

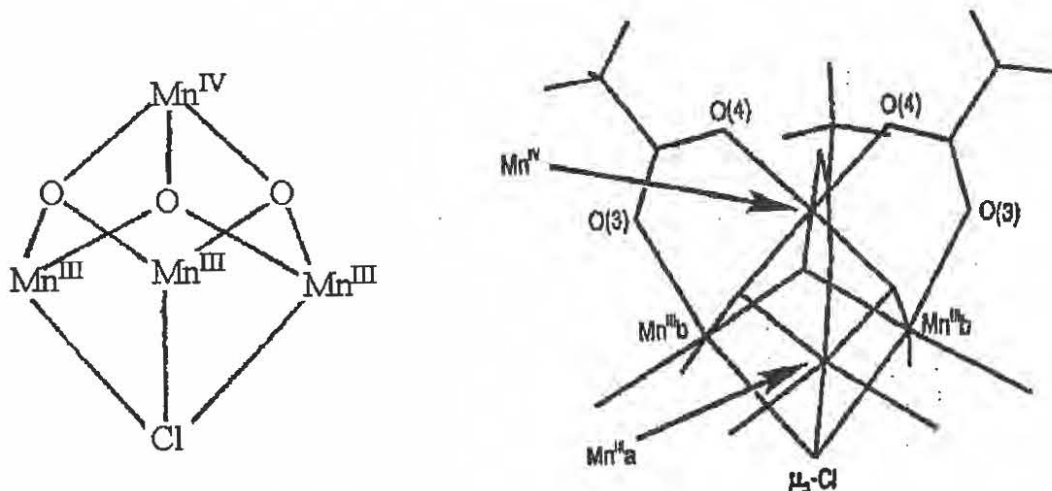
Characterization of the Electronic and Magnetic Properties of  
Four  $\text{Mn}_3^{\text{III}}\text{Mn}^{\text{IV}}$  Distorted Cubane Complexes

Edward A. Schmitt

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It has long been recognized that the oxygen evolving complex (OEC) of photosystem II (PSII) contains four Mn atoms and cycles through five discrete states,  $S_0$  through  $S_4$ , where the transition from one state to another is characterized by the loss of an electron [1,2]. Despite appreciable research efforts to understand or mimic this process, a precise structure of the OEC and mechanism for the oxidation of water has been elusive. There have been several proposed structures for the OEC, where each successive proposal is based upon new experimental or theoretical findings [3-5]. Though the most recent proposal is a dimer of dimers, the authors concede "we cannot rule out a highly distorted cubane" [5]. For the work presented here, the goal has been to develop a fundamental understanding of the electronic and magnetic properties of a series of four  $\text{Mn}_3^{\text{III}}\text{Mn}^{\text{IV}}$  distorted cubane complexes. A schematic representation of the distorted cubane core and one of the four complexes is shown below.



Characterization of the magnetic properties of these complexes relies upon a combination of theoretical models and experimental techniques [6]. From variable temperature magnetic susceptibility measurements and the Heisenberg-Dirac-Van Vleck (HDVV) model, it was determined that for all of the complexes studied the  $\text{Mn}^{\text{III}} - \text{Mn}^{\text{III}}$  interactions are ferromagnetic ( $J_{33} = 8.6$  to  $19.0 \text{ cm}^{-1}$ ) and the  $\text{Mn}^{\text{III}} - \text{Mn}^{\text{IV}}$  interactions are antiferromagnetic ( $J_{34} = -51.5$  to  $-20.8 \text{ cm}^{-1}$ ). In each case, the ground state has a spin of  $9/2$  and is isolated from the nearest excited spin state ( $S=7/2$ ) by a minimum of  $165.4 \text{ cm}^{-1}$ . This well isolated  $S=9/2$  ground state was further characterized by "high field" magnetization studies, which in conjunction with a full matrix magnetization model was used to determine that the zero-field splitting for two of the complexes ranged from  $0.28$ - $0.32 \text{ cm}^{-1}$ . Extending this model while using an average zero-field splitting value of  $0.30 \text{ cm}^{-1}$ , it was possible to predict X and Q-band electron paramagnetic resonance transitions that were in good agreement with experimental observations.

Relative to the  $S_2$  state of the OEC, it was shown that it is theoretically possible for a "cubane" complex to have anywhere from an  $S=1/2$  to  $15/2$  ground state depending upon the nature and relative magnitudes of  $J_{33}$  and  $J_{34}$ . Structural modifications that might lead to lower spin ground states in cubanes are discussed along with other molecular topologies and oxidation states.

To better understand the electronic structure and the effect of the core on the magnetic properties, Xa LCAO calculations were performed on the simplest of the four complexes [7]. These calculations correctly predicted the energetic ordering of the  $S=15/2$ ,  $9/2$  and  $1/2$  broken symmetry spin states. From these spin states, theoretical  $J_{33}$  and  $J_{34}$  values were calculated. Substituting these values into the HDVV model, the temperature dependence of the effective magnetic moment of this complex was predicted and found to be in good agreement with experimental results.

Careful examination of the electronic structure of these three spin states led to the proposal that ligand spin polarization plays a key role in the stabilization of the  $S=9/2$  spin state. The origin of this effect was described in terms of a simple model relating the energetic overlap of Mn "spin" orbitals to ligand orbitals.

The effects of protonating a single  $\mu_3$ -oxo and hydroxo substitution for the  $\mu_3$ -Cl were also considered. The most interesting result of these calculations was that for the latter case  $J_{33}=-11.7 \text{ cm}^{-1}$  is predicted to be antiferromagnetic, but the ground state remains the  $S=9/2$  state. This is attributable to the simultaneous destabilization of the  $S=15/2$  spin state and  $J_{34}$  increasing in magnitude from  $-46.6 \text{ cm}^{-1}$  to  $-97.0 \text{ cm}^{-1}$ . The opposite trend is observed for the protonated  $\mu_3$ -oxo form. In this case,  $J_{33}$  becomes more ferromagnetic and  $J_{34}$  becomes less antiferromagnetic. In both cases, the results correlated well with the proposed ligand spin polarization model.

## References

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