

SUPPORTING INFORMATION

Single-Molecule Magnetism Properties of the First Strontium-Manganese

Cluster [SrMn₁₄O₁₁(OMe)₃(O₂CPh)₁₈(MeCN)₂]

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Mn EXAFS Results

Comparison of Mn K-edge EXAFS (k^3 -weighted) spectra with those of the WOC in the S₁ state is shown in Figure S2 (top), and the Fourier transforms are shown in Figure S2 (bottom). The three main peaks, labeled I - III, have been assigned in the WOC to the Mn–ligand (peak I), di- μ -oxide-bridged Mn···Mn (peak II), and Mn···Mn and Mn···Ca (peak III) separations. Inspection of the FT spectra in Figure S2 (bottom) indicates significant differences in the peak positions and relative intensities between complex **1** and the WOC. Mn–O distances are longer in **1** than in the WOC, which is indicated by the shift of peak I to longer distances. This is consistent with the lower average Mn oxidation level in **1** (13Mn^{III}, Mn^{II}) compared with the WOC S₁ state (2Mn^{IV}, 2Mn^{III}), **Error! Bookmark not defined.** which will give longer average Mn–O bonds in the former. In general, Mn^{IV} ions (two Mn^{IV} in WOC S₁ state) are symmetric and isotropic, and have shorter Mn–O bond lengths (generally below 2 Å) when compared to the anisotropic JT distorted Mn^{III} ions of complex **1**. In the Mn₁₄Sr compound, only weak peaks are observed in the region for peaks II and III. This is clearly due to the many different Mn···Mn separations in the molecule spanning distances in a wide range of 2.9 – 4.0 Å. In such a case, the contribution of each individual vector is less pronounced in the spectrum normalized to one Mn atom, and the EXAFS oscillations are damped by the high distance distribution

Table S1. Least-squares fits of Fourier-filtered peaks I and II of Sr EXAFS data compared with structural parameters from the X-ray crystal structure on Complex **1** and the Sr-substituted WOC of Photosystem II in the S₁ state.^a

	Fit	Shell	R (Å)	N	$\sigma^2/10^3 \text{ \AA}^2$	$\Phi/10^3$	$\varepsilon^2/10^5$	XRD $R/\text{Å}$	XRD N
Mn₁₄Sr									
Peak I	I-1	Sr-O	2.59	8.8	12.0	0.27	0.10	Sr-O ~2.5 ~2.6	4 2
	I-2	Sr-O	2.56	5.2	7.1	0.22	0.084		
		Sr-N	2.73	2.3	6.0				
	I-3	Sr-O	2.54	4.0 ^b	6.7 ^c	0.22	0.084	Sr-N ~2.7	2
		Sr-O	2.62	2.0 ^b					
		Sr-N	2.74	2.0 ^b					
Peak II	II-1	Sr-Mn	3.34	1.4	6.0 ^c	1.10	0.76	Sr-Mn 3.3 3.7 3.9	1 1 1
		Sr-Mn	3.72	1.2					
	II-2	Sr-Mn	3.35	1.0 ^b	4.0	0.57	0.22		
		Sr-Mn	3.69	1.0 ^b	7.3				
		Sr-Mn	4.00	1.0 ^b	4.5				
Sr-Photosystem II S₁ ^d									
Peak I		Sr-O	2.57	9.0				-	-
Peak II		Sr-Mn	3.54	2.0	7.8	0.402	0.30	-	-

^a N , the number of interactions; σ^2 , Debye-Waller parameter; Φ and ε^2 , fit-quality parameters. S_0^2 value was fixed to 1.0. For details, see Supporting Information. ^b N is fixed to known values from XRD (crystal structure) data. ^c Single value of σ^2 is used for all the interactions. ^d Data was taken from references **Error! Bookmark not defined.** and **Error! Bookmark not defined.**a.

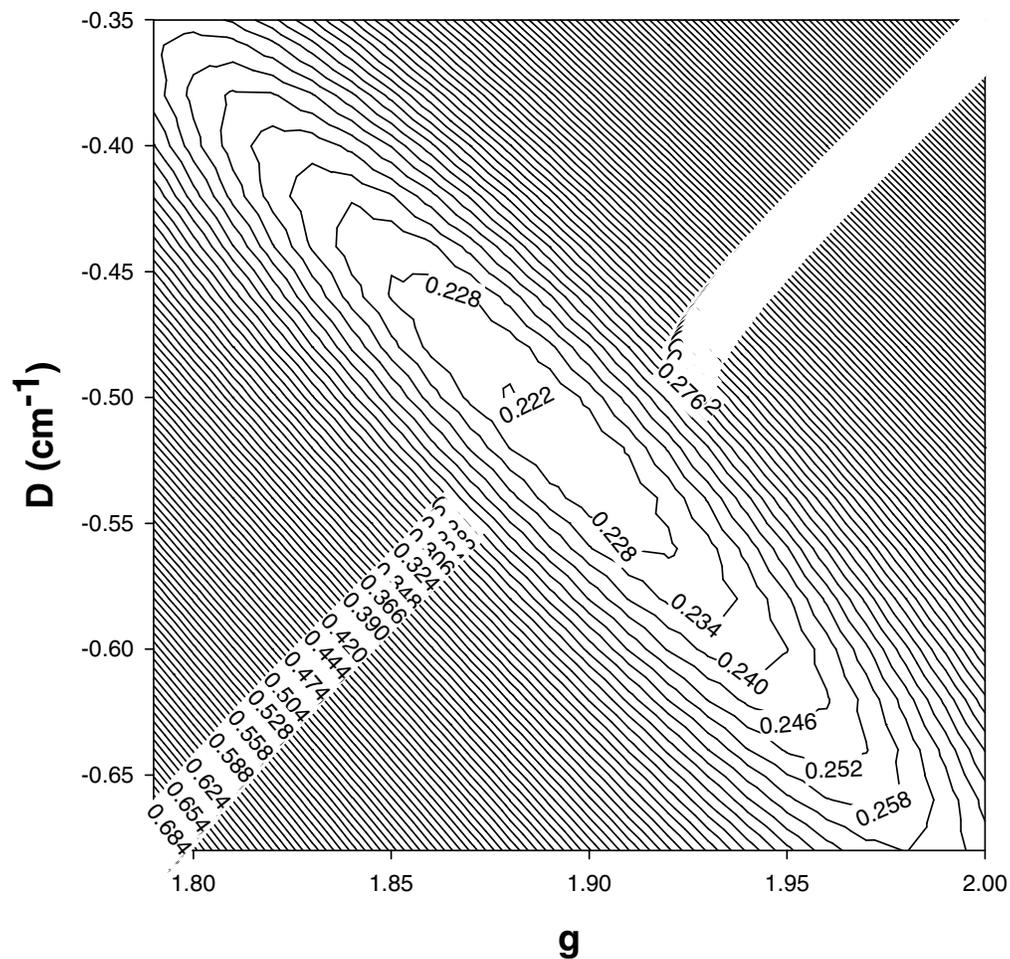


Figure S1. Two-dimensional contour plot of the root-mean-square error surface for the reduced magnetization ($M/N\mu_B$) vs H/T fit for complex **1** as a function of g and D . The asterisk marks the best-fit position.

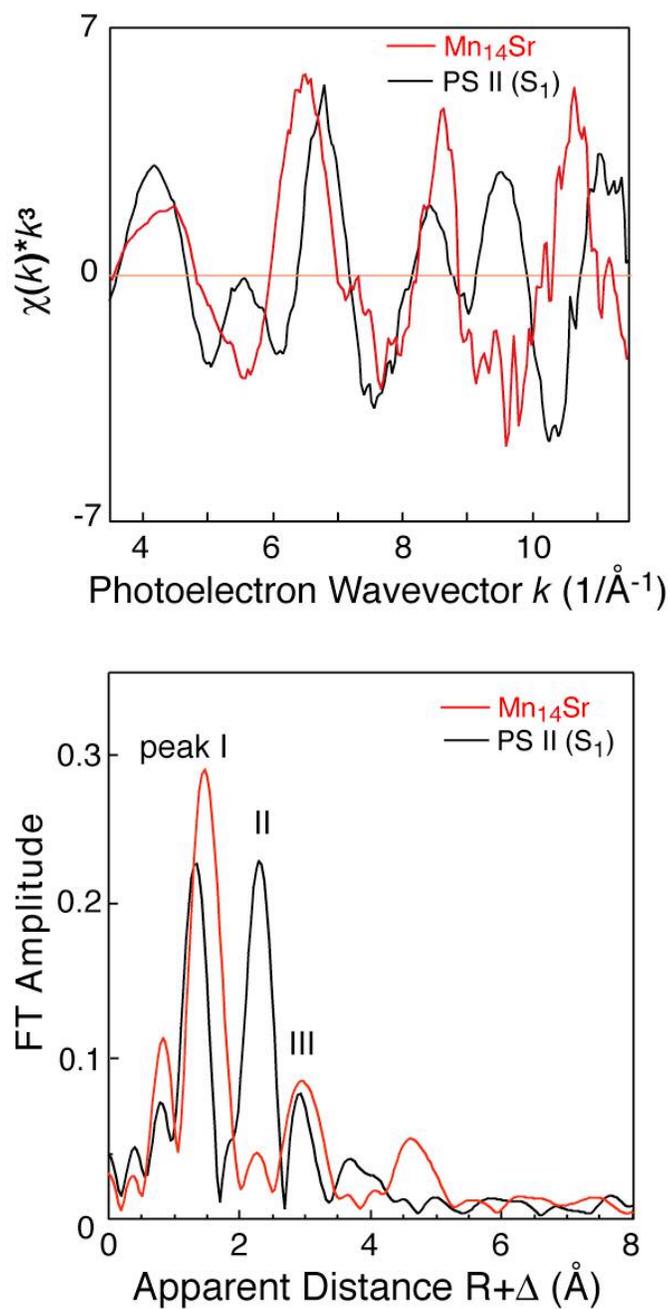


Figure S2. (Top) k^3 -weighted Mn K-edge EXAFS spectra of the Mn_{14}Sr compound (red) and PS II samples in the S_1 state (black). (Bottom) Fourier transforms of the averaged Mn K-edge EXAFS spectra for the Mn_{14}Sr complex **1** (red) and PS II samples in the S_1 state (black).

EXAFS Analysis Details

Data reduction of the EXAFS spectra was performed as described earlier.^{S1, S2} Curve fitting was performed using *ab initio*-calculated phases and amplitudes from the program FEFF 8.^{S3} These *ab initio* phases and amplitudes were used in the EXAFS equation:

$$\chi(k) = S_0^2 \sum_j \frac{N_j}{kR_j^2} f_{eff_j}(\pi, k, R_j) e^{-2\sigma_j^2 k^2} e^{-2R_j / \lambda_j(k)} \sin(2kR_j + \phi_{ij}(k))$$

The neighboring atoms to the central atom(s) are divided into j shells, with all atoms with the same atomic number and distance from the central atom grouped into a single shell. Within each shell, the coordination number N_j denotes the number of neighboring atoms in shell j at a distance of R_j from the central atom. $f_{eff_j}(\pi, k, R_j)$ is the *ab initio* amplitude function for shell j , and the Debye-Waller term $e^{-2\sigma_j^2 k^2}$ accounts for damping due to static and thermal disorder in absorber-backscatterer distances. The mean free path term $e^{-2R_j / \lambda_j(k)}$ reflects losses due to inelastic scattering, where $\lambda_j(k)$ is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term $\sin(2kR_j + \phi_{ij}(k))$, where $\phi_{ij}(k)$ is the *ab initio* phase function for shell j . This sinusoidal term shows the direct relation between the frequency of the EXAFS oscillations in k space and the absorber-backscatterer distance.

The EXAFS equation was used to fit the experimental data using N , R , and σ^2 as variable parameters. The coordination numbers, N , are evaluated on a per Sr basis. N values for Sr-Mn and Sr-ligand interactions are in multiples of 1, as there is only one Sr/PS II and one Sr in complex **1**.

Fit quality was evaluated using two different fit parameters, Φ and χ^2 . Φ is a normalized sum of residuals between the data and the simulations. The χ^2 error takes into account the number of variable parameters. S_0^2 is an amplitude reduction factor due to shake-up/shake-off processes at the central atom(s).

Fit-quality Φ is:

$$\Phi = \sum_1^{N_T} \left(\frac{1}{s_i} \right)^2 [\chi^{expt}(k_i) - \chi^{calc}(k_i)]^2$$

where N_T is the total number of data points collected, $\chi^{expt}(k_i)$ is the experimental EXAFS amplitude at point i , and $\chi^{calc}(k_i)$ is the theoretical EXAFS amplitude at point i .

The normalization factor s_i is given by:

$$\frac{1}{s_i} = \frac{k_i^3}{\sum_j^N k_j^3 |\chi^{expt}(k_j)|}$$

The ϵ^2 error takes into account the number of variable parameters p in the fit and the number of independent data points N_{ind} , as shown in:

$$\epsilon^2 = \left[\frac{N_{ind}}{N_{ind} - p} \right] N^{-1} \Phi$$

N is the total number of data points collected, and the number of independent data points N_{ind} is estimated from the Nyquist sampling theorem, as shown in

$$N_{ind} = \frac{2 \Delta k \Delta R}{\pi}$$

Δk is the k -range of the data and ΔR is the width of the Fourier-filtered peak in Å. ϵ^2 provides a gauge of whether the addition of another shell to the fit is justified.

Supplementary References

- S1. Robblee, J.H.; Messinger, J.; Cinco, R. M.; McFarlane, K. L.; Fernandez, C.; Pizarro, S. A.; Sauer, K.; Yachandra, V. K. *J. Am. Chem. Soc.* **2002**, *124*, 7459.
- S2. Cinco, R. M.; Robblee, J. H.; Rompel, A.; Fernandez, C.; Yachandra, V. K.; Sauer, K.; Klein, M. P. *J. Phys. Chem. B* **1998**, *102*, 8248.
- S3. Rehr, J. J.; Albers, R. C. *Rev. Mod. Phys.* **2000**, *72*, 621.