Characterization of Polynuclear Mixed-Valence Manganese Complexes As Models of the Water Oxidation Site in Photosystem II

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### Introduction

The most important biological role identified to date for manganese is the enzyme responsible for water oxidation/oxygen evolution in the photosynthetic apparatus of higher plants and cyanobacteria [1,2]. It is now generally believed that a tetranuclear manganese aggregate is found at the site of water oxidation in photosystem II(PSII) and cycles between five distinct oxidation levels labeled  $S_0$ ,  $S_1$ ,  $S_2$ ,  $S_3$  and  $S_4$  in the pioneering work of Joliot et al. [3] and Kok et al. [4]. The  $S_n$  states contain manganese ions in various combinations of oxidation states, including  $Mn^{II}$ ,  $Mn^{III}$  and  $Mn^{IV}$ , and ligation is provided by 0 and N atoms from amino acid residues [2,5].

Recently two research groups [6,7] independently reported on the EPR signal for the S<sub>2</sub> state of PSII. This signal has been attributed to either a binuclear  $Mn^{III}Mn^{IV}$  site [6] or a tetranuclear  $Mn_{2}^{III}Mn^{IV}$  site [8]. Even though the origin and exact characteristics of this S<sub>2</sub> EPR signal with 16-18 manganese hyperfine lines are matters of active discussion, vis-à-vis detailed power saturation, temperature dependence and sample history studies [9], the observation of this EPR signal has spawned a growing interest in characterizing mixed-valence multi-nuclear manganese complexes.

## Magnetochemistry of a Number of Polynuclear Manganese Complexes

The variable-temperature magnetic susceptibilities have been determined and theoretically modeled for several new polynuclear mixed-valence manganese complexes synthesized by the group of Professor G. Christou at Indiana University. These complexes include four manganese thiolate complexes, four trinuclear manganese acetate complexes of the composition  $[Mn_3O(O_2CR)_6L_3]^{O,+1}$ , where R is Me or Ph and L is a neutral donor group, three tetranuclear (butterfly arrangement) complexes with  $[Mn_4O_2]$  cores and a novel nonanuclear manganese complex with the composition  $Mn^{IT}Mn_8^{III}$ . The susceptibility data are well fit to suitable theoretical models according to the Kambe vector coupling model [11].

# Mixed-Valence Mn<sup>II</sup>Mn<sup>III</sup> Complexes

Until very recently only salts of the  $Mn^{III}Mn^{IV}$  complex [(bipy)<sub>2</sub>MnO<sub>2</sub>Mn-(bipy)<sub>2</sub>]<sup>3+</sup> and the analogous bipyridine N-oxide and phenanthroline (phen) complexes have been characterized [10]. In the last year Wieghardt et al. [12] and Christou et al. [13] each reported one new binuclear  $Mn^{III}Mn^{IV}$  complex, both of which exhibit interesting g = 2 EPR signals with considerable manganese hyperfine structure resembling that of the S<sub>2</sub> EPR signal.

In 1987, five new Mn<sup>II</sup>Mn<sup>III</sup> complexes were synthesized. These complexes have been characterized by several physical techniques including magnetochemistry, EPR and X-ray crystallography [13-16]. Two complexes of a Robson-type macrocyclic ligand L<sup>2-</sup> (shown below), formulated as [LMn<sub>2</sub>Cl<sub>2</sub>Br]·H<sub>2</sub>O (1) and [LMn<sub>2</sub>Br<sub>3</sub>]·1/2CH<sub>2</sub>Cl (2), are characterized to have a very weak antiferromagnetic exchange interaction with exchange parameters of  $J = -2 \text{ cm}^{-1}$  for 1 and  $= -1 \text{ cm}^{-1}$  for 2. These two complexes give broad EPR signals even at liquid-helium temperature.

The antiferromagnetic interactions in complex 3,  $[Mn_2(bpmp)(\mu-OAc)_2](ClO_4)_2$ and in complex 4,  $[Mn_2(bcmp)(\mu-OAc)_2](ClO_4)_2 \cdot 1/2CH_2Cl_2$  are somewhat larger in magnitude with J = -6 and -7.7 cm<sup>-1</sup>, respectively. (bpmp<sup>-</sup> and bcmp<sup>-</sup> ligands are shown below.)



Experimental and simulated X- and Q-band EPR spectra for the unusual 29line EPR features in the g = 2 region at low temperature for complexes 3 and 4 indicate that these hyperfine patterns are due to only the z-component of the g-tensor. The x- and y-components of the g-tensor are broadened to the point of not contributing, except as a background, to the observed EPR spectra. The differential broadening of transitions associated with the  $g_x$ ,  $g_y$  components relative to the  $g_z$  component could be a reflection of g- and A-strain effects and/or increased nitrogen superhyperfine interactions in the  $g_x$  and  $g_y$  directions.

The antiferromagnetic interactions for the 5 known  $Mn^{II}Mn^{III}$  complexes are quite weak relative to those reported for five known  $Mn^{II}Mn^{IV}$  complexes. In the former case J ranges from -7.7 to +0.9 cm<sup>-1</sup>. In the latter case J ranges from -40 to -220 cm<sup>-1</sup>. There are two possible explanations for this difference. First, the two electrons in an e orbital of a  $Mn^{II}$  ion provide more ferromagnetic exchange pathways than are present in  $Mn^{III}Mn^{IV}$  complexes. Second, the  $Mn^{III}$ -0 bond lengths (1.83 - 1.85Å) are only 0.04 - 0.07Å longer than the  $Mn^{IV}$ -0 bond lengths (1.78 - 1.80Å), but the  $Mn^{II}$ -0 bond lengths fall in the range of 2.17 - 2.39Å. This longer  $Mn^{II}$ -0 bond length in  $Mn^{III}Mn^{III}$  complexes could lead to a much weaker antiferromagnetic interactions in  $Mn^{II}Mn^{III}$  complexes compared to  $Mn^{III}Mn^{IV}$  complexes.

These results can be used to explain why the  $S_2$  state of PSII gives rise to an EPR signal, whereas, the  $S_0$  state does not. The  $S_2$  state is generally believed to be  $Mn_3^{III}Mn^{IV}$  unit, where relatively strong antiferromagnetic interactions could give a ground state with an energy far below that of excited states. In this case EPR spectra would be observed with well resolved hyperfine splitting. On the other hand, relatively weak antiferromagnetic interactions in the  $S_0$  state which could have the composition  $Mn_3^{III}Mn^{II}$  would lead to appreciable thermal populations in the ground state as well as in excited states even at liquid-helium temperatures. EPR signals for the  $S_0$  state would thus be broadened excessively and made very difficult to see as a result of Orbach relaxation mechanisms.

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