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Geometric and Electronic Structure of a Peroxomanganese(III) Complex Supported by a Scorpionate Ligand

Hannah E. Colmer, Robert A. Geiger, Domenick F. Leto, Gayan B. Wijeratne, Victor W. Day and Timothy A. Jackson*

Abstract. A monomeric Mn\textsuperscript{II} complex has been prepared with the facially-coordinating Tp\textsuperscript{Ph2} ligand, (Tp\textsuperscript{Ph2} = hydrotris(3,5-diphenylpyrazol-1-yl)borate). The X-ray crystal structure shows three coordinating solvent molecules resulting in a six-coordinate complex with Mn-ligand bond lengths that are consistent with a high-spin Mn\textsuperscript{II} ion. Treatment of this Mn\textsuperscript{II} complex with excess KO\textsubscript{2} at room temperature resulted in the formation of a Mn\textsuperscript{III}O\textsubscript{2} complex that is stable for several days at ambient conditions, allowing for the determination of the X-ray crystal structure of this intermediate. The electronic structure of this peroxomanganese(III) adduct was examined by using electronic absorption, electron paramagnetic resonance (EPR), low-temperature magnetic circular dichroism (MCD), and variable-temperature variable-field (VT/VH) MCD spectroscopies. Density functional theory (DFT), time-dependent (TD)-DFT, and multireference \textit{ab initio} CASSCF/NEVPT2 calculations were used to assign the electronic transitions and further investigate the electronic structure of the peroxomanganese(III) species. The lowest ligand-field transition in the electronic absorption spectrum of the Mn\textsuperscript{III}-O\textsubscript{2} complex exhibits a blue shift in energy compared to other previously characterized peroxomanganese(III) complexes that results from a large axial bond elongation, reducing the metal-ligand covalency and stabilizing the \sigma-antibonding Mn d\textsuperscript{2} MO that is the donor MO for this transition.

Introduction

Mononuclear peroxomanganese(III) species have been proposed to form in manganese-containing enzymes, including manganese superoxide dismutase (MnSOD),\textsuperscript{1-6} manganese-dependent homoprotocatechuate 2,3-dioxygenase (MndD),\textsuperscript{7,8} and the oxalate-degrading enzymes oxalate oxidase\textsuperscript{9,10} and oxalate decarboxylase.\textsuperscript{11-13} These biological peroxomanganese(III) species are highly unstable and relatively little is known concerning their structural and electronic properties. In contrast, a variety of synthetic peroxomanganese(III) species have been generated and characterized, offering insights into the structural, electronic, and reactivity properties of this class of compound.\textsuperscript{14-27} Members of this class of compound include side-on peroxomanganese(III) adducts (Mn\textsuperscript{III}-O\textsubscript{2}) and end-on alkylperoxomanganese(III) adducts (Mn\textsuperscript{III}-OOR).\textsuperscript{28,29}

While there are several examples of Mn\textsuperscript{III}-O\textsubscript{2} complexes with anionic supporting ligands,\textsuperscript{14,22,25,30} there are no detailed bonding descriptions of such complexes. As many enzymatic Mn\textsuperscript{III}-O\textsubscript{2} adducts are expected to feature anionic ligands, this represents a gap in knowledge. In addition, the electronic structures of crystallographically characterized Mn\textsuperscript{III}-O\textsubscript{2} adducts have not generally been explored in detail.\textsuperscript{30}

A mononuclear Mn\textsuperscript{III}-O\textsubscript{2} complex supported by the monoanionic facially-coordinating trispyrazolyl Tp\textsuperscript{Ph2} ligand (Tp\textsuperscript{Ph2} = hydrotris(3,5-diisopropylpyrazol-1-yl)borate) and an ancillary, monodentate 3,5-isopropylpyrazole (pz\textsuperscript{H}) ligand was previously reported to be stable at room temperature for a few hours.\textsuperscript{22} It was observed that the peroxo ligand in this Mn\textsuperscript{III}(O\textsubscript{2})(Tp\textsuperscript{Ph2})(pz\textsuperscript{H}) complex is bound to the Mn\textsuperscript{III} ion in a side-on (\eta\textsuperscript{2}) fashion, and the coordination sphere is completed by four N-donors from the Tp\textsuperscript{Ph2} ligand and the monodentate pz\textsuperscript{H} ligand. When this Mn\textsuperscript{III}-O\textsubscript{2} complex was cooled from 253 to 193 K, the pz\textsuperscript{H} ligand formed a hydrogen bond with one O atom of the peroxo unit, and this changed the absorption spectrum.\textsuperscript{22,27} Specifically, the absorption maxima shifted from 561 to 583 nm (17 820 to 17 150 cm\textsuperscript{-1}) causing the color of the complex to change from brown (at 253 K) to blue (at 193 K). In contrast, the frequency of the peroxo O-O vibration (v\textsubscript{O-O}), was not perturbed at all by this hydrogen bonding interaction. The absence of a shift in v\textsubscript{O-O} is surprising, but consistent with the statistically identical O-O bond lengths of the blue and brown isomers (1.43(1) and 1.428(7), respectively).\textsuperscript{22} A slightly higher-energy v\textsubscript{O-O} frequency of 896 cm\textsuperscript{-1} was observed for the related complex [Mn\textsuperscript{III}(O\textsubscript{2})(Tp)(Me-Im)], which displays an intermolecular hydrogen-bond in the solid-state crystal structure (O-O of 1.42(1) Å).\textsuperscript{22}

In a recent review,\textsuperscript{23} we noted that Mn\textsuperscript{III}-O\textsubscript{2} adducts supported by the Tp\textsuperscript{Ph2} ligand\textsuperscript{22,27} represent a unique geometry compared to other mononuclear Mn\textsuperscript{III}-O\textsubscript{2} adducts. Following a formalism proposed by Kitajima \textit{et al.},\textsuperscript{22} if the peroxo unit is viewed as a monoligand, the \tau parameter, as defined in Scheme 1, may be used to classify Mn\textsuperscript{III}-O\textsubscript{2} adducts along a spectrum of geometries from square pyramidal (\tau = 0) to trigonal bipyramidal (\tau = 1).\textsuperscript{22,31} In contrast, crystallographically-characterized mononuclear Mn\textsuperscript{III}-O\textsubscript{2} adducts supported by tetramethylcyclohexyl (TMC) and its derivatives (Scheme 1) show \tau parameters from 0 to 0.52, with the variation reflecting the size of the macrocyclic ring.\textsuperscript{14,21,24}

The Tp-supported Mn\textsuperscript{III}-O\textsubscript{2} adducts also appear distinct from...
other mononuclear Mn\(\text{II}\)-O \(_2\) species in terms of their electronic absorption properties, and this could be related to differences in geometric structure. While the blue and brown isomers of [Mn\(\text{II}\)(O\(_2\))(Tp\(\text{ph}_{\text{2}}\))(pz\(\text{ph}_{\text{2}}\)H)] show only very weak absorption features at \(\sim 560 - 580\) nm, Mn\(\text{III}\)-O\(_2\) adducts supported by a variety of neutral N\(_2\) ligands show moderately intense absorption bands from \(415 - 450\) nm (\(\varepsilon \approx 250 - 500\) M\(^{-1}\) cm\(^{-1}\)), with lower-intensity features at \(\sim 590 - 620\) nm.\(^{\text{25}}\) However, a complication in this comparison is that, while the onset of more intense features at wavelengths lower than 450 nm are apparent in the published electronic absorption spectra of [Mn\(\text{II}\)(O\(_2\))(Tp\(\text{ph}_{\text{2}}\))(pz\(\text{ph}_{\text{2}}\)H)], no absorption maxima were reported.

On the basis of these considerations, we investigated whether a Mn\(\text{III}\)-O\(_2\) unit could be supported by the related, but synthetically more accessible, Tp\(\text{ph}_{\text{2}}\) ligand (Scheme 1) in order to more fully understand the spectroscopic properties of a Tp-supported Mn\(\text{III}\)-O\(_2\) adduct and determine the consequences of the pseudo-trigonal bipyramidal geometry. Herein, we describe the synthesis, structural, and spectroscopic characterization of [Mn\(\text{III}\)(O\(_2\))(Tp\(\text{ph}_{\text{2}}\))(THF)], which is formed by treatment of the corresponding Mn\(^{\text{II}}\) complex with excess KO\(_2\). An X-ray diffraction (XRD) structure of [Mn\(\text{III}\)(O\(_2\))(Tp\(\text{ph}_{\text{2}}\))(THF)] reveals a mononuclear Mn\(\text{III}\)-O\(_2\) unit with the bulky phenyl groups shielding the peroxo ligand.

![Scheme 1. Representative Mn\(\text{III}\)-O\(_2\) with calculation of \(\tau\) (left), Tp type ligands (middle), and TMC type ligands (right).](image)

Electronic absorption, electron paramagnetic resonance (EPR), magnetic circular dichroism (MCD) and variable-temperature, variable-field (VTVH) MCD spectroscopies are used to determine ground-state zero-field splitting parameters and electronic transition energies for this complex. The spin-allowed \(d-d\) transitions of [Mn\(\text{III}\)(O\(_2\))(Tp\(\text{ph}_{\text{2}}\))(THF)], which are highly sensitive to the coordination sphere of the Mn\(\text{III}\) center, are found to be blue shifted in energy compared to those of other peroxomanganese(III) complexes. The electronic structure causing this perturbation was further investigated using density functional theory (DFT) and multi-reference \textit{ab initio} computations. Previously, spectroscopic changes in some Mn\(\text{III}\)-O\(_2\) complexes have been attributed to variations in the Mn-O\(_{\text{peroxo}}\) bond lengths;\(^{\text{16,32}}\) however, as the Mn-O\(_{\text{peroxo}}\) bond lengths of [Mn\(\text{III}\)(O\(_2\))(Tp\(\text{ph}_{\text{2}}\))(THF)] are within the range studied, they cannot account for the large spectroscopic perturbation observed. The combined spectroscopic and computational analysis presented here reveals that, for this system, ligand perturbations perpendicular to the Mn\(\text{III}\)-O\(_2\) unit can account for spectral differences. This work thus expands upon our previous investigations aiming at defining structural origins of spectral variations in peroxomanganese(III) complexes.\(^{\text{16,18,23,32}}\)

### Experimental

#### Materials

All chemicals and solvents were obtained from commercial vendors at ACS reagent-grade or better and were used without further purification. Synthesis of the Mn\(^{\text{II}}\) complex was carried out under argon using a glovebox.

#### Instrumentation

\(^{1}\)H NMR spectra were obtained on a Bruker DRX 400 MHz NMR spectrometer. Electronic absorption spectra were recorded on a Cary 50 Bio spectrophotometer (Varian) interfaced with a Unisoku cryostat (USP-203-A). ESI-mass spectrometry experiments were performed using an LCT Prims MicroMass electrospray-ionization time-of-flight instrument. EPR spectra were collected on Bruker EMXPlus instrument with a dual mode cavity. Magnetic circular dichroism (MCD) spectra were collected on a spectropolarimeter (Jasco J-815) interfaced with a magnetocryostat (Oxford Instruments SM-4000-8) capable of horizontal fields up to 8 T.

#### Preparation of [Mn\(\text{III}\)(Tp\(\text{ph}_{\text{2}}\))(DMF)](OTf)

Potassium tris(3,5-diphenylpyrazol)hydroborate (Tp\(\text{ph}_{\text{2}}\)) was prepared as previously described by condensing 3 molar equivalents of 3,5-diphenylpyrazole with KBH\(_4\).\(^{\text{33,34}}\) Mn(O\(_2\))(OTf)\(_2\) was prepared by a previously reported procedure by reacting 3,5-diphenylpyrazole with KBH\(_4\). An X-ray diffraction (XRD) structure of [Mn\(\text{II}\)(O\(_2\))(Tp\(\text{ph}_{\text{2}}\))(DMF)] reveals a mononuclear Mn\(\text{III}\)-O\(_2\) unit with the bulky phenyl groups shielding the peroxo ligand. The [Mn\(\text{III}\)(Tp\(\text{ph}_{\text{2}}\))(DMF)](OTf) complex was prepared by adding Tp\(\text{ph}_{\text{2}}\) (1.0 g, 1.411 mmol) in 30 mL DMF to a stirred solution of Mn(O\(_2\))(OTf)\(_2\) (0.497 g, 1.411 mmol) in 20 mL of DMF. The colorless solution was stirred for 4 hours. Precipitation of the crude product was obtained by addition of diethyl ether. [Mn\(\text{III}\)(Tp\(\text{ph}_{\text{2}}\))(DMF)](OTf) (1.39 g, 90%) \(M^*([\text{[Mn(Tp\text{ph}_{\text{2}})]}^+])^\text{246}\) 724.2; requires \(M^*\), 724.2.

#### In Situ Preparation of [Mn\(\text{III}\)(O\(_2\))(Tp\(\text{ph}_{\text{2}}\))(THF)] Complex

The yellow peroxomanganese(III) intermediate was formed by treating a THF solution of [Mn\(\text{III}\)(Tp\(\text{ph}_{\text{2}}\))(DMF)](OTf) with a KO\(_2\) slurry at ambient conditions. To optimize formation of the peroxomanganese(III) species, the slurry was prepared by stirring 25 equivalents of KO\(_2\) in a 50:50 mixture of 2-Me-tetrahydrofuran:THF for 20 minutes. Treatment with smaller amounts of KO\(_2\) resulted in lower yields of the Mn\(\text{III}\)-O\(_2\) species. 50 \(\mu\)L of the KO\(_2\) slurry was added to the [Mn\(\text{III}\)(Tp\(\text{ph}_{\text{2}}\))(DMF)](OTf) solution and stirred for 3 minutes, forming a brown precipitate. A second addition of 50 \(\mu\)L of the KO\(_2\) slurry was added and the solution was stirred for 15 minutes. The brown precipitate was filtered, a second addition of 50 \(\mu\)L of the KO\(_2\) slurry was added and the solution was stirred for 15 minutes. The brown precipitate was filtered from the solution, and a yellow solution was obtained. The peroxomanganese(III) intermediate was isolated by removing the solvent under vacuum and washing the solid residue with toluene to remove unreacted [Mn\(\text{III}\)(Tp\(\text{ph}_{\text{2}}\))(DMF)](OTf).

#### X-ray Crystallography

Single needle crystals of [Mn\(\text{III}\)(Tp\(\text{ph}_{\text{2}}\))(DMF)](OTf) were grown
by layering heptane on a THF solution of the metal complex at ambient temperature. Single needle crystals of [Mn(III)(O)(TPp^III)(THF)] were grown by vapor diffusion of diethyl ether into a 50:50 mixture of 2-Me-tetrahydrofuran:THF at -20 °C.

Diffracted intensities were measured for [Mn(III)(TPp^III)(DMF)][(OTf)] and [Mn(III)(O)(TPp^III)(THF)] using monochromated Cu-Kα radiation (λ = 1.54178) on a Bruker SHELXTL Version 6.10 software package. Kα Brilliance multilayer X-ray optics, an APEX II CCD detector, and a Bruker SAINT software package. The Bruker software package SHELXTL was used to solve the structure using “direct methods” techniques. All states of weighted full-matrix least-squares refinement were conducted using F_w^2 data with the SHELXTL Version 6.10 software package. Crystal data for [Mn(II)(TPp^II)(DMF)][(OTf)] and [Mn(II)(O)(TPp^II)(THF)] are supplied in Table 1, and full data collection and refinement parameters are summarized in the Electronic Supplementary Information (ESI) in Tables S1 and S2.

| Table 1. Crystal data for [Mn(TPp^II)(DMF)][(OTf)] (C_{36}H_{46}BF:MN_{12}O_{5}S) and [Mn(II)(O)(TPp^II)(THF)] (C_{54}H_{48}BN_{12}O_{5}S) |
|----------------------------------|----------------------------------|
| formula                         | CsCl cell monoclinic             |
| MW                              | 1164.99                         |
| T, K                            | 100(2)                          |
| unit cell                       | monoclinic                      |
| a, Å                            | 17.6441(10)                     |
| b, Å                            | 14.8052(8)                      |
| c, Å                            | 21.9441(11)                     |
| V, Å³                           | 5723.2(5)                       |
| Z                               | 4                               |
| d(calc), g/cm³                  | 1.352                           |
| space group                     | P2(1) / n                       |
| R                               | 0.0638                          |
| R_e                             | 0.1649                          |
| GOF                             | 0.928                           |

R = \sum ||F_o|| - |F_o| / \sum |F_o|
R_e = \{ \sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)] \}^{1/2}

EPR Experiments

A frozen sample of [Mn(III)(TPp^II)(DMF)][(OTf)] (250 µm) was prepared in THF at ambient temperature and flash-frozen in a quartz EPR tube in liquid N_2. Collection of EPR data in the same solvent as MCD experiments (75:25 mixture of 2-Me-tetrahydrofuran:THF, vide infra) was unsuccessful due to the propensity of this solvent system to partially melt during transfer of the EPR tube from the liquid nitrogen storage dewar to the EPR cryostat, resulting in shattered EPR tubes. An EPR sample of [Mn(II)(O)(TPp^II)(THF)] was prepared after filtering the brown precipitate from the yellow solution and confirming the characteristic spectrum of this complex by UV-visible spectroscopy. Frozen samples of [Mn(III)(O)(TPp^II)(THF)] (250 µm), prepared using both the crude yellow residue and the purified residue obtained through a toluene wash, were prepared in THF at ambient temperature and flash-frozen in quartz EPR tubes in liquid N_2. All data were collected on an X-band (9 GHz) Bruker EMX Plus spectrophotometer with an Oxford ESR900 continuous-flow liquid helium cryostat and an Oxford ITC503 temperature system to regulate the temperature. To collect perpendicular and parallel-mode spectra, a Bruker ER4116DM dual-mode cavity was used. Spectra were collected under non-saturated conditions with 9.3918 GHz microwave frequency, 20 dB microwave power, 0.6 mT modulation amplitude, 100 kHz modulation frequency and 163 ms time constant. The Matlab-based EPR simulation software package EasySpin, developed by Stoll, was used to simulate and fit all EPR spectra and determine zero-field splitting parameters of the peroxomanganate(III) complex.

Magnetic Circular Dichroism Experiments

A frozen glass sample of [Mn(III)(TPp^II)(THF)] (15 mM) was prepared in 75:25 mixture of 2-Me-tetrahydrofuran:THF at ambient temperature, transferred to MCD cells, and flash-frozen in liquid N_2. The obtained MCD spectra were measured in mdeg (θ) and converted to Δg (M^(-1) cm^(-1)) using the standard conversion factor Δg = 0.3290 c-d, where c is the concentration of the sample and d is the path length. MCD spectra were collected at 2, 4, 8, and 15 K for positive and negative field strengths of 1 to 7 T in 1 T increments. VTHV data were fit using the general method developed by Neese and Solomon. Fits were performed for an S = 2 system with isotropic g-values of 2.00. Using a previously described protocol, zero-field splitting (ZFS) parameters D and E/D were systematically varied while the transition moment products were optimized for a given set of ZFS parameters. The goodness of fit was evaluated by the χ^2 factor; where χ^2 is the sum of the squares of the differences between experimental and fit data sets.

X-ray Absorption Spectroscopy

The [Mn(II)(TPp^II)(DMF)][(OTf)] XAS sample was prepared as a 4% (w/w) dispersion by grinding 8 mg of [Mn(II)(TPp^II)(DMF)][(OTf)] with 192 mg boron nitride into a powder with a mortar and pestle. Solution phase XAS samples of [Mn(II)(O)(TPp^II)(THF)] were prepared by several methods and then transferred to XAS sample holders and flash frozen in liquid N_2. Methods of solution preparation included: 15 mM [Mn(II)(O)(TPp^II)(THF)] in 50:50 2-Me-tetrahydrofuran:THF, 5 mM [Mn(II)(O)(TPp^II)(THF)] in THF, and 15 mM [Mn(II)(O)(TPp^II)(THF)] in THF with isolation by toluene wash. All attempts at XAS data collection for [Mn(II)(O)(TPp^II)(THF)] were thwarted by photoreduction or sample degradation. XAS spectra were recorded on beamline X3B at the National Synchrotron Light Source (NSLS), Brookhaven National Lab (storage ring conditions, 2.8 GeV, 100 - 300 mA). Mn K-edge X-ray absorption spectra over the energy range 6.4 – 7.4 keV (Si(111) monochromer) were recorded on a powder sample maintained at 20 K with a helium Displex closed-cycle cryostat. XAS spectra were obtained as fluorescence excitation spectra using a solid-state 13-element germanium detector (Canberra). Contamination of higher harmonics radiation was minimized with a harmonic rejection mirror. Background fluorescence signal was
Density Functional Theory Calculations

The ORCA 3.0.1 software package was used for all DFT computations. An initial model of [Mn\textsuperscript{III}(O\textsubscript{2})(T\textsubscript{p}\textsuperscript{Ph\textsubscript{2}})](OTf) was built using the X-ray coordinates obtained in this work. Models were generated using the gOpenMol program using isodensity surfaces. The Mn\textsuperscript{III} species supported by Tp-based ligands. Specifically, the Mn-N pyrazole bond lengths of [Mn\textsuperscript{III}(T\textsubscript{p}\textsuperscript{Ph\textsubscript{2}})(DMF\textsubscript{3}))(OTf) and other mononuclear Mn\textsuperscript{III} complexes fall within the range of 2.149(2) to 2.319(1) Å (Table 3). Figure 1 (right) displays a view along the three-fold axis of the space filling model for [Mn\textsuperscript{III}(T\textsubscript{p}\textsuperscript{Ph\textsubscript{2}})(DMF\textsubscript{3}))(OTf) without the coordinated solvent molecules. This perspective highlights the

Figure 1. ORTEP diagram of [Mn\textsuperscript{III}(T\textsubscript{p}\textsuperscript{Ph\textsubscript{2}})(DMF\textsubscript{3}))(OTf) (left) and space filling model (right). For the ORTEP diagram, hydrogen atoms and the counter anion have been removed for clarity. For the space filling model, hydrogen atoms, coordinating solvents molecules, and the counter anion have been removed for clarity. The significant interatomic distances and angles are listed in Table 2.

Results and Discussion

Structural properties of [Mn\textsuperscript{III}(T\textsubscript{p}\textsuperscript{Ph\textsubscript{2}})(DMF\textsubscript{3}))(OTf)

The Mn\textsuperscript{III} complex [Mn\textsuperscript{III}(T\textsubscript{p}\textsuperscript{Ph\textsubscript{2}})(DMF\textsubscript{3}))(OTf)] was generated by treatment of Mn(OTf)\textsubscript{3} with Tp\textsuperscript{Ph\textsubscript{2}} in dimethylformamide (DMF). Diffraction quality crystals were obtained by vapour diffusion of diethyl ether into the DMF solution of [Mn\textsuperscript{III}(T\textsubscript{p}\textsuperscript{Ph\textsubscript{2}})(DMF\textsubscript{3}))(OTf). Figure 1 (left) displays an ORTEP diagram for [Mn\textsuperscript{III}(T\textsubscript{p}\textsuperscript{Ph\textsubscript{2}})(DMF\textsubscript{3}))(OTf). Selected bond distances and angles are given in Table 2. The tridentate Tp\textsuperscript{Ph\textsubscript{2}} ligand is bound facially, creating three coordination sites occupied by DMF ligands that complete the coordination sphere to give a six-coordinate Mn\textsuperscript{III} ion in a distorted octahedral geometry. The Mn-ligand bond lengths range from ~2.14 to 2.32 Å, typical of a high-spin Mn\textsuperscript{III} ion, and also consistent with reports of previously characterized Mn\textsuperscript{III} species supported by Tp-based ligands. Specifically, the Mn-N pyrazole bond lengths of [Mn\textsuperscript{III}(T\textsubscript{p}\textsuperscript{Ph\textsubscript{2}})(DMF\textsubscript{3}))(OTf) and other mononuclear Mn\textsuperscript{III} complexes fall within the range of 2.149(2) to 2.319(1) Å (Table 3).
Table 2. Selected bond lengths (Å) and angles (°) for [Mn\(^{III}\)(Tp\(^{Ph3}\))(DMF)](OTf).

<table>
<thead>
<tr>
<th>Manganese-Nitrogen</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-N(1)</td>
<td>2.286(1)</td>
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<tr>
<td>Mn-N(2)</td>
<td>2.250(3)</td>
</tr>
<tr>
<td>Mn-N(3)</td>
<td>2.250(1)</td>
</tr>
<tr>
<td>Mn-O(1)</td>
<td>2.193(5)</td>
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<tr>
<td>Mn-O(2)</td>
<td>2.141(6)</td>
</tr>
<tr>
<td>Mn-O(3)</td>
<td>2.191(1)</td>
</tr>
<tr>
<td>N(1)-Mn-O(3)</td>
<td>169.1(5)</td>
</tr>
<tr>
<td>N(2)-Mn-O(2)</td>
<td>172.0(2)</td>
</tr>
<tr>
<td>N(3)-Mn-O(1)</td>
<td>171.6(2)</td>
</tr>
</tbody>
</table>

Table 3. Mn-N\(_{pyrazole}\) bond lengths (Å) for [Mn\(^{III}\)(Tp\(^{Ph5}\))(DMF)](OTf) and other Mn\(^{III}\)(Tp) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mn-N(1)</th>
<th>Mn-N(2)</th>
<th>Mn-N(3)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
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<td>2.280(1)</td>
<td>2.250(3)</td>
<td>2.250(1)</td>
<td>This work</td>
</tr>
<tr>
<td><a href="ClO$_4$">Mn(Tp(^{Ph3})$_2$(H$_2$O)</a></td>
<td>2.254(4)</td>
<td>2.273(4)</td>
<td>2.307(4)</td>
<td>56</td>
</tr>
<tr>
<td>[Mn(OAc)(Tp(^{Ph3}))(pz$_2$Ph$_2$H)]</td>
<td>2.199(2)</td>
<td>2.282(2)</td>
<td>2.149(2)</td>
<td>37</td>
</tr>
<tr>
<td>[Mn(Cl)(Tp(^{Ph3}))(pz$_2$Ph$_2$H)]</td>
<td>2.151(2)</td>
<td>2.164(2)</td>
<td>2.243(2)</td>
<td>37</td>
</tr>
</tbody>
</table>

Figure 2. Electronic absorption spectra of [Mn\(^{III}\)(Tp\(^{Ph3}\))(DMF)](OTf) (black dashed trace) and the yellow intermediate, [Mn\(^{III}\)(O$_2$)(Tp\(^{Ph3}\))(THF)], (solid blue trace) at 298 K in THF.

Figure 3. ORTEP diagram of [Mn\(^{III}\)(O$_2$)(Tp\(^{Ph5}\))(THF)] (left) and space filling models (right). For the ORTEP diagram, hydrogen atoms have been removed for clarity. Select interatomic distances and angles are listed in Table 4.

The yellow intermediate is a peroxo manganese(III) adduct. Unlike the low-energy absorption band of the [Mn\(^{III}\)(O$_2$)(Tp\(^{Ph5}\))(pz$_2$Ph$_2$H)] complex that red-shifts and increases in intensity upon cooling from 253 to 193 K, the absorption bands of the yellow intermediate sharpen and show a slight blue-shift (~100 cm\(^{-1}\)) and increase in intensity (~17 % for the intense band at 26 320 cm\(^{-1}\)) when a 75:25 mixture of 2-Me-tetrahydrofuran:THF solution of the sample is cooled from 300 to 200 K (ESI Figure S1).

X-ray Diffraction Structure of the yellow intermediate: [Mn\(^{III}\)(O$_2$)(Tp\(^{Ph5}\))(THF)]

Because of the high thermal stability of the yellow intermediate (t$_{1/2}$ ≈ 4.5 days in THF), we were able to obtain single crystals suitable for XRD experiments. The XRD structure of the yellow needle crystals revealed a neutral mononuclear six-coordinate Mn\(^{III}\) complex with a side-on peroxo ligand and a coordinated THF molecule, [Mn\(^{III}\)(O$_2$)(Tp\(^{Ph5}\))(THF)] (Figure 3). Selected bond distances and angles are given in Table 4. The Mn\(^{III}\) ion is in a distorted octahedral geometry with an axial elongation along the (THF)O-Mn-N(1) axis (bond lengths of 2.313(7) Å and 2.375(2) Å, respectively). Here, the peroxo ligand and the N2 and N3 atoms of the Tp\(^{Ph5}\) ligand define the equatorial plane. The other Mn-N bond distances are nearly identical, with Mn-N(2) and Mn-N(3) bond lengths of 2.09 Å. The peroxo ligand is nearly symmetrically bound to the Mn\(^{III}\) ion with Mn-O distances of 1.865(2) and 1.859(2). The O-O bond length is 1.432(3) Å, which is typical of a peroxo ligand bound to a transition-metal ion and is in good agreement with other reported Mn\(^{III}\)-O$_2$ complexes (Table 2). Considering the peroxo as a monoligand, a τ parameter of 1.2 is obtained, indicating that this complex is at the open face of the metal ion that is shielded by the phenyl groups of the supporting ligand.

Conversion of [Mn\(^{III}\)(Tp\(^{Ph5}\))(DMF)](OTf) to [Mn\(^{III}\)(O$_2$)(Tp\(^{Ph5}\))(THF)]

No intense features are observed in the electronic absorption spectra of tetrahydrofuran (THF) solutions of [Mn\(^{III}\)(Tp\(^{Ph5}\))(DMF)](OTf) at energies below 33 000 cm\(^{-1}\) (Figure 2; dashed line). A weak feature is observed at ~28 000 cm\(^{-1}\) (ε = 20 M\(^{-1}\) cm\(^{-1}\)) that could arise from a Mn\(^{III}\)-to-ligand (Tp\(^{Ph5}\)) charge-transfer (CT) transition. While the intensity is very low for a CT feature, the intensity of this band is at least an order of magnitude larger than that expected for a spin-forbidden Mn\(^{III}\) ligand-field transition.

Treatment of [Mn\(^{III}\)(Tp\(^{Ph5}\))(DMF)](OTf) with excess K$_2$O at room temperature results in the formation of a yellow intermediate and a brown precipitate. After filtering the brown precipitate from the solution to obtain the yellow intermediate, new absorption features are present in the visible region. The absorption spectra of the yellow intermediate is characterized by a prominent band at 26 385 cm\(^{-1}\) and a weaker, broader band at 22 936 cm\(^{-1}\) (ε = 324 and 73 M\(^{-1}\) cm\(^{-1}\), respectively). For the previously reported [Mn\(^{III}\)(O$_2$)(Tp\(^{Ph5}\))(pz$_2$Ph$_2$H)] complex, a weak, broad band was observed at 17 800 cm\(^{-1}\) which shifted to 17 150 cm\(^{-1}\) when a pyrazole-peroxo hydrogen bond was formed. More intense features were apparent at higher energy, but no band maxima were reported. The extinction coefficient for the ~17 000 cm\(^{-1}\) transition of [Mn\(^{III}\)(O$_2$)(Tp\(^{Ph5}\))(pz$_2$Ph$_2$H)] (~50 M\(^{-1}\) cm\(^{-1}\)) is similar to that of the lowest-energy band of the yellow intermediate. Thus, these data are supportive of the formulation of the yellow intermediate as a peroxomanganese(III) adduct.
removing the solvent under vacuum and washing with toluene further decreased the intensity at 4.1 is present with hyperfine splitting of 9.1 mT, indicative of the O atom of the THF ligand (O(3)) refers to the O atom of the THF ligand.

**EPR Experiments**

X-band EPR spectra were collected for frozen solutions of [Mn(II)(TP)(DMF)][OTf] and [Mn(II)(TP)(THF)] at 5 K in perpendicular and parallel mode. In perpendicular mode, a THF solution of [Mn(II)(TP)(DMF)][OTf] exhibits a 6-line signal at \( g_1 = 2.03 \) with hyperfine splitting of 9.1 mT, indicative of mononuclear Mn(II) (Figure 4, left; black trace). Additionally, a weaker feature at \( g_2 = 4.1 \) is present with hyperfine splitting of 7.9 mT. Upon the treatment of this solution with an excess of KO \(_2\), we were unable to collect reliable IR data for solution samples of [Mn(II)(TP)(THF)].

Further Spectroscopic Characterization of [Mn(II)(O)(TP)(THF)]

IR data collected for a KBr pellet of [Mn(II)(O)(TP)(THF)] show a weak feature at 882 cm\(^{-1}\) (ESI, Figure S4) which is in the expected region for an O-O vibration of a mononuclear Mn(II)-O adduct (\( \nu_{O-O} = 875 - 896 \) cm\(^{-1}\)).

To gain additional insights into the ground- and excited-state properties of [Mn(II)(O)(TP)(THF)], we collected low-temperature MCD and VTVH MCD data. All MCD signals of [Mn(II)(O)(TP)(THF)] observed from 15 000 to 32 000 cm\(^{-1}\) show C-term behavior (i.e., their intensities show an inverse temperature dependence; see ESI Figure S5). Figure 5 (bottom) shows the 2 K, 7 T MCD spectra of [Mn(II)(O)(TP)(THF)]. The corresponding 298 K electronic absorption spectrum is included for comparison (Figure 5, top). In the absorption spectrum, [Mn(II)(O)(TP)(THF)] shows low-intensity features from \( \approx 1800 - 24 000 \) cm\(^{-1}\) with a slight maximum at 22 900 cm\(^{-1}\). This fairly indistinct region of the absorption spectrum corresponds to a set of MCD features at \( \approx 19000 \) (-), \( \approx 22000 \) (+), \( \approx 23500 \) (-, shoulder), and \( \approx 24100 \) (-) cm\(^{-1}\). The major absorption band at 26 320 cm\(^{-1}\) corresponds to an intense, positively-signed MCD band at roughly the same energy (26 200 cm\(^{-1}\)). An iterative Gaussian deconvolution of the absorption and MCD spectra reveals a total of nine electronic transitions from 16 500 to 31 000 cm\(^{-1}\) (ESI, Table S9). Tentative assignments can be made for these transitions on the basis of the different selection rules for electronic absorption and MCD spectroscopy, as well as previous spectral analysis of mononuclear Mn(II)-O adducts. More detailed band assignments developed using TD-DFT computations are discussed later. Bands 2, 8, and 9, which are fairly prominent in the absorption spectrum but carry comparatively little MCD intensity are assigned as peroxo-tomanganese(III) CT transitions (Table 5). Bands 4 and 6, which exhibit very narrow bandwidths in the MCD spectrum and carry the EPR signal.

Further Spectroscopic Characterization of [Mn(II)(O)(TP)(THF)]
essentially negligible absorption intensity, are assigned as spin-forbidden Mn$^{III}$ d-d transitions (Table 5). The narrow widths of these transitions are indicative of small excited state distortions.

Figure 5. 298 K electronic absorption (top) and 2 K, 7 T MCD (bottom) spectra of [Mn$^{III}$(O$_2$)(Tp$^{Ph_2}$)(THF)]. Inset: An 15-fold enhancement of the 2 K, 7 T MCD spectra from 17 500 to 25 000 cm$^{-1}$. Individual Gaussian curves (black dotted lines) and their sums (red dashed lines) obtained from iterative fits of these data sets are displayed on their respective spectra. Only Gaussian bands 1 – 4 are shown in the inset. Conditions: Absorption data were collected for a 2.5 mM sample in THF. MCD data were collected for a 15 mM frozen glass sample in 75:25 solution of 2-Me-THF:THF.

Table 5. MCD, electronic absorption, calculated TD-DFT, and NEVPT2 electronic transition energies (cm$^{-1}$) of [Mn$^{III}$(O$_2$)(Tp$^{Ph_2}$)(THF)]. Corresponding oscillator strengths are included in ESI, Table S14.

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*Band only apparent in low-temperature, 7 T MCD spectrum. $^{a}$Mn$^{III}$ spin-forbidden d-d transitions to triplet excited states. $^{b}$Assigned as a spin-allowed transition involving primarily the Mn 3d orbitals as indicated. $^{c}$Assigned as peroxo-to-manganese(III) charge transfer transition. $^{d}$Based on the low MCD intensity of band 9, this feature could arise from a Tp$^{Ph_2}$-based charge-transfer transition.

Figure 6. First coordination sphere of [Mn$^{III}$(O$_2$)(Tp$^{Ph_2}$)(THF)] and D-tensor coordinate system from CP-DFT computations. The $C_{5v}$ symmetry labels for the Mn 3d orbitals using the D-tensor coordinate system are provided.

16 630,16,18,32 For that series of complexes, this variation was related to slight differences in one Mn–O$_{peroxo}$ distance (1.869 – 1.907 Å). Because the Mn–O$_{peroxo}$ distances of [Mn$^{III}$(O$_2$)(Tp$^{Ph_2}$)(THF)] fall within this range (see Table 4), another structural perturbation must account for the high energy band 1 in this case.

VTVH MCD spectroscopy$^{37,61}$ was used to probe both the ZFS parameters and transition polarizations of [Mn$^{III}$(O$_2$)(Tp$^{Ph_2}$)(THF)]. VTVH MCD curves obtained for [Mn$^{III}$(O$_2$)(Tp$^{Ph_2}$)(THF)] at 26 180 cm$^{-1}$ are nested, indicating a moderate ZFS of the Mn$^{III}$ ion (Figure 7) and were systematically fitted to obtain zero field splitting parameters. The best fits ($\chi^2 < 0.04$) were obtained with $D = -2.0$ cm$^{-1}$, $E/D = 0.05$ and a predominant $z$-polarization ($<1\%$, $x$-, $<1\%$ $y$-, and 98% $z$-polarization). These ZFS parameters are in excellent agreement with those obtained from the EPR data ($D = -2.0(5)$ cm$^{-1}$; $E/D = 0.07(1)$). In addition, these ZFS splitting parameters fall in the range of those reported for other peroxomanganese(III) adducts ($D = -1.5$ to -3.0 and $E/D = 0.05$ to 0.30).16,19,20,25 Thus, the ZFS parameters of [Mn$^{III}$(O$_2$)(Tp$^{Ph_2}$)(THF)] are not reflective of the unique $\tau$ parameter of this complex.

Figure 7. Experimental VTVH MCD data collected at 26 180 cm$^{-1}$ for [Mn$^{III}$(O$_2$)(Tp$^{Ph_2}$)(THF)] (---) and theoretical fit (——) using the following parameters: $D = -2.00$, $E/D = 0.05$, $g_{//} = 2.00$, and 0.8% $x$, 0.8% $y$, and 98.4% $z$ polarization.

X-ray Absorption Spectroscopy of [Mn$^{III}$(Tp$^{Ph_2}$)(DMF)](OTf) and [Mn$^{III}$(O$_2$)(Tp$^{Ph_2}$)(THF)]
The Mn K-edge X-ray absorption data of [MnIII(Tp²)(DMF)](OTf) shows a rising edge at 6547.5 eV, characteristic of a MnIII species, as well as a pre-edge feature.

![Image](Figure 8. Fourier transform of Mn K-edge EXAFS data [k²γ(κ)] and raw EXAFS spectra (insets), experimental data (--) and fits (−) for [MnIII(Tp²)(DMF)](OTf).)

at 6540.6 eV (ESI, Figure S6). The Fourier transform of the extended X-ray absorption fine structure (EXAFS) data of [MnIII(Tp²)(DMF)](OTf) exhibits a primary peak at R' = 1.7 Å which was best fit with a shell of 3 O atoms at 2.16 Å and a shell of 3 N atoms at 2.28 Å (Figure 8, Table 6). Two smaller peaks are present in the Fourier transform at R'' = 2.5 and 3.1 which were fit with a shell of 4 N atoms at 3.09 Å, a shell of 1 B atom at 3.33 Å, and a shell of 6 C atoms at 3.49 Å. The fits of the EXAFS data show excellent agreement with the bond lengths determined through XRD, particularly with the EXAFS fits of the average Mn-N and Mn-O distances of 2.28 and 2.16 Å, respectively (ESI, Table S10).

We also attempted to collect Mn K-edge X-ray absorption data for [MnIII(THF)²(Tp²)(THF)]; however, all datasets showed signs of photoreduction or sample degradation which was evident by a shift in the edge energy and disappearance of the pre-edge feature (ESI, Figure S7). Several attempts were made to circumvent the sample instability, such as preparation with different solvents (50:50 mixture of 2-Me-tetrahydrofuran:THF, THF, and toluene) and by several methods of preparation, but sample degradation was observed in all cases when the sample was subjected to the X-ray beam.

### Ligand Exchange Reactions of [MnIII(O₃)(Tp²)](THF)

The observation of the solvent (THF) ligand in the X-ray structure of [MnIII(O₃)(Tp²)(THF)] appeared to present an opportunity to perform ligand substitution reactions cis to the MnIII-O₂ unit, under the assumption that the THF ligand might be labile. In a peroxomanganese(III) complex supported by the 13-

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Table 6. EXAFS Fitting Results for [MnIII(Tp²)(DMF)](OTf).a

a Fourier transform range is 2 – 14.5 Å (resolution 0.126 Å).

DFT Computations and Electronic Structure of [MnIII(O₃)(Tp²)](THF)

DFT computations were performed to provide a detailed comparison of the electronic structure of [MnIII(O₃)(Tp²)(THF)] with that of other peroxomanganese(III) adducts. The DFT-geometry-optimized model of [MnIII(O₃)(Tp²)(THF)] has metal-ligand bond lengths very similar to those observed crystallographically (Figure 9, top left panel). In particular, the Mn−Operoxo distances are within 0.03 Å of their crystallographic values (calculated: 1.881 and 1.894 Å; XRD: 1.859(2) and 1.865(2) Å). The calculated Mn-N distances are all predicted to be slightly larger than their crystallographic counterparts but all are within 0.07 Å of the experimental values. The Mn−O(THF) bond length shows a difference of in 0.04 Å between experimental and computed values. Overall, all calculated metric parameters are in quite acceptable agreement with the XRD structure of [MnIII(O₃)(Tp²)](THF).

Coupled-perturbed (CP) DFT calculations afforded the D-tensor orientation for [MnIII(O₃)(Tp²)](THF), (Figure 9, top left panel). The elongated N(1)−Mn−O(3) axis (see Figure 3 for atom numbering scheme) defines the z-axis of the D-tensor, and the y-axis bisects the O−O bond vector. The CP-DFT calculated ZFS parameters were D = -1.37 cm⁻¹ and E/D = 0.06. Although the CP-DFT method slightly underestimates the magnitude of D relative to the experimental value of -2.0 cm⁻¹, the relative magnitude agrees well with experimental value of D observed for other MnIII-O₂ adducts and is smaller than D values of other non-peroxo MnHI species (4 to -5 cm⁻¹). Additionally, D_{SOC} was also calculated using the state-

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averaged CASSCF/NEVPT2 method. In this case $D$ is
erestimated ($D_{SCF} = -2.91 \text{ cm}^{-1}$) and the system is predicted to
be too rhombic ($E/D = 0.28$). The CASSCF/NEVPT2 method
calculated a 29% contribution to $D_{SCF}$ in the same sign (-) from
components of the lowest-lying $^1T_1$ state (from parent $O_h$
symmetry) at 18 400, 19 200, and 20 400 cm$^{-1}$. Similarly, 30%
total contribution to $D_{SCF}$ comes from the lowest-lying quintet
states at 25 700 and 29 500 cm$^{-1}$. Additionally, a $^5A$ state at 30
500 cm$^{-1}$ contributed 27% to $D$ as well as 99% to $E$.

Contributions from individual excited states are listed in ESI,
Table S15.

Before discussing spectral assignments for
$[\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{PH}})(\text{THF})]$], we describe the bonding in this
complex, focusing on the frontier MOs. In the D-tensor
orientation, both the spin-up and spin-down $\text{Mn}^{\text{III}} 3d_{xy}$-based
MOs ($218\alpha$ and $230\beta$) are unoccupied and involved in $\text{Mn}^{\text{III}}\text{O}_2$
$\sigma$-antibonding interactions (Figure 9, top right panel). The $\text{Mn}^{\text{III}}$
$\text{O}_2$ $\pi$-antibonding interaction is distributed over the $\text{Mn}^{\text{III}} 3d_{z^2}$
($195\alpha$, $197\alpha$, $200\alpha$, $210\alpha$, and $219\beta$) and $3d_{xy}$ ($199\alpha$, and $225\beta$)
based MOs. For the $3d_{z^2}$ and $3d_{xy}$-based MOs, only the $\alpha$-spin
MOs are occupied. The strong $\sigma$-covalency of the $\text{Mn}^{\text{III}}\text{O}_2$ unit is
exemplified by the $34\%$ Mn $3d$ and $52\%$ $\text{O}_2$ $p$ character in the $\alpha$
spin Mn $3d_{xy}$ MO (218$\alpha$), which is essentially identical to that
calculated for other six-coordinate $\text{Mn}^{\text{III}}\text{O}_2$ complexes using the
same level of theory.$^{16}$ The Mn $3d_{z^2}$-based MO of
$[\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{PH}})(\text{THF})]$ largely reflects $\sigma$-interactions between the Mn–N(Tp) and Mn–O(THF) groups. The $\alpha$-spin Mn $3d_{xy}$
MO carries $21\%$ Mn $3d$, $23\%$ N(Tp$^{\text{PH}}$) $2p$, $2\%$ O(THF) $2p$, and $3\%
\text{O}_{\text{peroxo}}$ $2p$ character.

To develop detailed band assignments of the electronic transitions observed in the experimental absorption and MCD spectra (Figure 5, Table 5), electronic transition energies and intensities of $[\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{PH}})(\text{THF})]$ were calculated with the
TD-DFT method. Overall, the TD-DFT calculated absorption
spectrum for $[\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{PH}})(\text{THF})]$ shows good, qualitative
agreement with the experimental absorption spectrum albeit with

Figure 9. DFT-optimized structure of $[\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{PH}})(\text{THF})]$, with $\text{metal-ligand bond lengths and the D-tensor coordinate system from CP}$$\text{DFT computations (top left panel), and surface contour plots of quasi}$$\text{restricted Mn 3d-based orbitals (QROs). The sums of Mn 3d and ligand}
2p contributions to the spin-up Kohn-Sham orbitals are listed next to the
plots of the corresponding QROs.

a consistent overestimation of transition energies. In the
experimental absorption spectrum of $[\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{PH}})(\text{THF})]$, three absorption envelopes are observed (regions A, B, and C; see
Figure 10). Region A, which extends from 18 000 to 25 000 cm$^{-1}$
in the experimental absorption spectrum contains contributions from
bands 1 – 5. In the TD-DFT-calculated spectrum, region A contains contributions from the lowest-energy spin-allowed $\text{Mn}^{\text{III}}$
$d-d$ transition (state 2: $d_z^2 \rightarrow d_{xy}$; see Tables 5 and S12) at 20 500
$\text{cm}^{-1}$ as well as a set of three peroxo-tomanganese(III) CT
transitions from 23 000 to 25 500 $\text{cm}^{-1}$ (states 3, 4, and 5). The
calculated energy for the $d_z^2 \rightarrow d_{xy}$ transition is in excellent
greement with the experimental energy of band 1 (Table 5). Compared to other previously characterized peroxomanganese(III) species, the energy of the $d_z^2 \rightarrow d_{xy}$
transition is significantly shifted to higher energy. The peroxo-tomanganese(III) CT transitions in region A originate in the peroxo
$p^\pi$ orbitals that are perpendicular, or out-of-plane, with respect to the
$\text{Mn}^{\text{III}}\text{O}_2$ unit ($\pi_{\text{peroxo}}^\pi$) and terminate in the spin-down $\text{Mn}^{\text{III}}$
$3d$-based MOs. However, these transitions are highly mixed, and this
could account for the erroneously high TD-DFT-computed absorption intensity in this region. Nonetheless, these computations lend credence to the assignment of band 2 as a peroxo-tomanganese(III) CT transition.

Region B of the TD-DFT- computed absorption spectrum
extends from 25 000 to 31 000 $\text{cm}^{-1}$. This region contains
contributions from the three remaining spin-allowed $\text{Mn}^{\text{III}} d-d$
transitions ($d_{xy} \rightarrow d_{xy}$, state 8; $d_z^2 \rightarrow d_{xy}$, state 12; and $d_{xy} \rightarrow d_{xy}$,

Figure 10. Experimental (top) and TD-DFT-calculated (bottom)
asorption spectra of $[\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{PH}})(\text{THF})]$.}


state 17), as well as additional peroxyo-manganese(III) charge transfer transitions (Tables 5 and S12).\(^5\) Compared to experiment, transitions in region B are calculated at too high an energy by ~5 000 cm\(^{-1}\). Nonetheless, these calculations are generally supportive of the spectral assignments discussed previously. Additionally, state 17 is composed of the \(d_{x^2} \rightarrow d_{xy}\) transition, which corresponds to a \(z\)-polarized \(^4\text{B}_1 \rightarrow ^4\text{A}_2\) transition using the \(D\)-tensor coordinate system (Figure 6) and assuming idealized \(C_{2v}\) symmetry, with the \(y\) axis as the pseudo-\(C_2\) axis. This corroborates the assignment of band 7 as a \(d_{x^2} \rightarrow d_{xy}\) transition, as band 7 was characterized by VTVH MCD to be 98% \(z\)-polarized.

Region C of the TD-DFT absorption spectrum is composed of peroxyo-manganese(III) CT transitions with contributions from states 14 (29 500 cm\(^{-1}\)) and 15 (29 800 cm\(^{-1}\)). TD-DFT calculations incorrectly predict the ordering of these CT states with respect to the highest-energy \(d\)-\(d\) transition (state 17, 30 600 cm\(^{-1}\)), however, this is not unusual for TD-DFT calculations. Additionally, the excited state energies of \([\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{Pr}})(\text{THF})]\) were calculated by the CASSCF/NEVPT2 method to exclude the possibility of TD-DFT-calculated charge-transfer states with erroneously high intensity and low energy (so-called “intruder states”), that can occur as artifacts. The CASSCF/NEVPT2 method also has the advantage that spin-forbidden excited states can be treated. The \(d\)-\(d\) excited states from the CASSCF/NEVPT2 calculations agree well with the TD-DFT energies, confirming the presence of few intruder states in the latter spectrum. Importantly, two triplet excited states are predicted with energies (26 800 and 30 500 cm\(^{-1}\)) that interleave the quartet excited state energies (Table 5), supporting our assignment of bands 4 and 6 as spin-forbidden transitions. It should be noted that the TD-DFT method predicts a significant contribution to region B from state 10 in the TD-DFT calculations (Table S13); however, state 10 is predicted as a \(\text{Ph(Tp}^{\text{Pr}}) \rightarrow \text{Mn} \) intruder state. This transition is an anticipated artifact of the TD-DFT calculation and is not expected to contribute to the experimental absorption spectrum.

DFT Computations and Electronic Structure of the Blue and Brown Isomers of \([\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{Pr}})(\text{pz}^{\text{Pr}}\text{H})]\)

Due to the reasonable success in reproducing the spectroscopic properties of \([\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{Pr}})(\text{THF})]\) with these computational methods, a similar approach was utilized for the isomers of \([\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{Pr}})(\text{pz}^{\text{Pr}}\text{H})]\) in an attempt to explain the thermochromic shift in the electronic absorption spectrum. The 22 nm (670 cm\(^{-1}\)) red shift in the electronic absorption spectrum upon cooling from 253 to 193 K was associated with the formation of a hydrogen bond between the pyrazole ligand and one O atom of the peroxyo unit in the low-temperature isomer. TD-DFT calculations were performed on models of \([\text{Mn}^{\text{III}}(\text{O}_2)(\text{Tp}^{\text{Pr}})(\text{pz}^{\text{Pr}}\text{H})]\) built using the XRD coordinates of the isomers at 253 and 193 K (brown and blue isomers, respectively) in order to elucidate the nature of the changes in the absorption spectrum by determining the electronic structure. TD-DFT calculations were performed with both the unmodified XRD coordinates, as well as structures where the positions of the hydrogen atoms were optimized. Primarily, the optimization of the hydrogen atoms resulted in a shorter hydrogen bond, with a 0.139 Å decrease between the H-donor atom and the O(peroxo) acceptor in the blue isomer and a corresponding decrease of 0.049 Å in the brown isomer (Table 7).

TD-DFT calculations with both the hydrogen-optimized and XRD structures reproduce the experimental absorption spectra well. TD-DFT calculations performed with the hydrogen-optimized structures are predicted at 18 500 cm\(^{-1}\) for the brown isomer and a transition at 17 300 cm\(^{-1}\) for the blue isomer, in good agreement with the experimental values (17 820 and 17 150 cm\(^{-1}\)). The transition energies obtained through TD-DFT calculations with the hydrogen-optimized structures were at slightly higher energies of 18 900 and 17 500 cm\(^{-1}\) for the blue and brown.
isomers, respectively. Importantly, both the XRD and the hydrogen-optimized structures reproduce the red-shift that occurs as the complex is cooled from 253 to 193 K. With all TD-DFT calculations, this red-shifted transition involves a one-electron excitation between the α-spin Mn 3d_{x^2} MO (192a), which is highly mixed, and the unoccupied α-spin Mn 3d_{y^2} MO (192a). The acceptor orbital exhibits strong σ-covalency of the Mn(III)O unit, with 42 - 45% Mn 3d and 44 - 47% O 2p character (ESI, Tables S16 - S19), which is similar to other previously characterized Mn(III)O complexes. The band shift in the experimental absorption spectrum of the blue isomer of [Mn(III)(O_2)(Tp^Ph2)(pz^Ph2H)] is due to the stabilization of the Mn 3d_{y^2} acceptor MO, which carries significant peroxy ligand character, with the formation of the hydrogen bond (Figure 11).

The hydrogen-optimized structure of the blue isomer exhibits the shortest hydrogen bond at 2.017 Å which is accompanied by the greatest stabilization of 0.2294 eV of the Mn 3d_{y^2} acceptor MO (192a) relative to the corresponding orbital of the brown isomer (Table 7, Figure 11). TD-DFT calculations with the unmodified XRD structures display a similar trend with the blue isomer showing a hydrogen bond of 2.156 Å and a stabilization of the acceptor MO in the blue isomer of 0.1679 eV relative to the brown isomer. Notably, when both the brown and blue isomers were fully optimized (i.e. the positions of all atoms were energy-minimized), the computations yielded isomeric structures with a hydrogen bond distances of 1.891 and 1.890 Å and equivalent Mn—O distances of 1.858 and 1.910 Å (Table 7).

**Discussion**

Although there have been a variety of synthetic peroxy manganese(III) species supported by anionic ligands, there is still a lack of detailed bonding descriptions of such complexes. In particular, peroxy manganese(III) species supported by monoanionic and facially coordinating Tp ligands exhibit unusual electronic absorption spectra that have been unexplained by studies to date. In order to investigate the electronic structure of one of these species, a monomeric Mn(III)-O_2 adduct supported by the Tp^Ph2 ligand was synthesized and characterized by XRD, EPR, and MCD spectroscopies as well as TD-DFT and CASSCF/NEVPT2 computations. The high thermal stability of [Mn(III)(O_2)(Tp^Ph2)(THF)], presumably due in part to the steric bulk of the phenyl groups of the Tp^Ph2 ligand shielding the peroxy moiety, facilitated the determination of the crystal structure.

The XRD structure of [Mn(III)(O_2)(Tp^Ph2)(THF)] shows metric parameters in line with those collected for other peroxy manganese(III) species. The Mn(III) oxidation state was confirmed by EPR spectroscopy. Previously characterized peroxy manganese(III) species exhibit 6-line signals at ~80 mT with hyperfine splitting of 6-7 mT. As [Mn(III)(O_2)(Tp^Ph2)(THF)] displays a feature position of 84.6 mT and a hyperfine splitting of 5.1 mT. This hyperfine splitting is somewhat smaller than those of other non-peroxy manganese(III) species and previously studied peroxy manganese(III) adducts, possibly suggesting a higher degree of covalency in the Mn(III)(O_2)(Tp^Ph2)(THF) complex. Temperature dependence studies and simulation of the parallel-mode EPR feature yielded D = -2.0(5) cm⁻¹ and E/D = 0.07(1), which are very similar to the ZFS parameters for other Mn(III)-O_2 species which lie between -1.5 and -3.0 cm⁻¹ for D and 0.05 to 0.30 for E/D. In addition to supporting the assignment of this intermediate as a Mn(III) species, the determination of these zero field splitting parameters for [Mn(III)(O_2)(Tp^Ph2)(THF)] supply insight into the ground state properties of Mn(III)-O_2 species.

Figure 12: TD-DFT calculated d-d transitions in [Mn(III)(O_2)(Tp^Ph2)(THF)] and [Mn(III)(O_2)(L^py2^H)]. Following the hole formalism for these d^5 systems, the excited state is designated according to the d orbital hole. In D-tensor orientation of the [Mn(III)(O_2)(L^py2^H)] model, the x and y axes are swapped relative to [Mn(III)(O_2)(THF)]; the orbital labels corresponding to the coordinate system of [Mn(III)(O_2)(Tp^Ph2)(THF)] are shown in parentheses.
experimental spectrum. In general, the CASSCF/NEVPT2 method is accepted as a more reliable method for treating the excited states of transition metal complexes. In this present case, both methods overestimated the electronic transition energies compared to the experimentally observed bands, with the TD-DFT-calculated energies being closer to the experimental values. However, below 32 000 cm\(^{-1}\), the absorption spectra of [Mn\(^{III}\)(O\(_2\))\((\text{TPP})_2\)] calculated by both methods are comparable in their replication of the experimental spectrum with the exception of one intruder state in the TD-DFT calculation, which had a negligible effect on the primary features of the computed absorption spectrum. Here, TD-DFT calculations were sufficient to predict the electronic absorption spectrum, particularly the \(d-d\) transitions, and the use of the more input-rigorous CASSCF/NEVPT2 method may not be necessary in other similar cases.

TD-DFT calculations were extended to investigate the brown and blue isomers of [Mn\(^{II}\)(O\(_2\))\((\text{TPP})_2\)(pz\(^{-2}\)H)]. As previously reported, when the [Mn\(^{III}\)(O\(_2\))\((\text{TPP})_2\)(pz\(^{-2}\))\(\cdot\)H\(_2\)] species is cooled from 253 to 193 K, a hydrogen bond between the pyrazole ligand and one O atom of the peroxo unit is formed, and the absorption spectrum exhibits a 670 cm\(^{-1}\) red-shift. TD-DFT calculations permit the assignment of the red-shifted electronic transition to a Mn \(d_{\pi}\) → \(d_{\sigma}\) one-electron excitation. The Mn \(3d_{\alpha}\) acceptor MO of both isomers contains a significant amount of peroxo ligand character. The hydrogen bonding interaction with the peroxo moiety, and the concomitant Mn-O bond elongation, stabilizes this MO in the blue isomer by 0.2294 eV relative to the brown isomer (Figure 11).

The stabilization of the Mn-O \(\sigma\)-antibonding 3\(d_{\sigma}\) MO through a hydrogen-bonding interaction is of potential relevance to two recent reports describing activation of Mn\(^{III}\)-O \(=\)O intermediates. These elementary steps feature in the catalytic reduction of O\(_2\) to H\(_2\)O by the corresponding Mn\(^{II}\) complex. In a separate study, Anxolabéhère-Mallart, Policar, and Robert reported that the two-electron reduction of a Mn\(^{III}\)-O\(_2\) adduct supported by a trianionic tripodil ligand with a hydrogen-bonding cavity around the peroxo, Borovik and co-workers showed that the two-electron reduction of a Mn\(^{III}\)-O\(_2\) adduct using diphenyldihydrazine led to O-O bond cleavage and the eventual formation of a hybrid oxo-/hydroxo-manganese(III) adduct.\(^{39,26}\) A dihydroxomanganese(III) species was postulated as an intermediate in this process. These elementary steps feature in the catalytic reduction of O\(_2\) to H\(_2\)O by the corresponding Mn\(^{II}\) complex. In a separate study, Anxolabéhère-Mallart, Policar, and Robert reported that the two-electron reduction of a Mn\(^{III}\)-O\(_2\) adduct supported by a phenolate-containing N\(_2\)O\(_2\) ligand (the protonated, phenol form of the ligand is N(2)-hydroxybenzyl)-N,N'-bis[2-(N-methylimidazolyl)methyl]ethane-1,2-diamine) causes O-O bond cleavage when the reduction is carried out in the presence of water.\(^{26}\) Detailed electrochemical studies revealed that this process is kinetically controlled by the initial electron transfer that is also associated with a large reorganization energy. In both systems, hydrogen bonding to the peroxo ligand, either intramolecular with the supporting ligand or intermolecular with added water, is possible. On the basis of our computational work described here, hydrogen-bonding to the peroxo of a Mn\(^{III}\)-O\(_2\) unit stabilizes the Mn \(3d_{\alpha}\) orbital (Figure 11), which is the spin-\(\alpha\) LUMO, potentially facilitating reduction of the Mn\(^{III}\)-O\(_2\) unit. Because this MO contains a significant percentage of peroxo \(\pi^*\) character, the addition of an electron to this MO would weaken the O-O bond, priming it for cleavage.

**Conclusions**

The conversion of [Mn\(^{III}\)(TPP\(^{-2}\))(DMF)]\((\text{OTf})\) to [Mn\(^{II}\)(O\(_2\))(TPP\(^{-2}\))(THF)] by KO\(_2\) yielded a peroxomanganese(III) species exhibiting high thermal stability with unique spectral features in both the electronic absorption and MCD spectra. The nature of these spectral deviations from previously characterized peroxomanganese(III) species arises from an axial elongation along the molecular \(z\)-axis, reducing the metal-ligand covalency, stabilizing the \(\sigma\)-antibonding Mn \(d_{\sigma}\) MO, and affording higher energy \(d-d\) transitions. Compared to the peroxomanganese(III) species supported by the TPP\(^{-2}\) ligand, a hydrogen bonding interaction stabilizes the acceptor MO, causing the thermochromic shift observed as the complex is cooled from 293 to 193 K. These perturbations in the electronic transitions of these peroxomanganese(III) species represent an example of a deviation in symmetry and metal-ligand bonding in Mn\(^{III}\)-O\(_2\) intermediates and could be applied in the identification of similar changes in the first coordination sphere of short-lived intermediates in enzymatic and model systems.

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**Notes and references**

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† Electronic Supplementary Information (ESI) available:Crystal data and structure refinement information, variable-temperature electronic absorption spectra of [Mn\(^{II}\)(O\(_2\))(TPP\(^{-2}\))(THF)], temperature dependent EPR data for [Mn\(^{II}\)(O\(_2\))(TPP\(^{-2}\))(THF)], IR spectra of [Mn\(^{II}\)(TPP\(^{-2}\))(DMF)]\((\text{OTf})\) and [Mn\(^{II}\)(O\(_2\))(TPP\(^{-2}\))(THF)], variable-temperature 7T MCD spectra, deconvoluted MCD data, XAS spectra of [Mn\(^{II}\)(TPP\(^{-2}\))(DMF)]\((\text{OTf})\) and [Mn\(^{III}\)(O\(_2\))(TPP\(^{-2}\))(THF)], EXAFS fitting results for [Mn\(^{II}\)(TPP\(^{-2}\))(DMF)]\((\text{OTf})\), DFT-optimized cartesian coordinates, TD-DFT-calculated parameters, and CASSCF-NEVPT2-calculated parameters. CCDC reference numbers 1018686 and 1018687. See DOI: 10.1039/b600000ax/.

(60) Band 9 has exceptionally low MCD intensity and could also be assigned as a TpPh2 to manganese(III) CT transition.


(66) These transitions are all highly mixed, and the natures of the excited states were identified through visualization of electron density difference maps (EDDMs).


(69) The metric parameters in the crystal structure of this complex indicate that a proton is nearly equally shared between the supporting ligand and a coordinated oxygen atom.

A peroxomanganese(III) species supported by a scorpionate (Tp) ligand has been characterized by X-ray crystallography, electron paramagnetic resonance and magnetic circular dichroism spectroscopy, revealing a distinct electronic structure.