unequivocally that the dominant heme orientations are the same as those of their other derivatives, including the aquamet proteins precursory to the iron(III) nitrosyls.[15] In order to account for the different band shapes among the above derivatives, the rate of any ligand-dependent heme reorientation would need to be fast relative to the time required to prepare an adduct and obtain its optical spectrum. This seems unlikely: when horse heart myoglobin is reconstituted[15,28] from apoprotein by using Fe(CO)-(PPIX) at pH 7 (μ = 0.2 phosphate, 1 atm CO, 20 °C), the subsequent equilibrative reordering of the heme from its initially randomized orientational distribution may be followed by circular dichroism spectroscopy and is observed to occur with a first-order rate constant of only $(3.9 \pm 0.2) \times 10^{-7}$ s^{-1}. Although the reorientation rates are coordination-dependent[25] (with high-spin Fe(III) presumably having a lower activation barrier than low-spin Fe(II) hemes), all reorientations so far observed are very slow processes, the fastest having half-lives of a few hours.[29,30] Furthermore, when the slow nitrosyl autoredox reaction is inhibited by hexacyanoferrate(III), the optical spectra of Mb^{III}NO and Hb$_c$^{III}NO formed from NO and the aquamet proteins are stable in the 10^{-2}–10^6-s time scale.[13,31] Finally, the spectrum of oxymyoglobin shows no splitting of the α band; perturbations of the α band in myoglobin are intrinsically dependent on the nature of the distal ligand.

Therefore, we conclude that the splitting of the α band in iron heme proteins cannot readily be explained by the presence of different heme rotational components. Clearly, distal effects play an important role in determining the appearance of the α band in iron–porphyrin proteins.

In conclusion, although porphyrin orientational isomerism may lead to splitting of the optical absorption spectra of heme proteins reconstituted with non-iron porphyrins, the reverse logic does not apply for natural (iron) hemes.

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Physical Properties of a Manganese Tetramer with All-Oxygen Coordination

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The role of manganese in photosynthetic water oxidation is under intense study.[1] Since crystallographic data for the active site of photosystem II (PS II) are not available, current strategies include synthesis of model complexes whose properties correlate
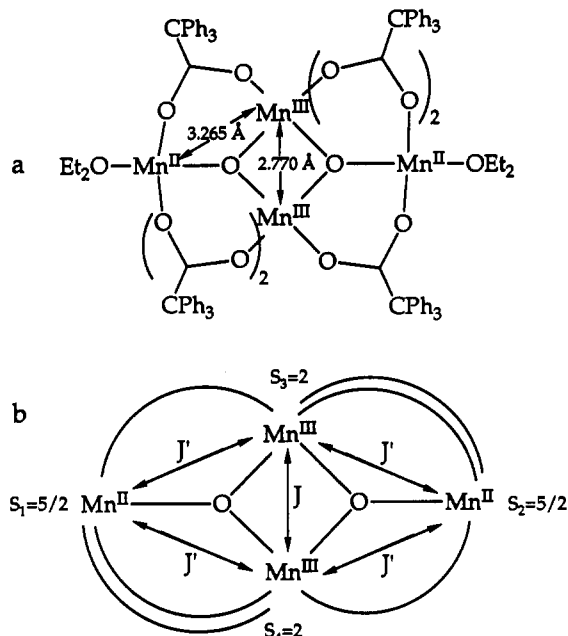
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Figure 1. (a) Structure of complex **1**, Mn$_4$O$_2$(O$_2$CCPh$_3$)$_6$(OEt$_2$)$_2$. (b) Vector-coupling scheme used for the analysis of the temperature-dependent magnetic susceptibility of **1**.

with existing physical data for the natural system.[2–5] Recent studies of PS II, particularly by EPR and X-ray spectroscopy,[1] have led to a greater understanding of the structure of the manganese water oxidation catalyst and have created a growing need for polynuclear manganese model complexes having suitable coordination geometries and oxidation states. The current data available for the natural system indicate that four manganese atoms are present with two distinct metal–metal separations of 2.7 and 3.3 Å[6–8] and that the coordination environment is primarily O donor in character.[9] Protein sequence data and indirect evidence for the location of the Mn binding site[10] are consistent with the primary protein-derived ligands being carboxylate groups; manganese coordination is completed by water-derived oxo, hydroxo, or aqua ligands.

Recently, we reported the structure of a tetranuclear manganese complex (Mn$_4$(μ_3-O)$_2$(O$_2$CCPh$_3$)$_6$(OEt$_2$)$_2$ (**1**) consisting of a central planar core of metal atoms (two Mn^{II}, two Mn^{III}) bridged by two μ_3-oxo ligands (Figure 1a).[11] The remaining ligands are carboxylate and Et$_2$O, leading to an all-oxygen coordination environment for each manganese center. As we have pointed out,[2b]

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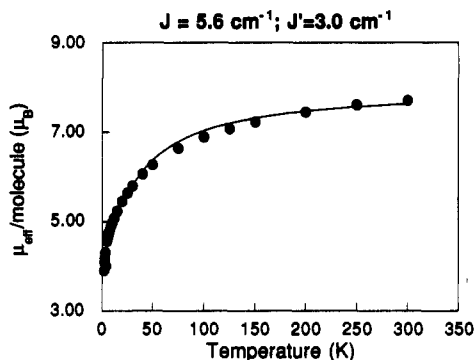
Figure 2. Temperature dependence of the magnetic moment (μ_{eff}) of **1**. Data were corrected for the sample diamagnetism. The data were analyzed by using the following exchange Hamiltonian: $\mathcal{H} = J(S_1 \cdot S_2) + J'(S_1 \cdot S_3 + S_1 \cdot S_4 + S_2 \cdot S_3 + S_2 \cdot S_4)$, where S_1, S_2, S_3, and S_4 are the spins of the Mn ions as given in Figure 1b. The solid line is a least-squares fit to the data using the indicated parameters.

1 is probably not an accurate structural model for Mn in PS II because it has only one Mn⋯Mn separation of 2.7 Å. Nonetheless, two structural features that may be relevant to the natural system are unique to **1**. First, this was the first reported high-valent manganese tetramer containing solely oxygen ligands. Second, the two Mn^{II} ions exhibit distorted-trigonal-bipyramidal geometry, which is unusual for this oxidation state and previously unobserved in an all-oxygen ligand environment.[2c] Consequently, the physical properties of this molecule are distinct from the properties of other complexes containing $Mn(II)$[12] and may be relevant to the interpretation of data from the natural system.

Experimental Section

Materials. Synthesis of **1** was performed as described previously.[11] Dichloromethane was distilled from calcium hydride immediately before use. The supporting electrolyte (tetra-*n*-butyl ammonium hexafluorophosphate) was recrystallized from hot ethanol. $Mn_4O_2(O_2CCH_3)_6(bpy)_2$ and $[Mn_4O_2(O_2CCH_3)_7(bpy)_2](ClO_4)$ were synthesized by literature methods (bpy = 2,2'-bipyridine).[12]

Physical Measurements. Low-temperature EPR spectra were measured at Yale on a home-built instrument[13] using an Oxford ESR-900 low-temperature cryostat. X-ray photoelectron spectroscopy was performed at the University of North Carolina as previously described.[14] Temperature-dependent magnetic susceptibility was measured by using the SQUID technique at the MIT Frances Bitter Magnet Laboratory. The data were fit with a nonlinear, least-squares program written at Yale. The electrochemistry was studied at Yale by using a PAR 273 potentiostat/galvanostat with a Pt-button working electrode, Pt-wire auxiliary electrode, and an SSCE reference electrode. Scan rates varied from 50 to 1000 mV/s in dichloromethane solution containing 0.1 M supporting electrolyte. The ferrocene/ferrocenium couple appears at +0.31 V under these conditions.

Results and Discussion

Magnetic Susceptibility. Figure 2 shows the temperature dependence from 2 to 300 K of the magnetic moment (μ_{eff}, units of μ_B) for complex **1**. The coupling scheme for analysis ($\mathcal{H} = JS_i \cdot S_j$) of the magnetic data is shown in Figure 1b. To simplify the analysis, the effects of zero-field splitting have not been considered, and the coupling between Mn^{II} and Mn^{III} ions is assumed to be equivalent (J') for all four pairs (1,3; 3,2; 2,4; 4,1), regardless of the number of carboxylate bridges. Similar assumptions have been applied to the analysis of the magnetic properties of an electronically and structurally related complex, $Mn_4O_2(O_2CCH_3)_6(bpy)_2$ (**2**), and have been shown to be valid.[12] Inclusion of coupling between the Mn^{II} ions (1,2) always gave
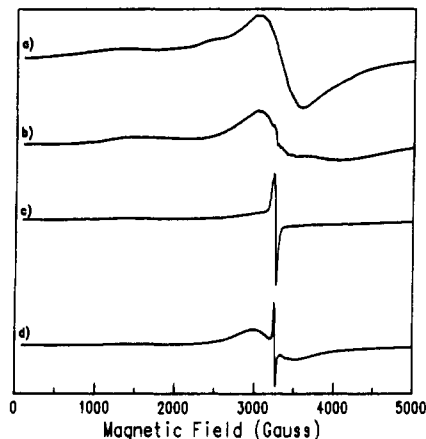

Figure 3. EPR spectrum of **1** at 10 K: (a) in dichloromethane solution; (b) after treatment with 2 equiv of triethylamine; (c) after UV photolysis of the triethylamine-treated sample at 77 K; (d) after annealing the sample in (c) at 200 K for 5 min and cooling to 77 K. The spectra in (a) and (b) are plotted with a 5-fold higher amplitude.

negligible values and did not improve the overall quality of the fit. The resulting spin Hamiltonian is thus

$$\mathcal{H} = J(S_3 \cdot S_4) + J'(S_1 \cdot S_3 + S_1 \cdot S_4 + S_2 \cdot S_3 + S_2 \cdot S_4) \quad (1)$$

The Kambe vector-coupling method,[15] when applied to eq 1, allows for determination of the eigenvalues using the following scheme:

$$S_1 + S_2 = S' \qquad S_3 + S_4 = S'' \qquad S = S' + S'' \quad (2)$$

The energies of the spin states are given in eq 3. Since $S = 0$–9, there are 110 individual spin states.

$$E = J/2[S''(S'' + 1) - 12] + $$
$$J'/2[S(S + 1) - S'(S' + 1) - S''(S'' + 1)] \quad (3)$$

An expression for μ_{eff} was derived from the Van Vleck equation[16] and from the spin-only definition of the magnetic moment ($2.828 \, (\chi_M T)^{1/2}$). A nonlinear least-squares procedure was used to fit this equation to the data in Figure 2, where the solid line represents the best fit obtained. The resulting coupling constants are $J = 5.6$ cm^{-1} and $J' = 3.0$ cm^{-1}. The fit confirms the observation of net antiferromagnetic coupling described above. An unusually low g value, 1.47, was determined from the fit. This may result from the assumption that all of the spin states have the same g value. A low g value was also obtained for **2**, and the magnitude of the antiferromagnetic coupling ($J = 6.24$ cm^{-1}, $J' = 3.94$ cm^{-1}) for **2** was similar to that for **1**.[12]

The energies of the spin states were determined by using the coupling parameters and eq 3. While the lowest spin state is an $S = 2$ state, there are a large number of other low-lying levels. It is noteworthy that there are two $S = 1$ states within 10 cm^{-1} of the ground state, especially with regard to the EPR spectrum that has been reported previously[11] and shown in Figure 3a.

Electrochemistry. Complex **1** cannot be oxidized electrochemically at potentials less than 2.0 V (vs SSCE), consistent with its electron-poor character. The complex is surprisingly resistant to reduction. Cyclic voltammetry in dichloromethane solution shows an irreversible reduction wave at −1.9 V, presumably corresponding to the reduction of Mn^{III} to Mn^{II} followed by complex decomposition. An anodic product wave at +0.75 V is seen, and this could arise from the one-electron oxidation of a Mn^{II} monomer. These features remained unchanged with increasing scan rates up to 1 V/s, consistent with a rapid, unimolecular decomposition process.

EPR Spectroscopy. In the case of FeS clusters, photolysis has been used successfully to prepare the mixed-valence state for EPR measurements.[17] We have used photolysis (254 nm) at 77 K to

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Table I. Mn 2p Binding Energies for Butterfly Complexes

complex	oxidn state	$2p_{3/2}$, eV	$2p_{1/2}$, eV
$Mn_4O_2(O_2CCPh_3)_6(OEt_2)_2$ (1)	2.5	642.2	653.8
$Mn_4O_2(O_2CCH_3)_6(bpy)_2$ (2)	2.5	641.8	653.4
$Mn_4O_2(O_2CCH_3)_7(bpy)_2^+$ (3)	3.0	642.2	653.8

photooxidize **1**, and low-temperature EPR measurements have been used to detect ligand binding and redox reactions of **1**. Figure 3a shows the EPR spectrum of **1** at 10 K in CH_2Cl_2. Addition of 2 equiv of triethylamine causes a pronounced change in the spectrum (Figure 3b), indicating that the amine coordinates to **1**, probably by displacement of Et_2O. Photolysis (254 nm) at 77 K leads to the formation of a carbon-centered radical via ejection of an electron from a phenyl ring of one of the carboxylate ligands (Figure 3c, spectrum plotted with a 5-fold smaller amplitude). Essentially identical spectra were observed after photolysis of either **1** or **1** plus 2 equiv of triethylamine. However, after the sample of **1** plus 2 equiv of triethylamine was annealed at 200 K (below the melting point of CH_2Cl_2), the radical signal was replaced by a much broader signal, which we assign to a mixed-valence manganese compound, possibly a $Mn^{III}_3Mn^{II}$ tetramer (Figure 3d).[18] This new signal was not obtained in the absence of triethylamine; in this case, annealing did not cause any change in the EPR spectrum. Amine coordination does not alter the electrochemistry or optical spectrum of **1**. If addition of triethylamine led to cluster decomposition, the Mn^{III} reduction at -1.9 V would certainly be affected, but coordination to Mn^{II} in the OEt_2 site would not be expected to change this potential, as we have observed.

The observation that **1** cannot be electrochemically oxidized to the (II, III, III, III) form can be understood in terms of the coordination environment for Mn^{II} in each cluster. In **1**, each Mn^{II} center is five-coordinate with a very poor donor ligand, Et_2O, in the terminal position. The EPR experiment shown in Figure 3, however, demonstrates two important features of the complex. First, the weak diethyl ether ligands can be replaced by triethylamine (Figure 3b). This is a very useful feature for studying the binding of exogenous ligands to polynuclear Mn clusters; there is a large body of data for reactions of this type in the natural system.[19] Second, the binding of triethylamine allows oxidation of a Mn^{II} center, showing that ligand binding can be used to tune the oxidation potential of the Mn_4O_2 core.

X-ray Spectroscopy. The Mn 2p binding energies for **1**, **2**, and $Mn_4O_2(OAc)_7(bpy)_2^+$ (**3**) were determined by X-ray photoelectron spectroscopy (Table I). Upon oxidation of **2** from the $Mn^{2.5+}$ level to the $Mn^{3.0+}$ level (**3**), the binding energies increase by 0.4 eV. This observation is consistent with a decrease in electron density at Mn brought about the oxidation. We have reported a 0.4-eV increase in binding energy for oxidation of $Mn_2O_2(bpy)_4^{3+}$ ($Mn^{3.5+}$) to $Mn_3O_4(bpy)_4(OH_2)_2^{4+}$.[20] The binding energies for **1** are 0.4 eV higher than those of the isoelectronic butterfly (**2**) and identical with those of **3**. This supports the idea that the Mn^{II} centers of **1** are relatively electron-poor, giving binding energies identical with those of a complex containing Mn^{III} in the same sites.

Conclusions

The physical properties of a Mn tetramer having biologically relevant coordination have been presented. The data show that the molecule contains a unique type of Mn^{II} center that is relatively electron-poor. The effects of these unique centers are evident in the Mn 2p binding energies and the redox chemistry, as detected by electrochemistry and EPR. It is notable that binding of strongly donating ligands permits oxidation of the Mn^{II} centers to occur, since binding of NH_3 has been shown to modulate the redox and EPR properties of Mn in PS II.[19] Finally, it has been suggested

that unusual Mn coordination environments could account for the X-ray absorption edge energies observed in PS II,[7] and the characterization of the unique Mn^{II} centers in **1** provides some evidence that this may be an important consideration.

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Synthesis and Characterization of a Dimeric Molybdenum(V) Anion [Br₂OMo(μ-S)₂MoOBr₂]²⁻: Conversion of Tetrahydrofuran to [ⁿBu₃P(CH₂)₄PⁿBu₃]²⁺

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Introduction

During our attempts to synthesize trinuclear sulfur-capped molybdenum clusters, we have inadvertently prepared and structurally characterized a molybdenum(V) dimer anion, $[Br_2OMo(\mu\text{-}S)_2MoOBr_2]^{2-}$. Many dinuclear molybdenum(V) and tungsten(V) compounds are known that have the general core formula $M_2O_nS_{4-n}^{2+}$ (M = Mo, W; n = 0-4).[1-9]

X = O, S
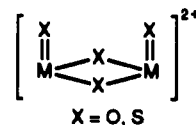
Typically, the dimers exhibit a bent MX_2M bridge with terminal syn M=X groups. A single metal–metal bond exists with an average length of 2.810 Å for molybdenum and 2.822 Å for tungsten.[3] Other ligands, such as dithiolates[2,5] and dithiocarbamates[4,5] as well as phosphines,[1] coordinate to the metal atoms, completing a square-pyramidal geometry (minus the M–M bond) about each metal atom. We report here a molybdenum(V) dimer that exhibits these characteristics, but contains four bromide ions completing the coordination sphere of each metal atom. A similar tungsten compound with terminal chlorides is known,[9] but this

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