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Isolation of the first ferromagnetically coupled Mn(III/IV) complex†

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Binuclear manganese complexes Mn_2(III/IV)(dtsalpn)$_2$DCBI, 1, Mn_2(III/III)(dtsalpn)$_2$HDCBI, 2, containing the ligand dicarboxyimidazole (DCBI) have been prepared in order to address the issue of imidazole bridged and ferromagnetically coupled Mn sites in high oxidation states of the OEC in Photosystem II (PS II). Temperature dependent magnetic susceptibility studies of 1 indicates that the interaction between the two Mn(III)/Mn(IV) ions is ferromagnetic (J = + 1.4 cm^{-1}). Variable temperature EPR spectra of 1 shows that a g = 2 multiline is as an excited state signal corresponding to S = 1/2.

Binuclear manganese complexes have been used as models of the Mn catalases and the Oxygen Evolving Complex (OEC) for many years. The OEC in Photosystem II (PSII) is responsible for the oxidation of water to dioxygen[1–5] and a low resolution X-ray structure of this enzyme has appeared.[6] The OEC contains a cluster of four manganese ions which undergoes a catalytic cycle with five relevant oxidation states (S_0–S_4).[7,8] The EPR-active S_2 state can show a multiline signal centered around g = 2[9,10] or a broad signal centered at $g \cong 4.1$ region.[11,12] Peloquin *et al.*[13] have suggested that a ferromagnetic exchange interaction between two of the four manganese ions is required to fit both types of EPR spectra. Structural elements leading to ferromagnetically exchanged manganese centers have also been of interest in the magnetic materials community due to an effort to make single molecule magnets that have high ground state magnetic moments. While ferromagnetically coupled manganese complexes are known, there has not been a report of a ferromagnetically coupled Mn(III/IV) complex.

We have been interested in Mn imidazole chemistry because a histidine appears to be bound to the manganese cluster,[14–17] and a structural model that is consistent with these data possesses an imidazole ring that could form a bridge between two manganese centers. To address the issue of imidazolate bridging in high oxidation states of the OEC, we first reported the structure of [Mn_2^{IV}(dtbsalpn)$_2$(DCBI)]PF$_6$.[18] This complex exhibited unprecedented low temperature EPR signals due to a very weak antiferromagnetic coupling between the two Mn(IV) ions. In this paper, we report the synthesis, X-ray structure, EPR and magnetic studies of $Mn_2^{III/IV}$(dtbsalpn)$_2$(DCBI) (**1**).‡ We also report the preparation of Mn_2^{III}(dtbsalpn)$_2$(HDCBI) (**2**), which is the precursor of both the dimanaganese(IV) complex mentioned above and the present mixed valent **1** which is the first example of a ferromagnetically coupled Mn(III)Mn(IV) dimer.

Compound **2** was synthesized from a mononuclear Mn(III) precursor and recrystallized from toluene.[19] The structure of this dimanganese (III) complex (Fig. S1†) is very similar to the dimanganese (IV) complex reported earlier.[18] The cyclic voltammogram of **2** (Fig. S2†) exhibits two oxidative waves with $E_{1/2}$ values of 575 and 850 mV *vs* Ag/AgCl reference electrode. When one equivalent of base ([Bu$_4$N][OH]) was added to deprotonate the carboxylate proton in the carboxyimidazolate bridge, these $E_{1/2}$ values shifted by approximately 400 mV to less positive potentials ($E_{1/2}$ = 490 and 165 mV, Fig. S2†) and the oxidation waves of Mn_2(III/III) → Mn_2(III/IV) → Mn_2(IV/IV) are better separated and more reversible.

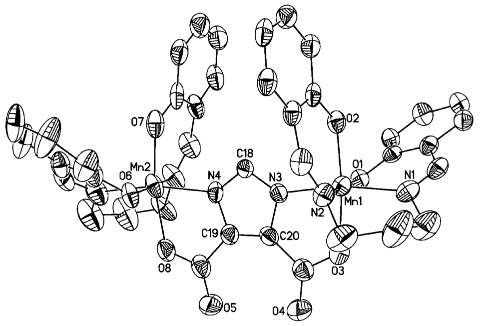

Fig. 1 ORTEP view of **1**. Selected bond distances (Å): Mn1–O1, 1.861(2); Mn1–O2, 1.899(2); Mn1–O3, 1.995(3); Mn1–N2, 1.983(3); Mn1–N1, 2.000(3); Mn1–N3, 2.023(3), Mn2–O6, 1.871(2); Mn2–O7, 1.962(3); Mn2-O8, 2.084(3); Mn2–N4, 2.082(3); Mn2–N5, 2.009(3); Mn2–N6, 1.997(3). Mn1–Mn2, 6.28 Å.

The mixed-valence dimanganese (III/IV) complex, **1**, was synthesized from bulk oxidation of **2** by addition of one equivalent of base[20] and also by the conproportionation of compound **2** and [Mn_2^{IV}(dtbsalpn)$_2$(DCBI)]PF$_6$ in presence of tetrabutyl ammonium hydroxide. An ORTEP diagram(Fig. S3) of **1** is shown as Fig. 1. The two Mn ions have identical first coordination sphere ligation; however, they are structurally inequivalent as the Mn2 has consistently longer Mn–O and Mn–N bonds (Mn1$_{avg}$ = 1.96 Å; Mn2 $_{avg}$ = 2.00 Å). We conclude that Mn2 is likely the Mn(III) ion and Mn1 is the Mn(IV) ion. The chemically equivalent distances Mn1–O1 and Mn2–O6 and Mn1–N2 and Mn2–N6 are essentially equal. In contrast, an equatorial plane of O7, O8, N4 and N5 show distances to Mn2 that are 0.06 Å longer than observed for O2, O3, N1 and N3 to Mn1. This suggests that Mn2 is a Jahn–Teller compressed Mn(III). The Mn–Mn distance in this mixed valence complex is intermediate (6.28 Å) between its dimanaganese(IV) (6.18 Å)[18] and dimanganese(III) (6.36 Å) analogs.

The variable temperature EPR spectra of the resulting solution (1.5 × 10^{-3} M) are shown in Fig. 2. At the lowest

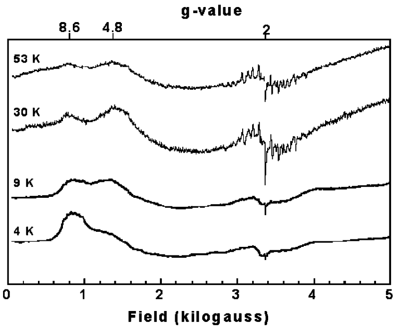

Fig. 2 X-band (9.45 GHz) EPR spectra of **1** at 53 K, 30 K, 9 K and 4 K (top to bottom).

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† Electronic supplementary information (ESI) available: Figures S1–S4. See http://www.rsc.org/suppdata/cc/b2/b212684m/

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temperature (4 K), the spectrum exhibits only low field resonances at g ~ 8.6, and ~ 4.8. When the temperature is raised to 9K, the g ~ 8.6 signal decreases in intensity while the intensity of the g ~ 4.8 transition increases. Interestingly, a novel $g = 2$ multiline (> 16 lines) feature appears at 30 K and the line width of this multiline signal (1200 G) is very similar to that observed for the ground $S = \frac{1}{2}$ spin state of strongly antiferromagnetically coupled dimanganese(III/IV) sites. However, the precise origin of the observed multiline for (Fig. S4†) is considerably more complex, owing to complications which derive from weak intramolecular exchange interactions and a potentially large single ion anisotropy (D) at the Mn(III) site. Regardless of these complications, the number of observed hyperfine lines clearly indicates that the manganese ions in **1** are exchange coupled. Furthermore, the resonance line position indicates that the transition likely derives from a Kramers doublet possessing considerable $m_s = \pm\frac{1}{2}$ character with $H \parallel z$. However, unlike antiferromagnetically coupled mixed-valence dimanganese (III/IV) complexes, the variable temperature EPR spectra of **2** indicate that the $m_s = \pm\frac{1}{2}$ transition does not derive from an $S = \frac{1}{2}$ ground state.

The complex EPR temperature dependence of **1**, coupled with an observed $g = 2$ multiline feature, is consistent with the two Mn ions being very weakly ferromagnetically exchange coupled. This is in accord with the variable temperature magnetic data presented in Fig. 3. Evidence for ferromagnetic exchange coupling derives from the fact that the magnetic moment begins to increase at ~150 K with decreasing temperature. This behavior is inconsistent with either antiferromagnetic pair wise exchange interactions, or antiferromagnetic coupling in the presence of a single ion anisotropy. The best fit to the data between 25–300 K yielded $J = +1.4$ cm^{-1} with $g = 1.9$. Below ~25 K the effects of a Mn(III) single ion anisotropy on the dimer are observed, resulting in a decrease in the effective moment with decreasing temperature. The combination of a weak exchange interaction in the presence of a moderate to large zero-field splitting lead to the complex EPR spectra at temperatures less than ~25 K. The simple exchange model predicts that the $S_T = \frac{1}{2}$ state lies ~ 20 cm^{-1} above the $S_T = 7/2$ ground state. Therefore, the origin of the $g = 2$ multiline resonance likely derives from a thermally excited $|S_T = \frac{1}{2}, m_s = -\frac{1}{2} > \rightarrow |S_T = \frac{1}{2}, m_s = +\frac{1}{2} >$ transition. A complete analysis of the complex EPR temperature dependence is ongoing and will be the subject of a future report. It should be noted that ferromagnetic coupling has never been observed in a Mn (III/IV) dimer, despite the fact that mixed valent manganese dimers have been known for over 20 years. As such, **1** is the first Mn (III/IV) dimer complex to possess a high spin, $S_T = 7/2$ ground state.

Binuclear manganese complexes with an imidazolate bridging ligand have shown interesting and unprecedented spectroscopic properties.[18] We have now shown that a mixed-valence dimanganese (III/IV) center can be weakly ferromagnetically exchange coupled and exhibit an excited state $g = 2$ multiline signal. In future studies, we will probe the unique electronic structure of this complex in order to understand the origin of the unusual intramolecular exchange interaction further.

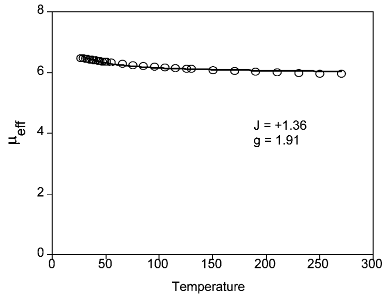

Fig. 3 Fit to the variable temperature magnetic data for **1**

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Notes and references

‡ Analytical data for **1**: Analysis found (calc): 65.0(65.2); H, 7.6(7.8); N, 6.7(6.4); Mn, 8.0(8.4)%. IR: ν(C=O) 1699 cm^{-1}, ν(C=N) 1614 cm^{-1}. Crystal data of **1**. ($C_{79}H_{109}Mn_2N_{10}O_8$): a = 16.6699(8) Å, b = 21.6736(11) Å, c = 24.3289(14) Å, $\alpha = \gamma = 90°$, β = 101.814(2)°, V = 8603(8) Å^3, Z = 4. Analytical data for **2**: Analysis Found (calc): C, 66.3 (66.9); H, 7.8 (7.8); N, 6.5(6.6); Mn, 8.4 (8.6)%. IR: ν(C=N) 1611 cm^{-1}. FAB$^-$ -MS: 1272 [M − H]$^-$. UV/Vis: 395 nm (shoulder, ε = 12,500 M^{-1} cm^{-1}). X-ray quality crystals were obtained from toluene. Crystal data of **2** with eight toluene solvent molecules ($Mn_2C_{99}H_{132}N_6O_8$): monoclinic, space group $C2/c$, a = 13.1300(14) Å, b = 35.455(3) Å, c = 20.564 (2) Å, $\alpha = \gamma = 90°$, β = 100.856(8)°, V = 9402(2) Å^3, Z = 4. X-ray diffraction data was collected on Siemens SMART CCD diffractometer and refined with full-matrix least-squares on F^2 using 9251 for **2** independent reflections (R1 = 0.0614, wR2 = 0.1672, GOF = 0.961, R_{int} = 0.0241) and 17626 for **1** independent reflections (R1 = 0.062, wR2 = 0.029, GOF = 1.097, R_{int} = 0.0502). CCDC reference number for **1** and **2**, are 195449 and 191509 respectively. See http://www.rsc.org/suppdata/cc/b2/b212684m/ for crystallographic data in CIF or other electronic format.

1 G. C. Dismukes, *Chem. Rev.*, 1996, **96**, 2909.
2 V. L. Pecoraro and W.-Y. Hsieh, in *Metal Ions in Biological Systems*, Vol 37, eds. A. Sigel and H. Sigel, Marcel-Dekker, Inc., Basel, 2000, 429.
3 R. D. Britt, in *Oxygenic Photosynthesis: The Light Reactions*, eds. D. R. Ort and C. F. Yocum, Kluwer Academic Publishers, Boston, 1996; p. 137.
4 V. K. Yachandra, K. Sauer and M. P. Klein, *Chem. Rev.*, 1996, **96**, 2927.
5 W. Rüttinger and G. C. Dismukes, *Chem. Rev.*, 1997, **97**, 1.
6 A. Zouni, H. T. Witt, J. Kern, P. Fromme, N. Kraub, W. Saenger and P. Orth, *Nature*, 2001, **409**, 739.
7 P. Joliot, G. Barbieri and R. Chabaud, *Photochem. Photobiol.*, 1969, **10**, 309.
8 B. Kok, B. Forbush and M. McGloid, *Photochem. Photobiol.*, 1970, **11**, 457.
9 G. A. Lorigan and R. D. Britt, *Biochemistry*, 1994, **33**, 12072.
10 G. C. Dismukes and Y. Siderer, *FEBS Lett.*, 1980, **121**, 78.
11 J. Cole, V. K. Yachandra, R. D. Guiles, A. E. McDermott, R. D. Britt, S. L. Dexheimer, K. Sauer and M. P. Klein, *Biochim. Biophys. Acta*, 1987, **890**, 395.
12 D. H. Kim, R. D. Britt, M. P. Klein and K. Sauer, *J. Am. Chem. Soc.*, 1990, **112**, 9389.
13 J. F. Peloquin, K. A. Campbell, D. W. Randall, M. A. Evanchick, V. L. Pecoraro, W. H. Armstrong and R. D. Britt, *J. Am. Chem. Soc.*, 2000, **122**, 10926.
14 R. D. Britt, J.-L. Zimmermann, K. Sauer and M. P. Klein, *J. Am. Chem. Soc.*, 1989, **111**, 3522.
15 V. J. DeRose, V. K. Yachandra, A. E. McDermott, R. D. Britt, K. Sauer and M. P. Klein, *Biochemistry*, 1991, **30**, 1335.
16 X. S. Tang, M. L. Gilchrist, G. A. Lorigan, B. Larson, R. D. Britt and B. A. Diner, *J. Am. Chem. Soc.*, 1993, **115**, 2382.
17 X.-S. Tang, B. A. Diner, B. S. Larsen, J. M. L. Gilchrist, G. A. Lorigan and R. D. Britt, *Proc. Nat. Acad. Sci., USA*, 1994, **91**, 704.
18 M. T. Caudle, J. W. Kampf, M. L. Kirk, P. G. Rasmussen and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1997, **119**, 9297.
19 To a mixture of 0.67 g (1.7 mmol) of $[C_4H_9)_4N]^+[H_2DCBI]^-$ and 0.44 g (1.7 mmol) of $[Bu_4N][CH_3CO_2]{\cdot}4H_2O$ in 50 mL CH_3CN, 2.5 g (3.4 mmol) of $[Mn^{III}(dtbsalpn)(H_2O)_2](PF_6)$ were added. The mixture was stirred overnight. A brown solid was collected by filtration and dried *in vacuo* to give 1.8 g (84% yield) of $Mn_2^{III}(dtbsalpn)_2(HDCBI)$, **2**.
20 $Mn_2^{III/IV}(dtbsalpn)_2(DCBI)$ (**1**) was prepared by anaerobic bulk oxidation of 20 mg (0.024 mmol) Mn_2^{III} (dtbsalpn)$_2$HDCBI dimer at 400 mV *vs* Ag wire/Pt gauze in CH_2Cl_2 with 0.10 M $[Bu_4N][PF_6]$ as the supporting electrolyte. One electron equivalent current was passed under nitrogen purging. A green solution of this electrochemistry experiment was transferred to an EPR tube for variable temperature EPR measurements.