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Synthesis and crystal structure of a dinuclear, monomeric Mn^{II} *p*-semiquinonato complex†

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Herein, we report the first crystal structure of a monomeric *p*-semiquinonato d-block complex and its reactivity toward dioxygen, closely associated with a biological system of an oxygen evolving centre of photosystem II.

The oxygen evolving centre (OEC) acts cooperatively with quinone cofactors in photosystem II (PSII), which play a key role in the electron transfer process coupled with O_2 evolution.[1–3] In the catalytic cycle of O_2 evolution from water, Mn^{III} and/or Mn^{IV} centres can react with *p*-hydroquinone to generate reduced Mn^{II} species concomitant with a *p*-semiquinone radical,[4–6] suggesting complexation between the Mn centres and the quinone species. Hence, studies of Mn^{II} *p*-semiquinonato complexes and their reactivity are considered to be of relevance in elucidating the true function of OEC in PSII.

Until now, however, there has been no report on the crystal structure of any monomeric *p*-semiquinonato d-block complex, though a crystal structure of a *p*-semiquinonato f-block, Sm mononuclear complex has been reported (Fig. S1 and S2, ESI†).[7–9] Here, we report the first example of a monomeric Mn^{II} *p*-semiquinonato complex and revealed its X-ray structure and reactivity toward O_2.

A dinuclear Mn^{II} *p*-semiquinonato complex, $[\mathrm{Mn^{II,II}}_2(\mathrm{cyclam})_2(\mu\text{-SQ})_2](\mathrm{ClO_4})_2$ $\{[\mathbf{1}](\mathrm{ClO_4})_2$, cyclam = 1,4,8,11-tetraazacyclotetradecane, SQ = *p*-semiquinonato$\}$, was synthesised by the reaction of a mixed-valence bis(μ-oxo) $\mathrm{Mn^{III,IV}}_2$ complex, $[\mathrm{Mn^{III,IV}}_2(\mathrm{cyclam})_2(\mu\text{-O})_2](\mathrm{ClO_4})_3$ $\{[\mathbf{2}](\mathrm{ClO_4})_3\}$, with *p*-hydroquinone, which was monitored by UV-vis spectroscopy (Fig. 1).

Upon addition of 3 equivalents of *p*-hydroquinone into **2** in acetonitrile under an N_2 atmosphere, characteristic bands of **2** disappeared together with the appearance of the absorption bands derived from **1** with an intense broad band at 634 nm (ε = 4370 M^{-1} cm^{-1}, Fig. S3, ESI†). This reduction process is concomitant with stoichiometric formation of 0.5 equivalent of *p*-benzoquinone, which was confirmed by quantitative analysis. The consequently formed water was confirmed by isotope-labelling experiments.

The structure of **1** has been determined by X-ray analysis by using dark blue crystals obtained from replacement of ClO_4^- in $[\mathbf{1}](\mathrm{ClO_4})_2$ by BPh_4^- in acetonitrile–diethyl ether (Fig. 2). This is the first crystal structure of a monomeric *p*-semiquinonato d-block complex, which is a single monomer molecule different from a polymeric structure comprising the repetition of a Mn *p*-semiquinonato porphyrin unit.[9a] Each Mn atom of **1** adopts a distorted-octahedral coordination which is surrounded by the cyclam and bridging *p*-semiquinonato ligands. The two Mn centres are tethered by two units of *p*-semiquinonato whose

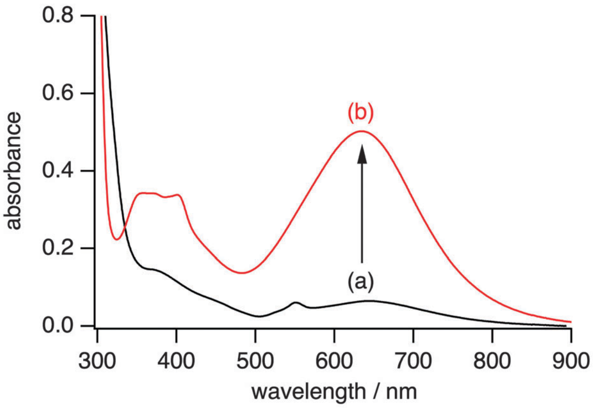

Fig. 1 (a) A UV-vis spectrum of **2** (1.0 mM) in acetonitrile under an N_2 atmosphere. (b) A UV-vis spectrum obtained upon the addition of 3 equivalents of *p*-hydroquinone into **2** (1.0 mM) in acetonitrile under an N_2 atmosphere.

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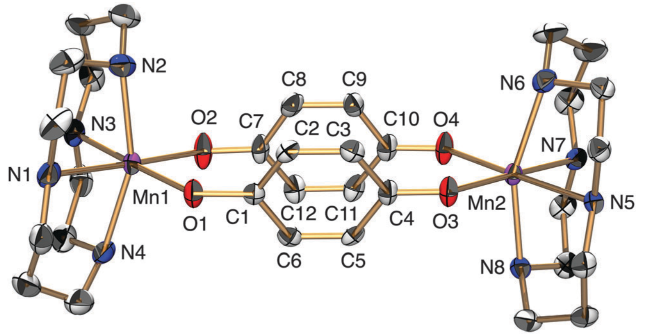

Fig. 2 An ORTEP drawing of [**1**]$(BPh_4)_2$ with ellipsoids at 50% probability. The counteranions (BPh_4), solvent (CH_3CN), and hydrogen atoms are omitted for clarity. Selected interatomic distances (l/Å): Mn1–O1 = 2.093(2), Mn1–O2 = 2.088(4), Mn1–N1 = 2.265(4), Mn1–N2 = 2.280(4), Mn1–N3 = 2.274(3), Mn1–N4 = 2.273(4), Mn2–O3 = 2.085(3), Mn2–O4 = 2.092(2), Mn2–N5 = 2.274(3), Mn2–N6 = 2.254(4), Mn2–N7 = 2.253(4), Mn2–N8 = 2.271(4), O1–C1 = 1.287(5), O2–C7 = 1.290(5), O3–C4 = 1.285(5), O4–C10 = 1.285(5).

arene rings are parallel with the π–π stacking interaction. The C–O bond distances {1.287(5), 1.290(5), 1.285(5) and 1.285(5) Å} are typical of that of *p*-semiquinonate.[9,10] An IR spectrum of **1** shows a characteristic band at 1510 cm^{-1} of ν(C–O) derived from the *p*-semiquinonato ligand (Fig. S4, ESI†).[9c,11] An ESR spectrum reveals that **1** is paramagnetic as evidenced by the appearance of its ESR signal in frozen *N*,*N*-dimethylformamide (DMF) at −150 °C (Fig. S5, ESI†).

Complex **1** was exposed to O_2 in acetonitrile to afford the mixed-valence bis(μ-oxo) $Mn^{III,IV}_2$ complex **2** concomitant with formation of *p*-benzoquinone and water. Complex **2** was characterised by UV-vis and ESR spectroscopy (Fig. 3 and Fig. S6, ESI†), corresponding to the previously reported data,[12] and electrospray ionization mass spectrometry (ESI-MS) (Fig. S7, ESI†). The stoichiometric formation of 2 equivalents of *p*-benzoquinone was confirmed by quantitative analysis. The generated water was confirmed by isotope-labelling experiments. This dinuclear Mn^{II}(cyclam) *p*-semiquinonato system is different from a mononuclear Mn^{II}(tpa) *o*-semiquinonato system {tpa = tris(2-pyridylmethyl)amine}, where oxygenation of the Mn^{II} *o*-semiquinonato complex forms a bis(μ-oxo) $Mn^{III,III}_2$ species. The difference in the oxidation state is probably due to the stronger donor ability of the cyclam over the tpa ligand.[13]

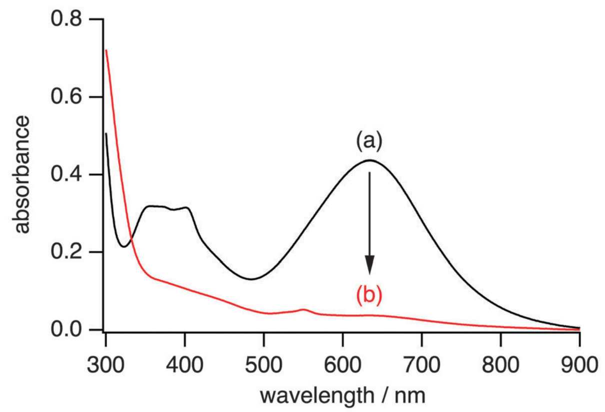

Fig. 3 (a) A UV-vis spectrum of **1** (1.0 mM) in acetonitrile under an N_2 atmosphere. (b) A UV-vis spectrum obtained upon the injection of O_2 into **1** (1.0 mM) in acetonitrile.

The UV-vis spectra showed that the absorption bands of **1** disappeared and the characteristic bands of **2** appeared by oxygenation of **1** (Fig. 3). An ESR spectrum of **2** in frozen DMF at −150 °C shows the typical 16-line pattern centred near $g = 2$, which has a hyperfine coupling characteristic of dinuclear complexes containing an $S = 2$ Mn^{III} ion and an $S = 3/2$ Mn^{IV} ion that are antiferromagnetically coupled to yield an $S = 1/2$ ground state (Fig. S6, ESI†). The hyperfine coupling constant A is estimated to be approximately 8 mT, which is similar to the previously reported value.[12b]

The ESI-MS results also indicate that the oxygenation of **1** is followed by formation of **2**. A negative-ion ESI mass spectrum of **2** in acetonitrile shows a prominent signal at *m*/*z* 940.2 (relative intensity = 100% in the range *m*/*z* 200–2000), which has a characteristic isotopic distribution that matches well with the calculated isotopic distribution for $[\mathbf{2} + 4(ClO_4)]^-$ (Fig. S7, ESI†). To shed light on the source of oxo ligands, an isotope-labelling experiment was conducted by using $^{18}O_2$ instead of $^{16}O_2$ (Fig. S7d, ESI†). The ESI-MS results show that the signal at *m*/*z* 940.2 shifts to *m*/*z* 944.2 corresponding to the $Mn^{III,IV}_2(\mu\text{-}^{18}O)_2$ species. This indicates that the two ^{18}O atoms from $^{18}O_2$ are incorporated.

A crossover experiment involving 50% $^{16}O_2$ and 50% $^{18}O_2$ was carried out for the oxygenation process of **1** to **2**. The ESI-MS results showed that the $Mn^{III,IV}_2(\mu\text{-}^{16}O)_2$, $Mn^{III,IV}_2(\mu\text{-}^{16,18}O)_2$ and $Mn^{III,IV}_2(\mu\text{-}^{18}O)_2$ species were formed in the ratio of 1 : 2 : 1 (Fig. S8, ESI†). It was confirmed that the $Mn^{III,IV}_2(\mu\text{-}^{16,18}O)_2$ species was not formed from the reaction of $Mn^{III,IV}_2(\mu\text{-}^{16}O)_2$ species with $Mn^{III,IV}_2(\mu\text{-}^{18}O)_2$ species. These results indicate that the oxo ligands scramble during the oxygenation process.

The bis(μ-oxo) ligands were sequentially exchanged for H_2O oxygen atoms, which was confirmed by isotope-labelling experiments using $H_2{}^{18}O$, monitored by ESI-MS (Fig. S9 and S10, ESI†).[14] Addition of 5000 equivalents of $H_2{}^{18}O$ into **2** in acetonitrile at 33 °C caused a consecutive exchange of ^{16}O ligands for ^{18}O atoms derived from $H_2{}^{18}O$. The oxo-exchange reaction was analysed as a consecutive reaction, where the observed rate constant for decrease of **2** at 33 °C was determined to be 2.1×10^{-3} s^{-1} (Fig. S10, ESI†).

We recognise that our assignment of the bridging oxo ligands as originating from O_2 is contrary to the assignment of Calvin and co-workers in their bis(μ-oxo) $Mn^{III,IV}_2$ complex.[12a] In their study, the authors proposed that the oxo ligands originated from H_2O, which is understandable given the fast exchange of the oxo ligands with H_2O oxygen atoms. However, our isotope studies on the complex confirm that the initial oxo ligands originate from O_2 (Fig. S11 and S12, ESI†).

Fig. 4 summarises the reaction cycle in this study. The dinuclear Mn^{II} *p*-semiquinonato complex **1** reacts with O_2 and H^+ to form the mixed-valence bis(μ-oxo) $Mn^{III,IV}_2$ complex **2** with *p*-benzoquinone and water. Then, reduction of **2** by *p*-hydroquinone results in formation of **1** with *p*-benzoquinone and water.

In conclusion, we have synthesised and fully characterised a monomeric, dinuclear *p*-semiquinonato Mn^{II} complex, which

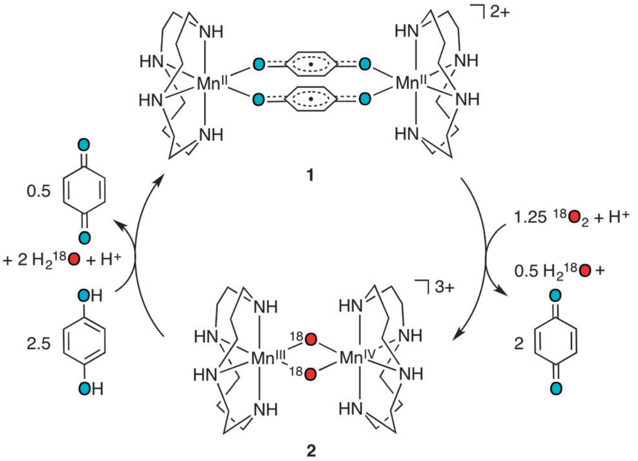

Fig. 4 A proposed mechanism for the oxidation of **1** with O_2 and the reduction of **2** with *p*-hydroquinone. H^+ is from the solvent of acetonitrile containing a small amount of H_2O.

constitutes the first monomeric *p*-semiquinonato d-block complex of any kind. We investigated its oxidation reaction with O_2 to access a mixed-valence bis(μ-oxo) $Mn^{III,IV}{}_2$ complex.

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References

1 (*a*) Y. Umena, K. Kawakami, J.-R. Shen and N. Kamiya, *Nature*, 2011, **473**, 55–61; (*b*) A. Zouni, H.-T. Witt, J. Kern, P. Fromme, N. Krauß, W. Saenger and P. Orth, *Nature*, 2001, **409**, 739–743; (*c*) K. N. Ferreira, T. M. Iverson, K. Maghlaoui, J. Barber and S. Iwata, *Science*, 2004, **303**, 1831–1838.
2 (*a*) J. Yano and V. Yachandra, *Chem. Rev.*, 2014, **114**, 4175–4205; (*b*) N. Cox and J. Messinger, *Biochim. Biophys. Acta*, 2013, **1827**, 1020–1030; (*c*) N. Cox, D. A. Pantazis, F. Neese and W. Lubitz, *Acc. Chem. Res.*, 2013, **46**, 1588–1596.
3 (*a*) F. Müh, C. Glöckner, J. Hellmich and A. Zouni, *Biochim. Biophys. Acta*, 2012, **1817**, 44–65; (*b*) I. Vass, *Biochim. Biophys. Acta*, 2012, **1817**, 209–217.
4 D. F. Ghanotakis, J. N. Topper and C. F. Yocum, *Biochim. Biophys. Acta*, 1984, **767**, 524–531.
5 U. Bergmann, M. M. Grush, C. R. Horne, P. DeMarois, J. E. Penner-Hahn, C. F. Yocum, D. W. Wright, C. E. Dubé, W. H. Armstrong, G. Christou, H. J. Eppley and S. P. Cramer, *J. Phys. Chem. B*, 1998, **102**, 8350–8352.
6 (*a*) N. Shaikh, M. Ali and P. Banerjee, *Inorg. Chim. Acta*, 2002, **339**, 341–347; (*b*) M. C. Ghosh, J. W. Reed, R. N. Bose and E. S. Gould, *Inorg. Chem.*, 1994, **33**, 73–78.
7 (*a*) J. Yuasa and S. Fukuzumi, *J. Am. Chem. Soc.*, 2007, **129**, 12912–12913; (*b*) H. Ohtsu and S. Fukuzumi, *Angew. Chem., Int. Ed.*, 2000, **39**, 4537–4539; (*c*) T. Kawashima, K. Ohkubo and S. Fukuzumi, *Phys. Chem. Chem. Phys.*, 2011, **13**, 3344–3352; (*d*) S. L. Scott, A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1992, **114**, 4605–4610; (*e*) S. Fukuzumi, H. Mori, H. Imahori, T. Suenobu, Y. Araki, O. Ito and K. M. Kadish, *J. Am. Chem. Soc.*, 2001, **123**, 12458–12465; (*f*) J. Yuasa, T. Suenobu and S. Fukuzumi, *J. Am. Chem. Soc.*, 2003, **125**, 12090–12091.
8 Â. Domingos, I. Lopes, J. C. Waerenborgh, N. Marques, G. Y. Lin, X. W. Zhang, J. Takats, R. McDonald, A. C. Hillier, A. Sella, M. R. J. Elsegood and V. W. Day, *Inorg. Chem.*, 2007, **46**, 9415–9424.
9 (*a*) E. J. Brandon, R. D. Rogers, B. M. Burkhart and J. S. Miller, *Chem. – Eur. J.*, 1998, **4**, 1938–1943; (*b*) M. Oh, J. A. Reingold, G. B. Carpenter and D. A. Sweigart, *J. Organomet. Chem.*, 2003, **687**, 78–84; (*c*) J. Moussa, C. Guyard-Duhayon, P. Herson, H. Amouri, M. N. Rager and A. Jutand, *Organometallics*, 2004, **23**, 6231–6238.
10 J.-M. Lü, S. V. Rosokha, I. S. Neretin and J. K. Kochi, *J. Am. Chem. Soc.*, 2006, **128**, 16708–16719.
11 (*a*) M. Bauscher and W. Mäntele, *J. Phys. Chem.*, 1992, **96**, 11101–11108; (*b*) X. Zhao, H. Imahori, C.-G. Zhan, Y. Sakata, S. Iwata and T. Kitagawa, *J. Phys. Chem. A*, 1997, **101**, 622–631.
12 (*a*) K. J. Brewer, M. Calvin, R. S. Lumpkin, J. W. Otvos and L. O. Spreer, *Inorg. Chem.*, 1989, **28**, 4446–4451; (*b*) P. A. Goodson and D. J. Hodgson, *Inorg. Chim. Acta*, 1990, **172**, 49–57.
13 T. Yatabe, M. Kikkawa, T. Matsumoto, H. Nakai, K. Kaneko and S. Ogo, *Dalton Trans.*, 2014, **43**, 3063–3071.
14 (*a*) R. Tagore, R. H. Crabtree and G. W. Brudvig, *Inorg. Chem.*, 2007, **46**, 2193–2203; (*b*) R. Tagore, H. Chen, R. H. Crabtree and G. W. Brudvig, *J. Am. Chem. Soc.*, 2006, **128**, 9457–9465.