SUPPORTING INFORMATION

TITLE: The effect of Ca/Sr substitution on the electronic structure of the oxygen-evolving complex of photosystem II: A combined multifrequency EPR, ^{55}Mn -ENDOR and DFT study of the S_2 state

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SUPPORTING INFORMATION S1 – ADDITIONAL THEORY (SECTION 3)

S1.1 The spin manifold. A mapping of the spin subspace in section 3.2 to the original basis set as described in section 3.1 can be made. This allows the intrinsic g and hyperfine tensors of the four Mn ions (g_i , a_i , see eq. 2) to be calculated from the effective $\mathbf{G}$ and hyperfine tensors ($\mathbf{A}$, see eq. 4). Here we consider only the electronic component of the basis functions. We adopted the coupling scheme: $|S_1 \ S_2 \ S_{12} \ S_3 \ S_4 \ S_{34} \ S \ M\rangle$, or more succinctly $|S_{12} \ S_{34} \ S \ M\rangle$, where $|S_1 - S_2| \leq S_{12} \leq |S_1 + S_2|$, $|S_3 - S_4| \leq S_{34} \leq |S_3 + S_4|$, and $|S_{12} - S_{34}| \leq S \leq |S_{12} + S_{34}|$. It can be readily shown that the $S = 1/2$ doublet has contributions from up to seven basis states of total spin $S = 1/2$, listed in the appendix, if only an isotropic exchange interaction between the four Mn is considered.

The contribution of each basis state to the ground state doublet is dependent on the coupling scheme. Here we consider that the electronic exchange term of the Spin Hamiltonian takes the form of a series of pair-wise interactions i.e.

$$H = - \sum_{i < j} J_{ij} S_i \cdot S_j \quad (\text{Eq. S1})$$

Expressions for all matrix elements of the Spin Hamiltonian are given in the supporting information S1. The matrix elements are given in generalized operator notation. The matrix is block diagonal. States of the same total spin appear in the same block.

Scaling factors can be calculated that describe the contribution of each of the Mn ions to a particular total spin state. These scaling factors are called spin projections. The projection of the total spin onto the individual Mn centers is defined as the ratio of the on-site spin expectation value $\langle S_Z^i \rangle$ of the i^{th} Mn to the ‘total spin’ $\langle S_Z \rangle^{1,2}$:

$$\rho_i = \frac{\langle S_Z^i \rangle}{\langle S_Z \rangle} \quad (\text{Eq. S2})$$

For the $S = 1/2$ electronic spin-manifold the expectation value of the spin operator $\langle S_Z \rangle$ is $1/2$ and thus Eq. 6 can re-expressed as:

$$\rho_i = 2 \cdot \langle S_Z^i \rangle \quad (\text{Eq. S3})$$

Analytical expressions for the spin projections ρ_i can be calculated using generalized operator notation as per the methodology outlined in chapter 3 of Bencini and Gatteschi³. These are given in the supporting information S2. The spin projections (ρ_i) now allow us to relate the effective isotropic G and hyperfine values to the intrinsic isotropic g and hyperfine values of the individual four Mn ions. It can be shown that the effective isotropic G and hyperfine values are a weighted linear sum of the intrinsic hyperfine values of the individual Mn ions (Eq. S4).

$$\begin{aligned} G &= \rho_1 g_1 + \rho_2 g_2 + \rho_3 g_3 + \rho_4 g_4 \\ A_1 &= \rho_1 a_1 \\ A_2 &= \rho_2 a_2 \\ A_3 &= \rho_3 a_3 \\ A_4 &= \rho_4 a_4 \end{aligned} \quad (\text{Eq. S4})$$

Where the weighting factor (ρ_i), corresponds to the projection of the total spin onto Mn_i .

S.1.2 Inclusion of the Zero-field Splitting (ZFS) of Mn^{III} . The spin projections calculated above can be corrected for the zero-field splitting (ZFS) of the only Mn^{III} ion of the $\text{Mn}_4\text{O}_x\text{Ca}$ cluster in the S_2 state.

$$H = - \sum_{i < j} J_{ij} S_i \cdot S_j + S_j \cdot d_j \cdot S_j \quad (\text{Eq. S5})$$

Where the j^{th} spin operator (S_j) refers to the Mn^{III} ion and d_j , is its corresponding fine structure tensor. The fine structure tensor is assumed to be axial and can thus be expressed in terms of a single parameter

(d):

$$d_j = \begin{bmatrix} -\frac{1}{3}d & 0 & 0 \\ 0 & -\frac{1}{3}d & 0 \\ 0 & 0 & \frac{2}{3}d \end{bmatrix} \quad (\text{Eq. S6})$$

The inclusion of the ZFS of the Mn^{III} requires the spin projections (ρ_i) to be expressed as a tensor as opposed to a scalar quantity. As we assume that all pair-wise exchange couplings (J_{ij}) are isotropic and that the fine structure tensor of the Mn^{III} is axial, the spin projection tensor of the i^{th} Mn can be expressed as a diagonal matrix of the form:

$$\rho_i = \begin{bmatrix} \rho_{\perp_i} & 0 & 0 \\ 0 & \rho_{\perp_i} & 0 \\ 0 & 0 & \rho_{\parallel_i} \end{bmatrix} \quad (\text{Eq. S7})$$

The effective $\mathbf{G}$ and hyperfine tensors ($\mathbf{A}_i$) are a weighted, linear sum of the intrinsic $\mathbf{g}$ and hyperfine tensors ($\mathbf{a}_i$) of the individual Mn ions as described above, (see Eq. S4).

S.1.3 Hyperfine couplings from broken-symmetry DFT. A quantum chemical approach that allows the extraction of hyperfine coupling constants (HFCs) from BS-DFT calculations of oligonuclear exchange-coupled clusters was developed recently⁴ and has been already applied to candidate models of the OEC.² The approach was shown to lead to predicted ^{55}Mn HFCs that can be meaningfully compared with experimental values and that can be used to distinguish between different cluster topologies and ligand environments of the Mn centers. Since the methodology has been previously described in detail,⁴ here we will only highlight the main concepts. Considering the system under study as composed of metal-centered subsystems, with nucleus K belonging to subsystem A, the general equation that directly connects the BS calculation to the observable HFC is

$$A_{\text{iso}}^{(\text{K})} = A_{\text{iso,site}}^{(\text{K})} \left(\frac{\langle S_z^{(\text{A})} \rangle}{S_{\text{t}}} \right) \quad (\text{Eq. S8})$$

where S_{t} is the effective total spin (1/2), $\langle S_z^{(\text{A})} \rangle$ is the on-site spin expectation value and $A_{\text{iso,site}}^{(\text{K})}$ is the site isotropic coupling constant

$$A_{\text{iso,site}}^{(\text{A})} = \pm A_{\text{iso,BS}}^{(\text{A})} \left(\frac{\langle S_z \rangle_{\text{BS}}}{S_{\text{A}}} \right) \quad (\text{Eq. S9})$$

S_{A} is the site-spin of subsystem A and the positive or negative sign depends on whether the fragment carries majority or minority spin. $\langle S_z \rangle_{\text{BS}}$ is the total M_S of the BS wavefunction and $A_{\text{iso,BS}}^{(\text{K})}$ the “raw” hyperfine coupling constant calculated directly from the BS calculation. The final projection of the site isotropic coupling constant into the correct effective HFC requires the determination of the site spin expectation value $\langle S_z^{(\text{A})} \rangle$, which for a given subsystem A is given by

$$\langle S_z^{(\text{A})} \rangle = \sum_{S_{\text{A}} M_{S_{\text{A}}} \dots S_N M_{S_N}} \left| C_I^{S_{\text{A}} M_{S_{\text{A}}} \dots S_N M_{S_N}} \right|^2 M_{S_{\text{A}}} \quad (\text{Eq. S10})$$

where $\left| C_I^{S_{\text{A}} M_{S_{\text{A}}} \dots S_N M_{S_N}} \right|^2$ is the weight of the basis state $|S_{\text{A}} M_{S_{\text{A}}}, \dots, S_N M_{S_N}\rangle$ in the ground-state eigenfunction describing the lowest-energy Kramers doublet. The TPSSh functional is also used in the calculation of effective ^{55}Mn HFCs for the models considered in the present study, following previous applications that established the reliability of the approach and the necessary scaling factors for the isotropic couplings.^{2,4,5} To ensure the accuracy of the results, the size of the integration grid was increased to “7” (ORCA convention) for the manganese atoms.

SUPPORTING INFORMATION S2 – SPIN PROJECTIONS

Spin projections were calculated as per the methodology outlined in chapter 3 of Bencini and Gatteschi³. We adopted the coupling scheme: $|S_1 \ S_2 \ S_{12} \ S_3 \ S_4 \ S_{34} \ S \ M\rangle$, or more succinctly $|S_{12} \ S_{34} \ S \ M\rangle$, where $|S_1 - S_2| \leq S_{12} \leq |S_1 + S_2|$, $|S_3 - S_4| \leq S_{34} \leq |S_3 + S_4|$, and $|S_{12} - S_{34}| \leq S \leq |S_{12} + S_{34}|$

The resultant basis set, for the subset where $S = \frac{1}{2}$ and assuming (S_1, S_2, S_3, S_4) is $(\frac{3}{2}, \frac{3}{2}, \frac{3}{2}, 2)$ or $(\frac{3}{2}, \frac{3}{2}, 2, \frac{3}{2})$ is:

$$\begin{array}{lll} |0 \ \frac{1}{2} \ \frac{1}{2} \ M\rangle & |2 \ \frac{3}{2} \ \frac{1}{2} \ M\rangle & |3 \ \frac{7}{2} \ \frac{1}{2} \ M\rangle \\ |1 \ \frac{1}{2} \ \frac{1}{2} \ M\rangle & |2 \ \frac{5}{2} \ \frac{1}{2} \ M\rangle & \\ |1 \ \frac{3}{2} \ \frac{1}{2} \ M\rangle & |3 \ \frac{5}{2} \ \frac{1}{2} \ M\rangle & \end{array}$$

Where M takes all half-integer values: $-\frac{1}{2} \leq M \leq \frac{1}{2}$

The complete set of basis vectors can be found in Table S1:

Table S2.1. Table of eigenstates $|S_{12} \ S_{34} \ S \ M\rangle$. M takes all half-integer values: $-S \leq M \leq S$, for each entry.

S		S ₁₂			
		0	1	2	3
S ₃₄	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}, \frac{3}{2}$	$\frac{3}{2}, \frac{5}{2}$	$\frac{5}{2}, \frac{7}{2}$
	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$	$\frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$
	$\frac{5}{2}$	$\frac{5}{2}$	$\frac{3}{2}, \frac{5}{2}, \frac{7}{2}$	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}$
	$\frac{7}{2}$	$\frac{7}{2}$	$\frac{5}{2}, \frac{7}{2}, \frac{9}{2}$	$\frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}$	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}, \frac{13}{2}$

The Spin Hamiltonian for the system takes the form of a series of pairwise interactions i.e.

$$H = \sum_{i < j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

Which can be re-expressed in generalized operator form:

$$H = \sum_k \sqrt{2k+1} \cdot O_k(k_1 \ k_2 \ k_{12} \ k_3 \ k_4 \ k_{34} \ k) \cdot \{ \{ T_{k1}(S_1) \otimes T_{k2}(S_2) \}_{k12} \otimes \{ T_{k3}(S_3) \otimes T_{k4}(S_4) \}_{k34} \}_k \\ = \sum_k \sqrt{2k+1} \cdot O_k(k_1 \ k_2 \ k_{12} \ k_3 \ k_4 \ k_{34} \ k) \cdot X_k(k_1 \ k_2 \ k_{12} \ k_3 \ k_4 \ k_{34} \ k)$$

Where O_k corresponds to the scalar exchange coupling term J i.e.

$$O_k(k_1 \ k_2 \ k_{12} \ k_3 \ k_4 \ k_{34} \ k) = -\sqrt{3} J_{ij};$$

$$\text{i.e. } O_0(1100000) = -\sqrt{3} J_{12}, O_0(1011010) = -\sqrt{3} J_{12} \text{ etc}$$

And the matrix elements X_k correspond to:

$$\langle S_1 S_2 S_{12} S_3 S_{34} S M | X_k | S_1 S_2 S'_{12} S_3 S'_{34} S M \rangle = (-1)^{S-M} \begin{pmatrix} S & k & S \\ -M & q & M \end{pmatrix} \cdot \langle S_1 S_2 S_{12} S_3 S_{34} S | X_k | S_1 S_2 S'_{12} S_3 S'_{34} S \rangle$$

The reduced matrix elements can be calculated using:

$$\langle S_1 S_2 S_{12} S_3 S_{34} S | X_k | S_1 S_2 S'_{12} S_3 S'_{34} S \rangle = (2S+1) \sqrt{(2k_{12}+1)(2S_{12}+1)(2S'_{12}+1)(2k_{34}+1)(2S_{34}+1)(2S'_{34}+1)} \\ \cdot \begin{Bmatrix} S_{12} & S'_{12} & k_{12} \\ S_{34} & S'_{34} & k_{34} \\ S & S & k \end{Bmatrix} \cdot \begin{Bmatrix} S_1 & S_1 & k_1 \\ S_2 & S_2 & k_2 \\ S_{12} & S'_{12} & k_{12} \end{Bmatrix} \begin{Bmatrix} S_3 & S_3 & k_3 \\ S_4 & S_4 & k_4 \\ S_{34} & S'_{34} & k_{34} \end{Bmatrix} \\ \langle S_1 || T_{k1} || S_1 \rangle \cdot \langle S_2 || T_{k2} || S_2 \rangle \cdot \langle S_3 || T_{k3} || S_3 \rangle \cdot \langle S_4 || T_{k4} || S_4 \rangle$$

The six reduced matrix elements corresponding to the six pair-wise interactions, that the form:

$$\left\langle S_1 S_2 S_{12} S_3 S_{34} S \| X_0(1100000) \| S_1 S_2 S'_{12} S_3 S'_{34} S \right\rangle = \frac{\delta_{S_{12} S'_{12}} \delta_{S_{34} S'_{34}}}{2} \sqrt{\frac{(2S+1)}{3}} [S_1(S_1+1) + S_2(S_2+1) - S_{12}(S_{12}+1)]$$

$$\left\langle S_1 S_2 S_{12} S_3 S_{34} S \| X_0(1011010) \| S_1 S_2 S'_{12} S_3 S'_{34} S \right\rangle = \frac{(-1)^{3(S_1+S_2+S_3+S_4+S_{34})+2(S_{12}+S'_{12})+S'_{34}+S}}{\sqrt{3}} \sqrt{(2S+1)(2S_{12}+1)(2S'_{12}+1)(2S_{34}+1)(2S'_{34}+1)} \cdot \sqrt{(2S_1+1)S_1(S_1+1)(2S_3+1)S_3(S_3+1)} \cdot \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_{34} & S'_{34} & S \end{Bmatrix} \cdot \begin{Bmatrix} S_1 & S_1 & 1 \\ S'_{12} & S_{12} & S_2 \end{Bmatrix} \cdot \begin{Bmatrix} S_3 & S_3 & 1 \\ S'_{34} & S_{34} & S_4 \end{Bmatrix}$$

$$\left\langle S_1 S_2 S_{12} S_3 S_{34} S \| X_0(1010110) \| S_1 S_2 S'_{12} S_3 S'_{34} S \right\rangle = \frac{(-1)^{3(S_1+S_2+S_3+S_4)+2(S_{12}+S'_{12}+S_{34}+S'_{34})+S}}{\sqrt{3}} \sqrt{(2S+1)(2S_{12}+1)(2S'_{12}+1)(2S_{34}+1)(2S'_{34}+1)} \cdot \sqrt{(2S_1+1)S_1(S_1+1)(2S_4+1)S_4(S_4+1)} \cdot \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_{34} & S'_{34} & S \end{Bmatrix} \cdot \begin{Bmatrix} S_1 & S_1 & 1 \\ S'_{12} & S_{12} & S_2 \end{Bmatrix} \cdot \begin{Bmatrix} S_4 & S_4 & 1 \\ S'_{34} & S_{34} & S_3 \end{Bmatrix}$$

$$\left\langle S_1 S_2 S_{12} S_3 S_{34} S \| X_0(0111010) \| S_1 S_2 S'_{12} S_3 S'_{34} S \right\rangle = \frac{(-1)^{3(S_1+S_2+S_3+S_4+S_{12}+S'_{34})+S'_{12}+S_{34}+S}}{\sqrt{3}} \sqrt{(2S+1)(2S_{12}+1)(2S'_{12}+1)(2S_{34}+1)(2S'_{34}+1)} \cdot \sqrt{(2S_2+1)S_2(S_2+1)(2S_3+1)S_3(S_3+1)} \cdot \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_{34} & S'_{34} & S \end{Bmatrix} \cdot \begin{Bmatrix} S_2 & S_2 & 1 \\ S'_{12} & S_{12} & S_1 \end{Bmatrix} \cdot \begin{Bmatrix} S_3 & S_3 & 1 \\ S'_{34} & S_{34} & S_4 \end{Bmatrix}$$

$$\left\langle S_1 S_2 S_{12} S_3 S_{34} S \| X_0(0111010) \| S_1 S_2 S'_{12} S_3 S'_{34} S \right\rangle = \frac{(-1)^{3(S_1+S_2+S_3+S_4+S_{12}+S'_{34})+S'_{12}+S_{34}+S}}{\sqrt{3}} \sqrt{(2S+1)(2S_{12}+1)(2S'_{12}+1)(2S_{34}+1)(2S'_{34}+1)} \cdot \sqrt{(2S_2+1)S_2(S_2+1)(2S_4+1)S_4(S_4+1)} \cdot \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S_{34} & S'_{34} & S \end{Bmatrix} \cdot \begin{Bmatrix} S_2 & S_2 & 1 \\ S'_{12} & S_{12} & S_1 \end{Bmatrix} \cdot \begin{Bmatrix} S_3 & S_3 & 1 \\ S'_{34} & S_{34} & S_4 \end{Bmatrix}$$

$$\left\langle S_1 S_2 S_{12} S_3 S_{34} S \parallel X_0(0001100) \parallel S_1 S_2 S'_{12} S_3 S'_{34} S \right\rangle = \frac{\delta_{S_{12} S'_{12}} \delta_{S_{34} S'_{34}}}{2} \sqrt{\frac{(2S+1)}{3}} [S_3(S_3+1) + S_4(S_4+1) - S_{34}(S_{34}+1)]$$

The resulting matrix is block diagonal; only terms with the same total spin mix.

The projection of the total spin onto the individual Mn ions can be calculated in a similar manner using the Wigner Echart Theorem. This reduced to calculating the matrix elements X_k , where X_k now refers to the spin operators S_x ($x = 1, 2, 3$ or 4). For instance, for $X_k = T_1(S_1)$:

$$\left\langle S_1 S_2 S_{12} S_3 S_{34} S \parallel T_1(S_1) \parallel S_1 S_2 S'_{12} S_3 S'_{34} S \right\rangle = (-1)^{S_1+S_2+S_{12}+S'_{12}+S_{34}+S} \delta_{S_{34} S'_{34}} (2S+1) \sqrt{(2S_{12}+1)(2S'_{12}+1)(2S_1+1)S_1(S_1+1)} \cdot \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S & S & S_{34} \end{Bmatrix} \cdot \begin{Bmatrix} S_1 & S_1 & 1 \\ S'_{12} & S_{12} & S_2 \end{Bmatrix}$$

The ratio of the matrix element $\langle \dots \parallel X_k \parallel \dots \rangle$ to the expectation value of the total spin $\langle \dots \parallel S \parallel \dots \rangle$ then yields the spin projection number (c_k) for each Mn center.

$$c_1 = \frac{\left\langle S_1 S_2 S_{12} S_3 S_{34} S \parallel T_1(S_1) \parallel S_1 S_2 S'_{12} S_3 S'_{34} S \right\rangle}{\left\langle S_1 S_2 S_{12} S_3 S_{34} S \parallel T_1(S) \parallel S_1 S_2 S'_{12} S_3 S'_{34} S \right\rangle} = (-1)^{S_1+S_2+S_{12}+S'_{12}+S_{34}+S} \delta_{S_{34} S'_{34}} \frac{\sqrt{(2S+1)(2S_{12}+1)(2S'_{12}+1)(2S_1+1)S_1(S_1+1)}}{\sqrt{S(S+1)}} \cdot \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S & S & S_{34} \end{Bmatrix} \cdot \begin{Bmatrix} S_1 & S_1 & 1 \\ S'_{12} & S_{12} & S_2 \end{Bmatrix}$$

$$c_2 = \frac{\langle S_1 S_2 S_{12} S_3 S_{34} S \| T_1(S_2) \| S_1 S_2 S'_{12} S_3 S'_{34} S \rangle}{\langle S_1 S_2 S_{12} S_3 S_{34} S \| T_1(S) \| S_1 S_2 S'_{12} S_3 S'_{34} S \rangle} = (-1)^{(S_1 + S_2 + 2S_{12} + 2S'_{12} + S_{34} + S)}$$

$$\delta_{S_{34} S'_{34}} \frac{\sqrt{(2S+1)(2S_{12}+1)(2S'_{12}+1)(2S_2+1)S_2(S_2+1)}}{\sqrt{S(S+1)}} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ S & S & S_{34} \end{Bmatrix} \cdot \begin{Bmatrix} S_2 & S_2 & 1 \\ S'_{12} & S_{12} & S_1 \end{Bmatrix}$$

$$c_3 = \frac{\langle S_1 S_2 S_{12} S_3 S_{34} S \| T_1(S_3) \| S_1 S_2 S'_{12} S_3 S'_{34} S \rangle}{\langle S_1 S_2 S_{12} S_3 S_{34} S \| T_1(S) \| S_1 S_2 S'_{12} S_3 S'_{34} S \rangle} = (-1)^{(S_3 + S_4 + S_{12} + 2S'_{34} + 2S_{34} + S)}$$

$$\delta_{S_{12} S'_{12}} \frac{\sqrt{(2S+1)(2S_{34}+1)(2S'_{34}+1)(2S_3+1)S_3(S_3+1)}}{\sqrt{S(S+1)}} \begin{Bmatrix} S_{34} & S'_{34} & 1 \\ S & S & S_{12} \end{Bmatrix} \cdot \begin{Bmatrix} S_3 & S_3 & 1 \\ S'_{34} & S_{34} & S_4 \end{Bmatrix}$$

$$c_4 = \frac{\langle S_1 S_2 S_{12} S_3 S_{34} S \| T_1(S_4) \| S_1 S_2 S'_{12} S_3 S'_{34} S \rangle}{\langle S_1 S_2 S_{12} S_3 S_{34} S \| T_1(S) \| S_1 S_2 S'_{12} S_3 S'_{34} S \rangle} = (-1)^{(S_3 + S_4 + S_{12} + 2S'_{34} + S_{34} + S)}$$

$$\delta_{S_{12} S'_{12}} \frac{\sqrt{(2S+1)(2S_{34}+1)(2S'_{34}+1)(2S_4+1)S_4(S_4+1)}}{\sqrt{S(S+1)}} \begin{Bmatrix} S_{34} & S'_{34} & 1 \\ S & S & S_{12} \end{Bmatrix} \cdot \begin{Bmatrix} S_4 & S_4 & 1 \\ S'_{34} & S_{34} & S_3 \end{Bmatrix}$$

For an arbitrary coupling scheme, the basis eigenstates take the form:

$$\Psi_a = \sum_{S_{12}} \sum_{S_{34}} C_{S_{12} S_{34}} |S_1 S_2 S_{12} S_3 S_{34} S\rangle$$

Thus, the calculation of the spin projection value requires the weighted sum over all matrix elements:

$$c_k = \sum_{S_{12}} \sum_{S_{34}} C_{S_{12} S_{34}} C_{S'_{12} S'_{34}} \frac{\langle S_1 S_2 S'_{12} S_3 S'_{34} S \| X_k \| S_1 S_2 S_{12} S_3 S_{34} S \rangle}{\langle S_1 S_2 S'_{12} S_3 S'_{34} S \| S \| S_1 S_2 S_{12} S_3 S_{34} S \rangle}$$

SUPPORTING INFORMATION S3: The magnetic field dependence of the ^{55}Mn -ENDOR spectra of the free Mn^{2+} artifact.

Figure S3. The field dependence of Q-band pulse ^{55}Mn Davies ENDOR of denatured (heat treatment) spinach PSII sample. The EPR settings are the same as described in the main text. Mn^{2+} has two characteristic peaks located the RF of ~ 114 MHz, ~ 158 MHz and at 375 MHz (not shown) under these experimental conditions described in Figure caption 2, see also ref⁶⁻⁸.

Mn^{2+} fitting parameters (Fig. 2 dashed green line)

$$g_{\text{iso}} = 1.996$$

$$[A_x \ A_y \ A_z] = 92.0 \text{ G}$$

$$D = -669 \text{ MHz}, E/D = 0.212$$

Supporting Information S4 – Monomeric Mn^{III} data

Mn ^{III}		g _⊥		g _∥	D	E	a _⊥	a _∥	a _{iso}	a _{aniso}
		g _x	g _y	g _z						
Mn ^{III} in rutile (TiO ₂) ⁹		2.00		1.99	-3.4	0.116	256	158	233	-98 (-33)
Mn(H ₂ O) ₆ ³⁺¹⁰		2.000		1.984	-4.514	-0.162	261	159	197	-102 (-34)
[Mn(dbm) ₃] Octahedral/ tetrahedral elongated ¹¹		1.99		1.87	-4.35	0.26	-		-	
[(terpy)Mn ^{III} (N ₃) ₃] Octahedral/ tetrahedral elongated ¹²		2.00	1.98	2.01	-3.29	0.51	-		-	
[Mn(cyclam)I ₂]I Octahedral/ tetrahedral elongated ¹³		2.00		1.99	0.604	0.034	-		-	
[Mn(bpia)(OAc)-(OCH ₃)]PF ₃ Octahedral/ tetragonally compressed ¹⁴		1.981	1.952	1.978	3.526	0.589	-		-	
Mn ^{III} -Porphyrins 15-17	Mn(TPP)Cl	2.005		1.982	-2.29	0.00	-		-	
	MnPcCl	2.005		2.00	-2.31	0.00			-	
	Mn(ODMAP ₂)Cl	-		1.984	-2.33	~0	-		-	
	Mn(ODMAP ₂)DTC	-		1.983	-2.61	~0	-		-	
	Mn(DP-IX_DME)Cl	-		-	-2.53	~0	-		-	
	Mn(DPDME)Cl	2		2	-2.53	~0.01	-		-	
	Mn(DPDME)Br	2		2	-1.1	~0	-		-	
Mn ^{III} -Corrole ^{18,19}	(tpfc)Mn(OPPh ₃)	1.994		1.980	2.69	0.03	-		-	
	Mn ^{III} C ³⁻	2.002			-2.66 - - 2.78	0.13 – 0.15	-		-	
Mn-Salen ^{20,21}	+ NMO (CH ₂ Cl ₂)	2.0		1.98	-2.5	0.269	190	126	167	-64 (-21)
	+ 4-PPNO (CH ₂ Cl ₂)	2.0		1.98	-2.5	0.249	190	119	166	-71 (-24)
	HFEPR (CH ₂ Cl ₂ /toluene 3:2 v/v)	2.00			-2.47	0.17	-		-	
PS II Mn ^{III} bound to the high affinity site ²²		2.0		1.98	-2.5	0.269	190	123	168	-67 (-22)
MnSOD Trigonal-bipyramidal ²³		2.00	1.99	1.98	2.10	0.243	283	280	282	-2 (-1)

Monomeric Mn^{IV} data

Mn ^{IV}		g _⊥		g _∥	D	E (E/D)	a _⊥		a _∥	a _{iso}	a _{aniso}
		g _x	g _y	g _z			a _x	a _y	a _z		
Mn ^{IV} in MgO (Octahedral) ²⁴		1.994			-	-	212			212	-
Mn ^{IV} in MgO (Tetragonal) ²⁴		1.9940		1.993 1	0.5287	-	213			213	-
Mn ^{IV} in Al ₂ O ₃ (tetragonal distorted) ²⁵		1.993		-	-0.1957	-	209		211	210	2 (1)
Mn ^{IV} in SnO ₂ /TiO ₂ (octahedral, rhomically distorted) ^{26,27}		1.98 79	1.98 70	1.987 0	0.8818	0.2635	252	209	226	229	-26 (-1.5)
K ₂ MnCl ₆ (perfect octahedron) ²⁸		~2.00			0	0	-			-	-
[Mn(MePH) ₃]PF ₆ ²⁹		~2.00			<<0.31	-	266			-	-
Mn ^{IV} tridentate ONO ligands ³⁰	[Mn ^{IV} (azpSS) ₂] ⁻⁴	2.01			0.0115	-	272			-	-
	[Mn ^{IV} (□mps) ₂] ⁻⁴	2.00			0.0116	-	272			-	-
	[Mn ^{IV} (azpSa) ₂] ⁻⁴	2.03			0.0117	-	263			-	-
	[Mn ^{IV} (azpSb) ₂] ⁻⁴	2.02			0.0117	-	272			-	-
Schiff base (N ₂ O ₂ coordination environment) ³¹⁻³³	Mn(SALAHE) ₂ .2H ₂ O	g _{eff} 5.45			>>0.31	(0.32)	-			-	-
	Mn(SALAHF) ₂ .3H ₂ O	g _{eff} 5.91			>>0.31	(0.07)	216			216	-
	Mn(SALAHF) ₂ .2D MF	g _{eff} 5.15, 4.38, 1.96			>>0.31	(0.22)	-			-	-
	Mn(SALATHM) ₂ . H ₂ O	g _{eff} 4.32			>>0.31	(0.06)	-			-	-
	Mn(SALAPDH) ₂ . DMF	g _{eff} 4.98			>>0.31	(0.19)	-			-	-
	Mn(L) ₂ .2THF (2 phenolic O)	g _{eff} ~ 4.0			>>0.31	~0	-			-	-
	Mn(als) ₂ (carbox ligand)	g _{eff} ~ 3.86, 2.02			>>0.31	~0	a _{av} ~ 216			216	-
Mn(salen) ³⁴		g _{eff} ~ 5.02			>>0.31	-	210			210	-
[Mn ^{IV} H ₃ burea(O)] ⁻ (terminal oxo) ³⁵		g _{eff} ~5.15, 2.44, 1.63			3.0	(0.26)	190			190	-
Mn ^{IV} (dbpip) ₂ (N ₂ O ₂ coordination environment) ³⁶		~2.00			<<0.31		-			-	-
[Mn ^{IV} (HIB) ₃] ²⁻ (hydroxyl acid ligands) ³⁷		g _{eff} ~ 3.9 (crossover)			>>0.31	0.05	198			198	-
[Mn ^{IV} Br(T _{piv} PP)] (Mn-porphyrins) ³⁸		g _{eff} ~ 4.0			>>0.31	~0	-			-	-

Mn^{III}Mn^{IV} mixed valance complexes

Mn ^{III} Mn ^{IV} complexes		g _⊥		g _∥	a _⊥		a _∥	a _{iso}	a _{aniso}
		g _x	g _y	g _z	a _x	a _y	a _z		
[(phen) ₂ Mn ^{III} O ₂ -Mn ^{IV} (phen) ₂](ClO ₄) ₃ (J = -150 cm ⁻¹) ³⁹	Mn ^{III}	-	-	-	245		189	227	-56 (-18.6)
	Mn ^{IV}	-	-	-	-	-	-	-	-
[Mn ^{III} Mn ^{IV} O ₂ (OAc)(HB(pz) ₃) ₂] (J < -150 cm ⁻¹) ³⁹	Mn ^{III}				228		163	206	65 (-21.7)
	Mn ^{IV}	-	-	-	-	-	-	-	-
[(phen) ₂ Mn ^{III} O ₂ -Mn ^{IV} (phen) ₂](ClO ₄) ₃ (J = -150 cm ⁻¹) ^{40a}	Mn ^{III}	-	-	-	237 to 249		178 to 187	220	-59 (-19.7) to -62 (-20.7)
	Mn ^{IV}	-	-	-	208 to 229		226 to 249	218	18 (6) to 20 (7)
Mn ^{III} Mn ^{IV} -[2-OH-3,5-Cl ₂ -salpn] ₂ (THF)(ClO ₄) (J = -10 cm ⁻¹) ^{40a}	Mn ^{III}	-	-	-	-	-	-	170-180	60 (20) to 30 (10)
	Mn ^{IV}	-	-	-	-	-	-	200-210	15 (5) to -27 (-9)
[Mn ^{III} Mn ^{IV} (μ-O) ₂ bipy ₄](ClO ₄) (BIPY) (J = -144 to -150 cm ⁻¹) ^{41,42b}	Mn ^{III}	1.991	1.988	1.984	253	242	183	226	-70 (-21.5)
	Mn ^{IV}	1.988	1.987	1.991	214	219	223	219	9 (2.2)
[Mn ^{III} Mn ^{IV} (μ-O) ₂ (μ-OAc)tacn ₂]BPh ₄ (TACN) (J = -110 cm ⁻¹) ^{41,42b}	Mn ^{III}	1.995	1.994	1.988	209	233	143	195	-90 (-26.0)
	Mn ^{IV}	1.988	1.987	1.991	227	198	213	213	15 (0.2)
[Mn ^{III} Mn ^{IV} (μ-O) ₂ (μ-OAc)dtne]BPh ₄ (DTNE) (J = -110 cm ⁻¹) ^{41,42b}	Mn ^{III}	1.995	1.992	1.987	212	238	144	198	-94 (-27.0)
	Mn ^{IV}	1.988	1.987	1.991	227	199	201	209	-26 (-4.0)
[Mn ^{III} Mn ^{IV} (μ-O) ₂ (μ-OAc)Me ₄ dtne]BPh ₄ (MDTN) (J = -130 cm ⁻¹) ^{41,42b}	Mn ^{III}	1.995	1.992	1.987	212	244	153	203	-51 (-25.0)
	Mn ^{IV}	1.988	1.987	1.991	226	198	206	210	-20 (-2)
MnCat 1 (J < -175 cm ⁻¹) ³⁹	Mn ^{III}	-	-	-	245		157	192	-88 (-29.3)
	Mn ^{IV}	-	-	-	-	-	-	-	-
MnCat 2 (J < -175 cm ⁻¹) ^{41,42b}	Mn ^{III}	1.996	1.995	1.989	215	208	147	190	-68 (21.5)
	Mn ^{IV}	1.988	1.987	1.991	228	237	245	237	17 (4.2)

^aUsing the range of acceptable D values (see Peloquin et al.⁴⁰ Fig. 4); ^bUsing the literature D values of Gerristen et al.⁹ and From et al.²⁷ (see table 4.4 Schäfer doctoral thesis⁴¹)

SUPPORTING INFORMATION S5

Table S5.1. Pair-wise exchange coupling constants J (cm^{-1}) for the literature coupling schemes referred to in the text (assuming $-JS_iS_j$ convention).

	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}
Kulik (1) ⁴³	-180	0	0	-52	-5	-42
Kulik (3) ⁴³	-117	0	0	-40	-12	-32
Peloquin (3) ⁴⁰	-115	0	0	-150	0	-15
Peloquin (4) ⁴⁰	-150	0	0	-150	0	-16
Pantazis (1) – EXAFS I ²	-94	10	-2	-18	24	-86
Pantazis (2) – EXAFS II ²	-2	6	-2	-16	24	2
Pantazis (3) – EXAFS IIb ²	0	6	0	-12	22	-36
Pantazis (4) – EXAFS III ²	-20	0	-2	14	-16	-74
Pantazis (5) – EXAFS III ²	-6	0	-4	-6	-16	-54
Pantazis (10) – EXAFS III ²	-4	-2	-8	10	-52	28
Pantazis (11) – Siegbahn ²	-16	6	20	30	18	-68

Figure S5. Panel A: The dependence of the spin projection ($\rho_{\perp}$, $\rho_{\parallel}$) on the zero-field splitting parameter (d) of the Mn^{III} ion assuming the EXAFS I core exchange coupling (scheme Fig. 1F). Tile B: The dependence of the on-site hyperfine tensor components ($a_{\perp}$, $a_{\parallel}$) of the $\text{Mn}_4\text{O}_x\text{Ca}$ cluster for each of the four manganese ions on the on the zero-field splitting parameter (d) of the Mn^{III} ion (see text). The bottom panel (C) shows the difference (a_{Δ}) between the parallel ($a_{\parallel}$ or a_z) and perpendicular ($a_{\perp}$ or a_x , a_y) hyperfine components of the three Mn^{IV} ions. The green shaded region represents the range of ZFS values for the Mn^{III} seen in model complexes (when $d < 0$). The red shaded region represents the range of acceptable ZFS values for the Mn^{III} which are consistent with the electronic model i.e. the range over which the intrinsic hyperfine anisotropy of the Mn^{IV} ions are within the range seen for model complexes. Their intersection is shown by the orange shaded region. Panels D and E are exactly the same as tiles B and C, except that here the Sr containing OEC was examined. Table 5 lists the intrinsic hyperfine tensor components for all four Mn ions calculated at the mid-point of the range of consistent d values i.e. the yellow shaded region.

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