 (diphos is 1,2-bis(diphenylphosphino)ethane) and Cu(prophos)BH_4 (prophos is 1,3-bis(diphenylphosphino)propane). Sensitization is accompanied by quenching of the emissive $^3(\sigma\text{–}a_\pi)$ excited state in each copper(I) complex, and the two processes occur with identical Stern–Volmer kinetics. Measurements of the trans/cis diene ratio at the photostationary state can be used to estimate the triplet-state energy as 60–61 kcal for Cu(diphos)BH_4 and >61 kcal for Cu(prophos)BH_4; additional evidence suggests that 66–67 kcal is a reasonable value for the latter complex. Collectively, the results support the assignment of triplet–triplet energy transfer as the primary mechanism for sensitization and quenching in these systems. This mechanism also can accommodate earlier reports that Cu(diphos)BH_4 and Cu(prophos)BH_4 sensitize the valence isomerization of norbornadiene to quadricyclene with markedly different quantum efficiencies.

Introduction

Copper(I) complexes of general formula CuP_nX, where P is a monodentate or polydentate arylphosphine, X is a uninegative group such as Cl^-, Br^-, or BH_4^-, and $n = 1–3$, possess a number of interesting spectral and photochemical properties.[1a,2,3] Exemplary in this respect is the behavior of the triphenylphosphine, diphos (1,2-bis(diphenylphosphino)ethane), and prophos (1,3-bis(diphenylphosphino)propane) complexes pictured in Figure 1. As summarized in Table I, each member of this series luminesces in room-temperature fluid solution and also functions as a photosensitizer, with limiting quantum efficiency $\phi^\infty_{\text{isom}}$, for the valence isomerization of norbornadiene (NBD) to quadricyclene (Q) (eq 1). A detailed investigation of the $Cu(PPh_3)_2BH_4$/NBD system



(1)

led us to propose that sensitization arises from the bimolecular interaction of the photoexcited copper(I) complex (denoted by an asterisk) with the ground-state diene molecule (eq 2).[2a,b] Direct support for this proposal came from a related study in which it was observed that quenching of the phosphorescence of Cu(prophos)BH_4 by NBD and sensitized production of Q (eq 1) occur concurrently and with identical Stern–Volmer kinetics.[2c] The simplest interpretation of this parallel behavior is that both processes result from the bimolecular encounter of the organic substrate with the emissive triplet state of the copper(I) complex.

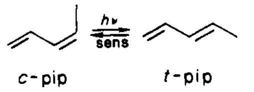
$$^*Cu(PPh_3)_2BH_4 + NBD \rightarrow \underset{\text{encounter pair}}{[^*Cu(PPh_3)_2BH_4,NBD]} \rightarrow Cu(PPh_3)_2BH_4 + Q \quad (2)$$

Table I. Properties of (Arylphosphine)copper(I) Complexes[a]

complex	λ_{em},[b] nm	τ,[c] μs	$\phi^\infty_{\text{isom}}$[d]
$Cu(PPh_3)_2BH_4$	475	<0.01	0.76
Cu(diphos)BH_4	537	1.1[e,f]	<0.01
Cu(prophos)BH_4	510	3.9[e]	0.88

[a] Measured in benzene at 25 °C; unless noted otherwise, data were taken from ref 2b,c. [b] Wavelength of luminescence maximum. [c] Luminescence lifetime. [d] Limiting quantum yield for sensitized isomerization of NBD to Q. [e] Measured in this study. [f] This lifetime is considerably longer than the one reported in ref 2b.

Since relatively little is known about the bimolecular chemistry of (arylphosphine)copper(I) excited states, we have undertaken additional studies of the triplet-state behavior of the two model complexes Cu(diphos)BH_4 and Cu(prophos)BH_4 in the presence of isomerizable dienes. Our primary goal has been to characterize the key excited-state interaction responsible for quenching and sensitization in these systems. In this report we investigate the use of the two copper(I) complexes as photosensitizers for the isomerization of *cis*- and *trans*-piperylene (hereafter abbreviated as *c*-pip and *t*-pip, respectively (eq 3)). The well-characterized



(3)

interconversion of these acyclic 1,3-dienes proceeds efficiently upon population of the lowest triplet state of either isomer and thereby

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(1) (a) Part 3: Borsub, N; Chang, S.-C.; Kutal, C. *Inorg. Chem.* **1982**, *21*, 538. (b) Permanent address: Department of Chemistry, University of the Witwatersrand, Johannesburg 2001, South Africa.

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