

Supplementary Online Material

Ca XAS data collection

Ca X-ray absorption spectra were measured at beamline 10.3.2 of the Advanced Light Source (ALS) operating at electron energy of 1.9 GeV (an average current of 300 mA). The radiation was monochromatized by a Si(111) double-crystal monochromator. Intensity of the incident X-ray was monitored by an N₂-filled ion chamber (I₀) in front of the sample. XAS samples were made by gently grinding ~1 mg of compound and sealing in a sample holder with Mylar tape. Fluorescence spectra were recorded by using a seven-element Ge detector array. Energy was calibrated by the edge peak of calcium acetate (4050 eV) for Ca XAS. All spectra were collected at room temperature. Each XANES and EXAFS scan required 17 and 30 minutes to complete. From a radiation damage study on each sample prior to data collection, it was considered safe to collect three scans per spot for XANES and two scans per spot for EXAFS with a spot size of 100 (H) * 10 (V) μm² using a defocused beam.

Sr XAS data collection

X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 9-3 at electron energy of 3.0 GeV with an average current of 70-90 mA. The radiation was monochromatized by a Si(220) double-crystal monochromator. The intensity of the incident X-ray was monitored by an N₂-filled ion chamber (I₀) in front of the sample. XAS samples were made by carefully grinding 5-10 mg of compound and diluting it with a 10-fold excess of boron nitride. The mixture was packed into 0.5-mm-thick sample holders and sealed with Mylar windows. For Mn₁₄Sr

complex, the data were collected as fluorescence excitation spectra with a Lytle detector.^[S1] Energy was calibrated by the edge peak of strontium acetate (16120 eV) for Sr XAS. The standards were placed between two N₂-filled ionization chambers (I₁ and I₂) after the sample. The X-ray flux at 16-17 keV was between 2 and 5*10⁹ photons s⁻¹mm⁻² of the sample. Samples were kept at a temperature of 10 K in a liquid helium flow cryostat to minimize radiation damage.

Data reduction and analysis

Data reduction of the EXAFS spectra was performed as described earlier.^[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 . S_0^2 is an amplitude reduction factor due to shake-up/shake-off processes at the central atom(s). The EXAFS equation was used to fit the experimental data using N , R , and σ^2 as variable parameters.

Fit quality was evaluated using a fit parameter, Φ :

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

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 . It is a normalized sum of residuals between the data and the simulations. 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 least-square fits of Fourier-filtered peaks I and II of Ca and Sr EXAFS data (Fig. 5 in the main paper) compared with the complexes, are shown in Tables S1 and S2, respectively. For both Sr and Ca EXAFS, the best fit was obtained when the structural parameters (i.e. coordination numbers, N) from the X-ray crystal structures of $Mn_{13}Ca_2$ and $Mn_{14}Sr$ complexes were used. The fitting results of the Ca PS II and Sr-reconstituted PS II S_1 state are also shown in the tables.

Refinement of the structures of complexes 1 and 2

The structures of **1**·10MeCN and **2**·12MeCN were solved by direct methods in *SHELXTL6*,^[S4] and refined on F^2 using full-matrix least squares. The asymmetric unit of **1**·10MeCN contains half the cluster and 5 MeCN molecules of crystallization. The asymmetric unit of **2**·12MeCN contains the complete $SrMn_{14}$ cluster and 12 MeCN molecules of crystallization. The 10 and 12 MeCN solvent molecules of **1** and **2**, respectively, were disordered and could not be modeled properly, thus program SQUEEZE,^[S5] a part of the PLATON^[S6] package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.

Table S1. Least-square fits^(a) of Fourier-filtered peaks I and II of Ca EXAFS data compared with structural parameters from the X-ray crystal structures from Mn₁₃Ca₂ complex **1**,^[S7] and the OEC of Photosystem II in the S₁ state.^[S8]

| | Fit No. | Shell | R ^(b) (Å) | N ^(c) | σ ² (Å ²) | Φ/10 ³ | XRD ^(b) R /Å | XRD N |
|--|---------|-------|----------------------|--------------------|----------------------------------|-------------------|-------------------------|-------|
| Mn ₁₃ Ca ₂ | | | | | | | | |
| Peak I | I-2 | Ca-O | 2.37 | 7.0 | 0.012 | 1.3 | Ca-O | |
| | I-2 | Ca-O | 2.35 | 6.0 ^(d) | 0.010 | 0.84 | 2.3-2.5 | 6 |
| | | Ca-O | 2.83 | 1.0 ^(d) | 0.001 | | ~2.8 | 1 |
| Peak II | II-1 | Ca-Mn | 3.43 | 3.0 | 0.016 | 1.57 | Ca-O | |
| | | Ca-Mn | 3.79 | 2.0 | 0.019 | | ~3.0 | 1 |
| | II-2 | Ca-O | 3.06 | 1.0 ^(d) | 0.003 | 0.26 | Ca-Mn | |
| | | Ca-Mn | 3.45 | 3.0 ^(d) | 0.017 | | 3.5-3.6 | 3 |
| | | Ca-Mn | 3.86 | 2.0 ^(d) | 0.025 | | 3.8-3.9 | 2 |
| | | | | | | | | |
| Photosystem II S _I ^(e) | | | | | | | | |
| Peak I | | Ca-O | 2.4 | 5 - 6 | - | - | - | - |
| Peak II | | Ca-Mn | 3.40 | 1.0 | 0.009 | 0.70 | - | - |

(a) N, the number of interactions; σ^2 , Debye-Waller parameter; Φ , fit-quality

parameter. S_0^2 value was 1.0. For details, see ref. S2.

(b) Ca···Mn distances longer than 4.0 Å were not included in the fitting for Mn₁₃Ca₂.

(c) Bold letter shows the fixed number.

(d) N is fixed to known values from the XRD data.

(e) The data was taken from ref. S7.

Table S2: Least-square fits^(a) of Fourier-filtered peaks I and II of Sr EXAFS data compared with structural parameters from the X-ray crystal structure of Mn₁₄Sr complex and the Sr-substituted OEC of Photosystem II in the S₁ state.^[s9]

| | Fit No. | Shell | R (Å) | N ^(b) | $\sigma^2 / \text{Å}^2$ | $\Phi / 10^3$ | XRD R / Å | XRD N |
|--|---------|-------|-------|--------------------------|-------------------------|---------------|-----------|-------|
| Mn₁₄Sr | | | | | | | | |
| Peak I | I-1 | Sr-O | 2.59 | 8.8 | 0.012 | 0.29 | Sr-O | |
| | I-2 | Sr-O | 2.56 | 5.0 | 0.007 | 0.23 | 2.5 | 4 |
| | | Sr-N | 2.73 | 2.4 | 0.006 | | 2.6 | 2 |
| | I-3 | Sr-O | 2.55 | 4.0^(c) | 0.006 | 0.22 | Sr-N | |
| | | Sr-O | 2.66 | 2.0^(c) | 0.009 | | 2.7 | 2 |
| | | Sr-N | 2.71 | 2.0^(c) | 0.007 | | | |
| Peak II | II-1 | Sr-Mn | 3.34 | 1.4 | 0.006 ^(d) | 1.10 | Sr-Mn | |
| | | Sr-Mn | 3.72 | 1.2 | | | 3.3 | 1 |
| | II-2 | Sr-Mn | 3.35 | 1.0^(c) | 0.004 | 0.57 | 3.7 | 1 |
| | | Sr-Mn | 3.69 | 1.0^(c) | 0.007 | | 3.9 | 1 |
| | | Sr-Mn | 4.00 | 1.0^(c) | 0.005 | | | |
| | | | | | | | | |
| Sr-Photosystem II S₁^(e) | | | | | | | | |
| Peak I | | Sr-O | 2.57 | 9.0 | - | - | - | - |
| Peak II | | Sr-Mn | 3.54 | 2.0 | 0.008 | 0.402 | - | - |

(a) N, the number of interactions; σ^2 , Debye-Waller parameter; Φ and ϵ^2 , fit-quality parameters. S_0^2 value was 1.0. For details see ref. S2.

(b) Bold letter shows the fixed number.

(c) The data was fixed to the known values from the XRD data.

(d) Single value of σ^2 was used for all the interactions.

(e) Data was taken from ref. S9.

References:

- [S1] E.A. Stern and S.M. Heald, *Rev. Sci. Instrum.*, 1979, **50**, 1579.
- [S2] J. H. Robblee, J. Messinger, R.M. Cinco, K.L. McFarlane, C. Fernandez, S. A. Pizarro, K. Sauer and V.K. Yachandra, *J. Am. Chem. Soc.*, 2002, **124**, 7459.
- [S3] Rehr, J. J.; Albers, R. C. *Rev. Mod. Phys.* **2000**, 72, 621.
- [S4] G. M. Sheldrick, *SHELXTL6*, Bruker-AXS: Madison, WI, 2000.
- [S5] P. van der Sluis and A. L. Spek, *Acta Crystallogr.*, 1990, **A46**, 194.
- [S6] A. L. Spek, *Acta Crystallogr.*, 1990, **A46**, C34.
- [S7] A. Mishra, W. Wernsdorfer, K. A. Abboud and G. Christou, *Chem. Commun.*, 2005, 54.
- [S8] R. M. Cinco, K. L. M. Holman, J. H. Robblee, J. Yano, S. A. Pizarro, E. Bellacchio, K. Sauer and V. K. Yachandra, *Biochemistry*, 2002, **41**, 12928.
- [S9] R. M. Cinco, J. H. Robblee, A. Rompel, C. Fernandez, V. K. Yachandra, K. Sauer and M. P. Klein, *J. Phys. Chem. B*, 1998, **102**, 8248.