ELECTRONIC SUPPORTING INFORMATION

Towards models of the oxygen-evolving complex (OEC) of photosystem II: A Mn_4Ca cluster of relevance to low oxidation states of the OEC

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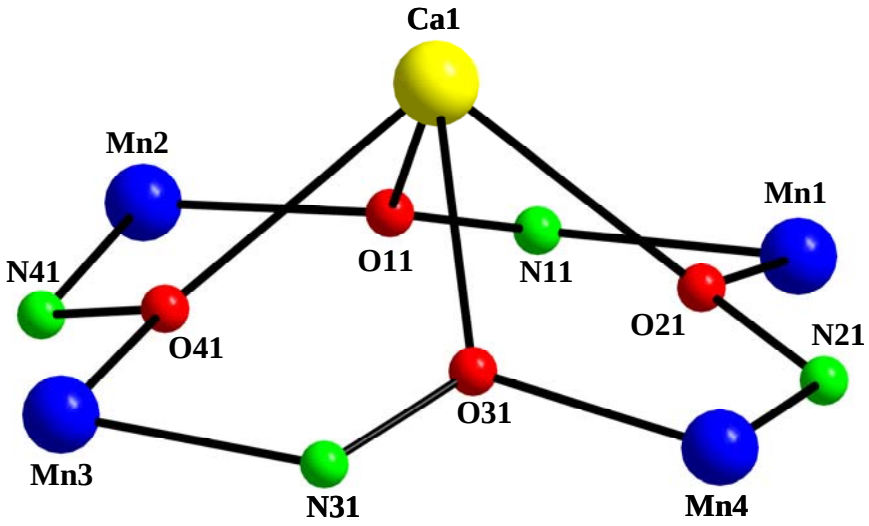
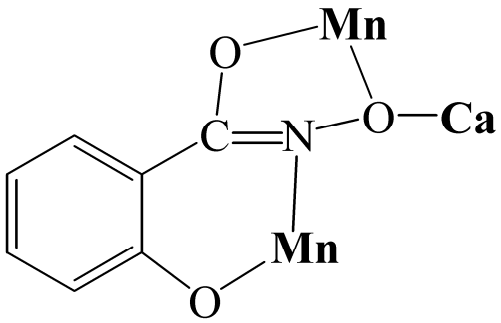


Fig. S1 Labeled PovRay representation of the complete $[Mn_4Ca(\mu\text{-}NO)_4]^{10+}$ core of **1**. Color scheme: Ca, yellow; Mn^{III}, blue; O, red; N, green.

The Mn-Mn-Mn, Mn-Mn-Ca, and Mn-Ca-Mn angles are in the ranges 89.5(2)-90.6(2)°, 51.6(3)-52.3(3)°, and 75.9(4)-123.3(5)°, 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.



shi^{3-}

$\eta^1:\eta^1:\eta^1:\eta^2:\mu_3$

Fig. S2 The coordination mode of shi^{3-} ligand in complex **1**.

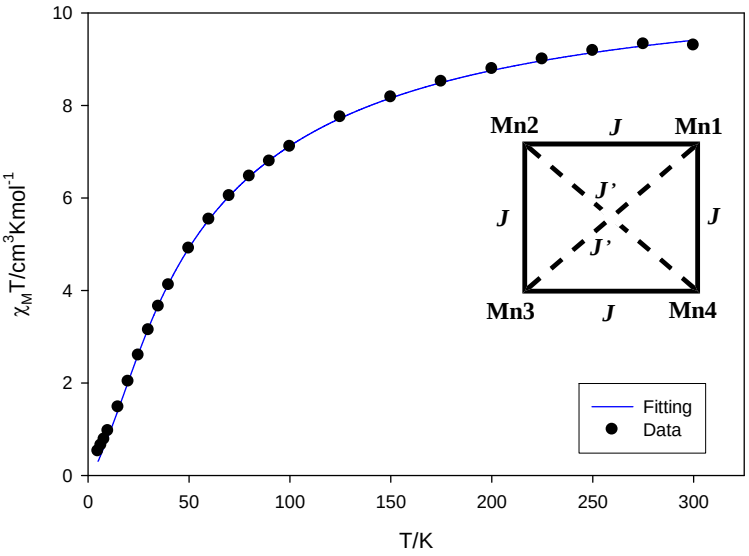


Fig. S3 $\chi_M T$ vs T plot for **1**·CH_2Cl_2. The blue solid line is the fit of the data. Inset: 2-J coupling scheme for **1**.

The fit (solid blue line in Fig. S3) gave fit parameter values ($\mathcal{H} = -2J\hat{S}_i \cdot \hat{S}_j$ 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 × 10^{-6} cm^3 mol^{-1}. The agreement factor was R^2 = 0.99.