

The First Binuclear Mn(IV) Complex Containing a Bridging Imidazolate Ligand Exhibits Unique EPR Spectral Features

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The oxygen-evolving complex (OEC) is a component of photosystem II (PS II) whose function is to facilitate the four-electron oxidation of water to dioxygen.¹ Essential to this activity is a cluster proposed to contain four manganese ions. While high-resolution structural information is currently unavailable for PS II, information on the structure of the OEC has come from comparisons between spectroscopic data collected on synthetic manganese complexes and on the OEC in its various catalytically relevant oxidation states,² $S_0 - S_4$.³ The most spectroscopically rich of these is the EPR-active S_2 state, which has an $S = 1/2$ ground state and is currently proposed to contain three Mn(IV) ions and one Mn(III) ion.⁴ This OEC oxidation level exhibits either a multiline EPR signal at $g = 2$ or a broad signal at $g = 4.1$.⁵ The only information currently available on specific ligands bound to the manganese cluster comes from ESEEM ¹⁴N/¹⁵N-labeling studies⁶ and ¹⁵N ENDOR spectroscopy⁷ on the S_2 state, which have shown that nitrogen-containing ligands are bound to manganese in PS II. More recently, ESEEM studies by Tang and Britt on PS II preparations incubated on histidine exclusively labeled with ¹⁵N at the imidazole nitrogen positions have shown that the nitrogen hyperfine interactions observed in these experiments arise from histidine ligation to the manganese cluster.⁸ Britt furthermore suggested that the bidentate nature of the imidazole unit might facilitate a bridging function for histidine in a manner analogous to the bridging imidazolate group in CuZn superoxide dismutase, the only biological center currently known to possess a bridging imidazolate.⁹ There are structurally-characterized examples of non-porphyrin complexes with imidazole bridging two Mn(II)¹⁰ or Mn(III)¹¹ ions, but no examples of corresponding dimanganese(IV) imidazolate-bridged complexes, which can address the specific issue of imidazole bridging in high oxidation states of the OEC. We therefore report the structure and spectroscopy

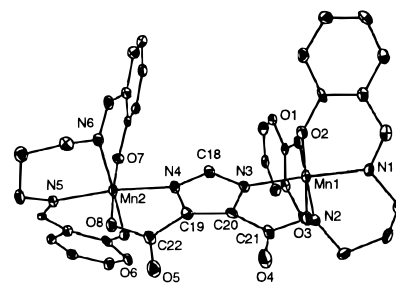


Figure 1. [Mn(IV)(dtbsalpn)]₂DCBI⁺ cation with *tert*-butyl groups removed from the 3,5-positions of the aromatic rings for clarity. Selected bond distances (Å) and angles (deg). Mn1–O1, 1.869(3); Mn1–O2, 1.849(3); Mn1–O3, 1.917(3); Mn1–N1, 1.981(3); Mn1–N2, 2.003(4); Mn1–N3, 1.994(3); Mn1···Mn1a, 6.18; O3–C21, 1.322(5); O4–C21, 1.221(5); Mn1–N3–C18, 140.3(3); Mn1–N3–C20, 112.1(3); O3–Mn1–N3, 81.6(1); Mn1–O3–C21, 119.3(3); O3–C21–C20, 111.7(4); N3–C20–C21, 114.8(4).

of the first imidazolate-bridged dimanganese(IV) complex that, due to its weak antiferromagnetic exchange coupling, exhibits a broad low-field EPR spectrum unprecedented in dimanganese(IV) complexes.

The cation [Mn(IV)(dtbsalpn)]DCBI⁺ ($H_2dtbsalpn = 1,3$ -bis((3,5-di-*tert*-butylsalicylidene)amino)propane, $H_3DCBI = 4,5$ -dicarboxyimidazole) was prepared by chemical or electrochemical oxidation of the dimanganese(III) precursor and crystallized as the hexafluorophosphate salt.¹² The ORTEP view (Figure 1) shows the cation with the *tert*-butyl groups at the 3,5-positions of the aromatic rings removed for clarity. The primary symmetry element is a single C_2 axis bisecting the imidazolate bridge and relating both of the manganese centers. There is one hexafluorophosphate anion per cation, and the overall structure is highly solvated, with three benzene and two acetonitrile molecules associated with each cation. The assignment of the cation as containing two manganese(IV) ions was confirmed by iodometric titration, which gave four oxidizing equivalents per cation. The short manganese–ligand bond lengths and highly octahedral ligand arrangement are consistent with a Mn(IV) center, with no evidence of an axial Jahn–Teller distortion characteristic of Mn(III) ions. Examination of the ligated carboxylate groups reveals distinct long (1.322 Å) and short (1.221 Å) C–O bond lengths, consistent with monodentate carboxylate coordination to an electron-poor metal center. The imidazole ring and the two Mn(IV) ions are coplanar with a Mn···Mn separation of 6.18 Å.

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(12) The preparation and characterization of the [Mn(III)(dtbsalpn)]₂HDCBI precursor will be detailed in a subsequent full paper. [Mn(III)(dtbsalpn)]₂HDCBI (1.5 g, 1.2 mmol) was slurried in 120 mL of distilled CH₃CN containing 0.10 M tetrabutylammonium hexafluorophosphate and was carefully reacted with 1 equiv of tetrabutylammonium hydroxide under anaerobic conditions. Bulk electrolysis of the solution at 500 mV vs Ag wire on a Pt gauze under N₂ sparging gave a dark green solution after passage of 230 C. The CH₃CN solvent was allowed to evaporate, and the green residue was extracted with CH₂Cl₂. Storage of the solution at –45 °C overnight gave 0.85 g (51% yield) of green microcrystalline [Mn(IV)(dtbsalpn)]₂DCBI·PF₆[–]. Anal. Found (calcd): C, 60.5 (60.1); H, 7.1 (7.0); N, 5.6 (5.9); Mn, 7.3 (7.8). IR: $\nu_{C=O}$ 1710 cm^{–1}, $\nu_{C=N}$ 1603 cm^{–1}. Visible: λ_{max} 682 nm, $\epsilon = 9500$ M^{–1} cm^{–1}. $\chi_m = 5.4 \mu_B$ (298 K). Vapor diffusion of benzene into an acetonitrile solution of [Mn(IV)(dtbsalpn)]₂DCBI⁺PF₆[–] yielded dark-green X-ray quality crystals with three benzene and two acetonitrile molecules of crystallization (Mn₂C₉₃F₆H₁₂₁N₈O₈P, orthorhombic, space group $P_{bc}a$, $a = 21.0211(3)$, $b = 26.8006(2)$, and $c = 32.6466(6)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 18392.4(4)$ Å³, $Z = 8$. X-ray diffraction data was collected on a Siemens SMART CCD diffractometer and refined with full-matrix least-squares on F^2 using 21 826 independent reflections ($R = 0.1188$, GOF = 1.179).

Plots of the temperature-dependent magnetic susceptibility (χ_m) and effective magnetic moment (μ_{eff}) are shown in Figure S2, Supporting Information. At room temperature, μ_{eff} is 5.4 μ_B per dimer, consistent with two weakly-coupled $S = 3/2$ ions in the high temperature limit. As the sample is cooled below 100 K, χ_m exhibits a maximum at 8.5 K and μ_{eff} continuously decreases to 1.4 μ_B at 2.5 K, consistent with weak antiferromagnetic coupling between the two Mn(IV) ions. Neglecting zero-field effects,¹³ the Heisenberg exchange Hamiltonian for this system is $H = -2J\mathbf{S}_i\cdot\mathbf{S}_j$. This yields four energy levels n having total spin quantum numbers $S_n = 0, 1, 2, 3$ with relative energies E_n of 0, $-2J$, $-6J$, and $-12J$. The temperature dependence of the molar susceptibility, χ_m , is then given by eq 1 where P_n is the spin degeneracy of each level. Fitting the temperature-dependent magnetic susceptibility data to this expression results in an excellent fit with J equal to -2.3 cm^{-1} and a g value of 1.98.

$$\chi_m = \sum P_n (Ng^2\beta^2/3kT) S_n(S_n + 1) e^{(-E_n/kT)} / \left(\sum P_n e^{(-E_n/kT)} \right) \quad (1)$$

While coupling in this system is substantial in light of the very long Mn...Mn separation, it is the smallest value for J yet reported for a dimanganese(IV) complex. Because all of the unpaired electrons in this complex are in the t_{2g} orbital set, the primary exchange pathway is likely to be through overlap of the t_{2g} orbitals with the aromatic π system of the deprotonated dicarboximidazolate group. In d^9 dicopper(II) imidazolate-bridged complexes,¹⁴ which possess a filled t_{2g} set and a single unpaired electron in the e_g set, the exchange is mediated primarily through σ orbital pathways, resulting in considerably larger J values (-20 to -80 cm^{-1}).

Because the ground state of an antiferromagnetically-coupled dimanganese(IV) dimer is $S = 0$, strong exchange gives rise to EPR-silent complexes. The fact that there are no prior examples of an EPR-active coupled dimanganese(IV)₂ system is consistent with this premise, though EPR signals have been observed in tetranuclear Mn(IV) clusters which should formally have an $S = 0$ ground state.¹⁵ However, in [Mn(IV)(dtbsalpn)]₂DCBI⁺, the weak exchange coupling allows for population of higher spin states at relatively low temperatures, resulting in observation of a number of EPR signals from integer-spin excited states.

The X-band EPR spectrum of [Mn(IV)(dtbsalpn)]₂DCBI⁺ is shown in Figure 2a. The complicated spectrum at 50 K is a result of the population of all three excited spin states ($S_n = 1, 2, 3$) at this temperature. While these integer spin states are non-Kramers states, the small zero-field splitting (ZFS) char-

(13) We have collected temperature-dependent magnetic susceptibility data for a mononuclear Mn(IV) complex with exactly the same ligand set and geometry as our dimanganese(IV) complex and explicitly determined the ZFS parameter $|D_{\text{mono}}| = 0.58 \text{ cm}^{-1}$. The ZFS for the monomer is nearly an order of magnitude smaller than the exchange splitting ($2J = -4.6 \text{ cm}^{-1}$) between the single and triplet. Under the approximation of minimal zero-field mixing between exchange coupled states, D_{mono} can be related to D_{dimer} via the familiar Judd–Owen equations. This gives estimates for D_{dimer} of $1.7D_{\text{mono}}$, $0.5D_{\text{mono}}$, and $0.3D_{\text{mono}}$ (0.99, 0.29, and 0.17 cm^{-1}) for the $S_T = 1, 2,$ and 3 states of the dimer. It is clear that only the triplet will possess an appreciable ZFS, which is still approximately five times smaller than the singlet–triplet exchange splitting. At 5.65 K, a temperature well below the turnover of the susceptibility, the differential population of the $|1, \pm 1\rangle$ and $|1, 0\rangle$ components of the triplet is $< 8\%$. This indicates that the ZFS has a small effect on the J determined for the dimer, especially since the susceptibility data has been collected over a wide temperature range where all of the exchange coupled states are eventually thermally populated.

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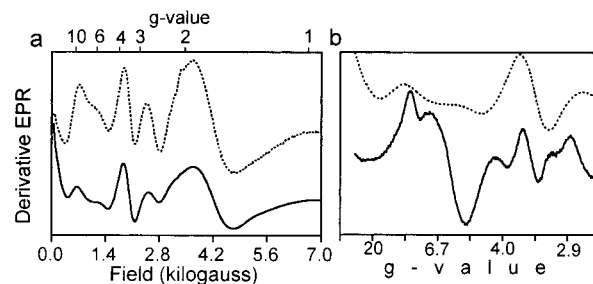


Figure 2. EPR spectra of [Mn(IV)(dtbsalpn)]₂DCBI⁺ in glassy butyronitrile solution: (a) X-band EPR spectra (9.45 GHz) were measured at 20 mW (no saturation) on a Bruker ER-200E spectrometer with a TE₁₀₂ cavity. Solid line = 5.5 K. Dashed line = 50 K. (b) Comparison of the low-field X-band and Q-band EPR spectra of [Mn(IV)(dtbsalpn)]₂DCBI⁺ at 5.5 K. Q-band EPR spectra were measured on a Bruker EMX spectrometer and Q-band helium cryostat. Solid line = Q-band (34.04 GHz). Dashed line = X-band (9.45 GHz).

acteristic of Mn(IV) allows observation of allowed $\Delta m_s = 1$ transitions. As the sample is cooled to 5.5 K, the zero-field feature of the spectrum becomes more intense at the expense of the other signals in the spectrum, indicating that this signal arises from either the $S = 1$ or $S = 2$ excited spin state. A complete assignment of the X-band EPR spectrum awaits further analysis. However, considerable information can be gleaned from the low-temperature Q-band spectrum. The low-field ($g \approx 10$) resonance strongly indicates that the ZFS of the excited triplet state is very close to the microwave quantum ($\sim 1.1 \text{ cm}^{-1}$). If this resonance is assigned as a transition between the $|1, -1\rangle$ and $|1, 0\rangle$ states (Happ along z) of the triplet, the calculated value for $|D_{S=1}|$ is $\sim 0.9 \text{ cm}^{-1}$, in excellent agreement with the 0.99 cm^{-1} splitting determined for the triplet from $|D_{\text{mono}}|$.¹³

Only recently has the dogma that biologically-relevant dimanganese(IV) complexes will be strongly antiferromagnetically coupled been challenged.¹⁶ Because the spin state of a tetranuclear complex with a formal $S = 0$ ground state is exquisitely sensitive to the relative magnitudes of individual exchange couplings,^{15,17} it is important to understand the relationship between structural motifs and magnetic interactions if we seek to fully understand the electronic structure of the OEC. The complex reported herein demonstrates that dimanganese(IV) complexes can exhibit extremely weak antiferromagnetic exchange through a structural motif established to be biologically relevant. As a consequence of this weak coupling, low-field temperature-dependent EPR signals consistent with the population of EPR-active higher spin states can be observed even at temperatures as low as 5.5 K. In future studies, we will explore the magnetic exchange and spectroscopic signatures of these fascinating binuclear complexes in other biologically relevant oxidation levels.

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Supporting Information Available: Crystallographic data for [Mn(IV)(dtbsalpn)]₂DCBI⁺PF₆⁻ including tables of positional and thermal parameters, an ORTEP drawing with full numbering scheme, and details of crystallographic data collection and refinement and Figure S2 showing the temperature-dependent magnetic susceptibility for [Mn(IV)(dtbsalpn)]₂DCBI⁺PF₆⁻ (15 pages). See any current masthead page for ordering and Internet access instructions.

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