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 S0, S1, S2, S3, and S4 in the pioneering work of Joliot et al. [3] and Kok et al. [4]. The S2 states contain manganese ions in various combinations of oxidation states, including MnII, MnIII, and MnIV, and ligation is provided by O and N atoms from amino acid residues [2,5].

Recently two research groups [6,7] independently reported on the EPR signal for the S2 state of PSII. This signal has been attributed to either a binuclear MnII-MnIV site [6] or a tetranuclear MnIII-MnIV site [8]. Even though the origin and exact characteristics of this S2 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 multinuclear 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 [Mn3O(RCOO)6L3]+, where R is Me or Ph and L is a neutral donor group, three tetranuclear (butterfly arrangement) complexes with [Mn4O2] cores and a novel nonanuclear manganese complex with the composition Mn11-Mn8. The susceptibility data are well fit to suitable theoretical models according to the Kambe vector coupling model [11].

Mixed-Valence MnII-MnIII Complexes

Until very recently only salts of the MnIII-MnIV complex [(bipy)2MnO2Mn(bipy)2]3+ 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 MnIII-MnIV complex, both of which exhibit interesting g = 2 EPR signals with considerable manganese hyperfine structure resembling that of the S2 EPR signal.

In 1987, five new MnII-MnIII 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 L2- (shown below), formulated as [LMn2Cl2Br]+H2O (1) and [LMn2Br3]•1/2CH2Cl (2), are characterized to have a very weak
The antiferromagnetic interactions in complex 3, \([\text{Mn}_2(\text{bpmp})(\mu-OAc)_2](\text{ClO}_4)_2\) and in complex 4, \([\text{Mn}_2(\text{bcmp})(\mu-OAc)_2](\text{ClO}_4)_2\cdot 1/2\text{CH}_2\text{Cl}_2\) are somewhat larger in magnitude with \(J = -6\) and \(-7.7\) cm\(^{-1}\), respectively. (bpmp and bcmp ligands are shown below.)

\[
\text{bpmp}^- \quad \text{bcmp}^-
\]

Experimental and simulated X- and Q-band EPR spectra for the unusual 29-line 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 \(\Lambda\)-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\(^{III}\)Mn\(^{IV}\) complexes. In the former case \(J\) ranges from \(-7.7\) to +0.9 cm\(^{-1}\). In the latter case \(J\) ranges from \(-40\) to \(-220\) cm\(^{-1}\). There are two possible explanations for this difference. First, the two electrons in an \(e_g\) orbital of a Mn\(^{II}\) ion provide more ferromagnetic exchange pathways than are present in Mn\(^{III}\)Mn\(^{IV}\) complexes. Second, the Mn\(^{III}\)-O bond lengths (1.83 - 1.85A) are only 0.04 - 0.07A longer than the Mn\(^{IV}\)-O bond lengths (1.78 - 1.80A), but the Mn\(^{III}\)-O bond lengths fall in the range of 2.17 - 2.39A. This longer Mn\(^{II}\)-O bond length in Mn\(^{II}\)Mn\(^{IV}\) 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\(^{III}\)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\(^{II}\)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.
References


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