

Spectroscopic Models for the $S_2Y_z^\bullet$ State of Photosystem II – $Mn^{III}Mn^{IV}$ Complexes with Covalently Tethered Organic Radicals

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Distance measurement by EPR techniques has received healthy usage for the long distance magnetic interaction between tyrosyl radical Y_z^\bullet and the manganese cluster at the reaction center (RC) of Photosystem II (PSII) in the $S_2Y_z^\bullet$ state. In the S_2 state the Mn_4 cluster has an overall spin ground state $S = 1/2$ and shows a multi-line EPR spectrum that resembles that of an AF coupled Mn^{III} - Mn^{IV} dimer, although in full three Mn^{III} and a Mn^{IV} are present. The tyrosine/tyrosyl radical switch at Y_z has been proposed as the first link in the electron transfer chain of events at the RC, and therefore, accurate knowledge of the distance and the type of interaction between these two paramagnetic centers is important. We studied the angular and distance dependence of through-bond and through space interactions for a synthetic dimeric Mn_2 -radical model system.

A series of six isostructural dimeric manganese complexes of the type $[(Me_4dtne)Mn_2(\mu-O)_2(\mu-R)]^{2+}(X^-)_2$ have been prepared and characterized ($Me_4dtne = 1,2$ -bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane). The complexes differ by the organic residue tethered to the core unit: **1** ($R = ^-OAc$), **2** ($R = ^-O_2BPh$), **3** ($R = ^-O_2C$ -PROXYL), **4** ($R = ^-O_2C$ -TEMPO), and **5** ($R = ^-O_2BPhNIT$), and **6** ($R = ^-O_2CPhNIT$). Molecular structures for the entire series have been obtained from X-ray diffraction measurements, and the rich redox properties have been explored.

Complexes **1**, **3**, **4**, and **6** contain a mixed-valent $Mn^{III}Mn^{IV}$ core with an isolated magnetic ground state of $S=1/2$. The exchange coupling between the manganese ions is strong throughout the series ($J \approx -130 \pm 10 \text{ cm}^{-1}$, $H = -2JS_1S_2$). Complexes **3**, **4**, and **6** carry an organic radical and exhibit, in addition, *long-range exchange* interaction between that group and the dimanganese core, which are separated by 6.9Å, 7.7Å, and 8.8Å, respectively. The intramolecular *anisotropic coupling* was determined from cw-EPR line shape analyses at S-, X-, and Q-band frequencies, and from the intensity of half-field signals detected in normal- and parallel-mode ($J_{d,z} = -120 \times 10^{-4} \text{ cm}^{-1}$, $-105 \times 10^{-4} \text{ cm}^{-1}$, $-140 \times 10^{-4} \text{ cm}^{-1}$, for **3**, **4**, **6** respectively). Distance information was obtained for the dimanganese core and the organic radicals from these values by using a three-spin dipole model and local spin contributions for the manganese ions.

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