ELECTRONIC SUPPORTING INFORMATION

Towards models of the oxygen-evolving complex (OEC) of photosystem II: A Mn₄Ca cluster of relevance to low oxidation states of the OEC

Evangelia S. Koumousi, a Shreya Mukherjee, b Christine M. Beavers, c Simon J. Teat, c George Christou b and Theocharis C. Stamatatos a,d

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a Department of Chemistry, University of Patras, 26500 Patras, Greece. Fax: +30-2610-997118; Tel: +30-2610-996020; E-mail: thstama@chemistry.upatras.gr

b Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, USA.

c Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Mail Stop 2-400, Berkeley, CA 94720, USA.

d Department of General and Inorganic Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki, P.O. Box 135, 54124 Thessaloniki, Greece.
Fig. S1 Labeled PovRay representation of the complete $[\text{Mn}_4\text{Ca}(\mu\text{-NO})_4]^{10+}$ core of 1. Color scheme: Ca, yellow; Mn$^{III}$, blue; O, red; N, green.

The Mn-Mn-Mn, Mn-Mn-Ca, and Mn-Ca-Mn angles are in the ranges $89.5(2)$-$90.6(2)^\circ$, $51.6(3)$-$52.3(3)^\circ$, and $75.9(4)$-$123.3(5)^\circ$, respectively. The Ca$^{II}$ atom lies 1.804 Å out of the Mn$_4$ plane. All Ca-O bonds are in the range 2.346(4)-2.465(4) Å.

Fig. S2 The coordination mode of shi$^{3-}$ ligand in complex 1.
**Fig. S3** $\chi_M T$ vs $T$ plot for 1·CH$_2$Cl$_2$. The blue solid line is the fit of the data. Inset: 2-$J$ coupling scheme for 1.

The fit (solid blue line in Fig. S3) gave fit parameter values ($\mathcal{H} = -2\mathbf{S}_i \cdot \mathbf{S}_j$ convention) of $J = -3.33(5)$ cm$^{-1}$, $J' = -1.15(9)$ cm$^{-1}$, and $g = 1.91(2)$, indicating an $S = 0$ ground state and an $S = 1$ first excited state at 6.66 cm$^{-1}$ higher in energy. A temperature-independent paramagnetism (TIP) term was included, held fixed at $200 \times 10^{-6}$ cm$^3$ mol$^{-1}$. The agreement factor was $R^2 = 0.99$. 

Electronic Supplementary Material (ESI) for Chemical Communications
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