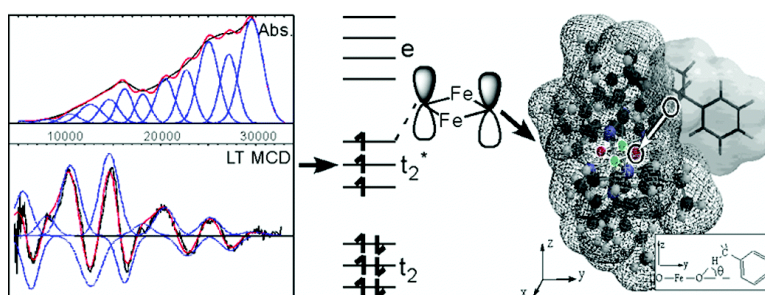


## Spectroscopic Study of [FeO(5-Et-TPA)]: Nature of the FeO Diamond Core and Its Possible Relevance to High-Valent Binuclear Non-Heme Enzyme Intermediates

Andrew J. Skulan, Melissa A. Hanson, Hua-fen Hsu, Lawrence Que., and Edward I. Solomon

*J. Am. Chem. Soc.*, **2003**, 125 (24), 7344-7356 • DOI: 10.1021/ja021137n • Publication Date (Web): 21 May 2003

Downloaded from <http://pubs.acs.org> on March 29, 2009



### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 6 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

## Spectroscopic Study of $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2]^{3+}$ : Nature of the $\text{Fe}_2\text{O}_2$ Diamond Core and Its Possible Relevance to High-Valent Binuclear Non-Heme Enzyme Intermediates

Andrew J. Skulan,<sup>†</sup> Melissa A. Hanson,<sup>†</sup> Hua-fen Hsu,<sup>‡</sup> Lawrence Que, Jr.,<sup>\*,‡</sup> and Edward I. Solomon<sup>\*,†</sup>

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305, and Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455

Received August 30, 2002; Revised Manuscript Received February 20, 2003; E-mail: Edward.Solomon@stanford.edu; que@chem.umn.edu

**Abstract:** The spectroscopic properties and electronic structure of an  $\text{Fe}_2(\text{III,IV})$  bis- $\mu$ -oxo complex,  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2](\text{ClO}_4)_3$  where 5-Et<sub>3</sub>-TPA = tris(5-ethyl-2-pyridylmethyl)amine, are explored to determine the molecular origins of the unique electronic and geometric features of the  $\text{Fe}_2\text{O}_2$  diamond core. Low-temperature magnetic circular dichroism (MCD) allows the two features in the broad absorption envelope (4000–30000  $\text{cm}^{-1}$ ) to be resolved into 13 transitions. Their C/D ratios and transition polarizations from variable temperature–variable field MCD saturation behavior indicate that these divide into three types of electronic transitions;  $t_2 \rightarrow t_2^*$  involving excitations between metal-based orbitals with  $\pi$  Fe–O overlap (4000–10000  $\text{cm}^{-1}$ ),  $t_2/t_2^* \rightarrow e$  involving excitations to metal-based orbitals with  $\sigma$  Fe–O overlap (12500–17000  $\text{cm}^{-1}$ ) and LMCT (17000–30000  $\text{cm}^{-1}$ ) and allows transition assignments and calibration of density functional calculations. Resonance Raman profiles show the  $C_{2h}$  geometric distortion of the  $\text{Fe}_2\text{O}_2$  core results in different stretching force constants for adjacent Fe–O bonds ( $k_{\text{str}}(\text{Fe}-\text{O}_{\text{long}}) = 1.66$  and  $k_{\text{str}}(\text{Fe}-\text{O}_{\text{short}}) = 2.72$   $\text{mdyn}/\text{\AA}$ ) and a small (~20%) difference in bond strength between adjacent Fe–O bonds. The three singly occupied  $\pi^*$ -metal-based orbitals form strong superexchange pathways which lead to the valence delocalization and the  $S = 3/2$  ground state. These orbitals are key to the observed reactivity of this complex as they overlap with the substrate C–H bonding orbital in the best trajectory for hydrogen atom abstraction. The electronic structure implications of these results for the high-valent enzyme intermediates **X** and **Q** are discussed.

### 1. Introduction

The oxygen-activating binuclear non-heme iron enzymes ribonucleotide reductase (RR), methane mono-oxygenase (MMO), and  $\Delta^9$ -desaturase ( $\Delta 9\text{D}$ ) utilize high-valent iron–oxo intermediates in performing a variety of vital reactions including generation of a tyrosine radical for nucleotide biosynthesis (RR), substrate hydroxylation (MMO), and desaturation ( $\Delta 9\text{D}$ ).<sup>1,2</sup> The final intermediate in oxygen activation by MMO (intermediate **Q**) is generally described as an  $\text{Fe}_2(\text{IV,IV})$  bis- $\mu$ -oxo structure.<sup>3</sup> A related structure has been proposed for the  $\text{Fe}_2(\text{III,IV})$  intermediate **X**, of RR,<sup>4–6</sup> while a high-valent intermediate has not yet been trapped for  $\Delta 9\text{D}$ .<sup>7,8</sup> The bis- $\mu$ -oxo core,

$\text{M}_2(\mu\text{-O})_2$ , is a structural motif observed or proposed in metalloenzyme systems using metals other than iron and has been implicated in proteins which both form (oxygen-evolving complex of the photosystem-II)<sup>9–11</sup> and activate molecular dioxygen.<sup>12,13</sup> Thus, understanding the electronic structure of the  $\text{Fe}_2\text{O}_2$  core will provide insight into the reactivity of both the binuclear non-heme iron enzymes and the wide family of metalloenzymes and model complexes which utilize this structure.

Spectroscopic evidence of the structure of high-valent intermediates **Q** and **X** has been attained from extended X-ray absorption fine structure (EXAFS) and Mössbauer data.<sup>3,14–18</sup>

<sup>†</sup> Stanford University.

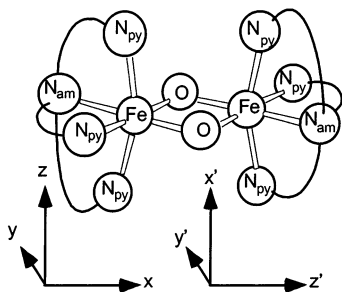
<sup>‡</sup> University of Minnesota.

- (1) Solomon, E. I.; Brunold, T. C.; Davis, M. I.; Kemsley, J. N.; Lee, S. K.; Lehnert, N.; Neese, F.; Skulan, A. J.; Yang, Y. S.; Zhou, J. *Chem. Rev.* **2000**, *100*, 235–349.
- (2) Wallar, B. J.; Lipscomb, J. D. *Chem. Rev.* **1996**, *96*, 2625–2658.
- (3) Shu, L. J.; Nesheim, J. C.; Kauffmann, K.; Münck, E.; Lipscomb, J. D.; Que, L. *Science* **1997**, *275*, 515–518.
- (4) Edmondson, D. E.; Huynh, B. H. *Inorg. Chim. Acta* **1996**, *252*, 399–404.
- (5) Que, L.; Dong, Y. H. *Acc. Chem. Res.* **1996**, *29*, 190–196.
- (6) Que, L. *J. Chem. Soc., Dalton Trans.* **1997**, 3933–3940.
- (7) Broadwater, J. A.; Ai, J. Y.; Loeher, T. M.; Sanders-Loehr, J.; Fox, B. G. *Biochemistry* **1998**, *37*, 14664–14671.

- (8) Broadwater, J. A.; Achim, C.; Münck, E.; Fox, B. G. *Biochemistry* **1999**, *38*, 12197–12204.

- (9) Yachandra, V. K.; Sauer, K.; Klein, M. P. *Chem. Rev.* **1996**, *96*, 2927–2950.
- (10) Latimer, M. J.; DeRose, V. J.; Yachandra, V. K.; Sauer, K.; Klein, M. P. *J. Phys. Chem. B* **1998**, *102*, 8257–8265.
- (11) Liang, W. C.; Roelofs, T. A.; Cinco, R. M.; Rompel, A.; Latimer, M. J.; Yu, W. O.; Sauer, K.; Klein, M. P.; Yachandra, V. K. *J. Am. Chem. Soc.* **2000**, *122*, 3399–3412.
- (12) Solomon, E. I.; Sundaram, U. M.; Machonkin, T. E. *Chem. Rev.* **1996**, *96*, 2563–2605.
- (13) Que, L.; Tolman, W. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 1114–1137.
- (14) Lee, S. K.; Nesheim, J. C.; Lipscomb, J. D. *J. Biol. Chem.* **1993**, *268*, 21569–21577.

**Chart 1.** Core Geometry of [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>]<sup>3+</sup> Cation Showing the Relationship between the Molecular Coordinate System (*x*, *y*, *z*) and the Magnetic Coordinate System (*x'*, *y'*, *z'*)<sup>a</sup>



<sup>a</sup> This study is presented in terms of the molecular (*x*, *y*, *z*) coordinate system. The short Fe–O bonds are trans to the amine nitrogen donors, *N*<sub>am</sub>.

Intermediate **Q** has an Fe–Fe distance of 2.46 Å and both short and long Fe–O bonds of 1.77 and 2.0 Å. The two irons are indistinguishable by Mössbauer with simulation parameters consistent with a pair of high-spin antiferromagnetically (AF) coupled Fe(IV) ions. This is consistent with a bis-μ-oxo structure for **Q**. Intermediate **X** has inequivalent high-spin, AF coupled Fe(III) and Fe(IV) ions and at least one μ-oxo bridge. ENDOR studies on **X** suggest that O<sub>2</sub> is split to form a bridging μ-oxo and a terminal hydroxo/water ligand.<sup>19,20</sup> Unfortunately, the body of data on these high-valent intermediates is not extensive. Neither **Q** nor **X** have been generated in crystals, and the use of other structural probes, such as resonance Raman and magnetic circular dichroism (MCD) spectroscopies have thus far not been reported.

The only structurally characterized high-valent, binuclear non-heme iron complex is [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>, where 5-Et<sub>3</sub>-TPA = tris(5-ethyl-2-pyridylmethyl)amine.<sup>21</sup> It has a bis-μ-oxo core supported by the tetradentate alkyl-substituted TPA ligand which coordinates via a pyridine and a tertiary amine in the Fe<sub>2</sub>O<sub>2</sub> plane along with two axial pyridines (see Chart 1). The bis-μ-oxo core displays *C*<sub>2h</sub> symmetry with alternating short (1.806 Å) and long (1.860 Å) Fe–O bonds, paralleling the *C*<sub>2h</sub> core symmetry proposed for intermediate **Q** of MMO.<sup>3</sup> The dimer has been described as a class III valence-delocalized Fe<sub>2</sub>-(III,IV) dimer with two low-spin irons generating an *S* = 3/2 ground state.<sup>22,23</sup> Its ground-state magnetic properties were found to be unusual, with a very large zero field splitting (ZFS), *D* = 35 ± 15 cm<sup>-1</sup>, while monomeric iron complexes typically show

*D* < 3 cm<sup>-1</sup>.<sup>24</sup> The electron paramagnetic resonance (EPR) spectrum shows a near axial electronic environment with *g*<sub>z</sub> = 2.01, *g*<sub>x</sub> = 2.08, and *g*<sub>y</sub> = 2.10, where (*x'*, *y'*, *z'*) is the magnetic coordinate system.<sup>22,25</sup> In a companion study we have evaluated the orbital origin of these unique magnetic signatures; a near-axial EPR spectrum accompanied by very large ZFS.<sup>26</sup> This study also determined the relationship of the molecular coordinate system (*x* = Fe–Fe vector, *y* ≈ O–O vector (the angle between the Fe–Fe and O–O vectors is 88°), *z* = perpendicular to the Fe<sub>2</sub>O<sub>2</sub> core) to the magnetic coordinate system (Chart 1) and identified the relative importance of spin-allowed versus spin-forbidden spin–orbit interactions to the large ZFS. The present study is presented in terms of the molecular (*x*, *y*, *z*) coordinate system; hence *g*<sub>x</sub> = 2.01, *g*<sub>z</sub> = 2.08, and *g*<sub>y</sub> = 2.10. Analysis of Raman data has suggested that the Fe<sub>2</sub>O<sub>2</sub> core is near *D*<sub>2h</sub> symmetry, with near equal Fe–O stretching force constants (*k*(Fe–O<sub>long</sub>) = 3.151, *k*(Fe–O<sub>short</sub>) = 3.186 mdyn/Å),<sup>27</sup> while density functional calculations were used to describe the *S* = 3/2 ground state in terms of two ferromagnetically coupled low-spin iron centers.<sup>28</sup>

The Fe<sub>2</sub>(III,IV) 5-Et<sub>3</sub>-TPA bis-μ-oxo complex is a member of a family of structurally and spectroscopically similar [Fe<sub>2</sub>O<sub>2</sub>(*x*-TPA)<sub>2</sub>]<sup>3+</sup> complexes (*x* = 5-Et<sub>3</sub>-, 5-Me<sub>3</sub>-, 3-Me<sub>3</sub>-, or no substitution).<sup>22,27</sup> These show small variations in their EXAFS, absorption and vibrational spectra, indicating that their geometric and electronic structures are quite similar. An exception is the [Fe<sub>2</sub>O<sub>2</sub>(6-Me<sub>3</sub>-TPA)<sub>2</sub>](Ce(NO<sub>3</sub>)<sub>6</sub>) complex which has a pair of high-spin AF-coupled iron ions generating a *S* = 1/2 spin ground state. Analysis of resonance Raman spectra suggests this complex has a mono-μ-oxo, terminal oxo structure (i.e., Fe–O–Fe=O).<sup>29</sup>

[Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> displays reactivity paralleling that of the binuclear non-heme iron enzymes: hydroxylation (monooxygenases), desaturation (desaturases), and radical formation (ribonucleotide reductases) with select organic substrates.<sup>30,31</sup> 2,4-Di-*tert*-butyl phenol is converted to its phenoxy radical with the high-valent complex acting as a one-electron oxidant as occurs in RR. Cumene can be either hydroxylated or desaturated to cumyl alcohol or α-methylstyrene, while ethylbenzene is converted to a mixture of 1-phenylethanol and styrene. Hydroxylation and desaturation are two-electron processes and require 2 equiv of the high-valent dimer to perform the reaction. This is proposed to occur via a hydrogen atom abstraction step involving one [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>]<sup>3+</sup> ion based upon the large deuterium isotope effect (*k*<sub>H</sub>/*k*<sub>D</sub> = 20) of this step. This is

- (15) Liu, K. E.; Wang, D. L.; Huynh, B. H.; Edmondson, D. E.; Salifoglou, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 7465–7466.  
 (16) Lee, S. K.; Fox, B. G.; Froland, W. A.; Lipscomb, J. D.; Münck, E. *J. Am. Chem. Soc.* **1993**, *115*, 6450–6451.  
 (17) Sturgeon, B. E.; Burdi, D.; Chen, S. X.; Huynh, B. H.; Edmondson, D. E.; Stubbe, J.; Hoffman, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 7551–7557.  
 (18) RiggsGelasco, P. J.; Shu, L. J.; Chen, S. X.; Burdi, D.; Huynh, B. H.; Que, L.; Stubbe, J. *J. Am. Chem. Soc.* **1998**, *120*, 849–860.  
 (19) Burdi, D.; Sturgeon, B. E.; Tong, W. H.; Stubbe, J. A.; Hoffman, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 281–282.  
 (20) Burdi, D.; Willems, J. P.; RiggsGelasco, P.; Antholine, W. E.; Stubbe, J.; Hoffman, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 12910–12919.  
 (21) Hsu, H. F.; Dong, Y. H.; Shu, L. J.; Young, V. G.; Que, L. *J. Am. Chem. Soc.* **1999**, *121*, 5230–5237.  
 (22) Dong, Y. H.; Fujii, H.; Hendrich, M. P.; Leising, R. A.; Pan, G. F.; Randall, C. R.; Wilkinson, E. C.; Zang, Y.; Que, L.; Fox, B. G.; Kauffmann, K.; Münck, E. *J. Am. Chem. Soc.* **1995**, *117*, 2778–2792.  
 (23) “Class III valence-delocalized” means the two metal centers are electronically equivalent (Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247–403). This assignment is made based on [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>]<sup>3+</sup> displaying one sharp Mössbauer doublet, indicating the two iron atoms are equivalent. This is consistent with the *C*<sub>2h</sub> Fe<sub>2</sub>O<sub>2</sub> core symmetry as the two metal atoms are related by the *C*<sub>2</sub> rotation element.

- (24) Two notable exceptions are the Fe(IV)=O(cyclam-acetato)<sup>+</sup> complex, *D* = 23 cm<sup>-1</sup> (Grapperhaus, et al. *Inorg. Chem.* **2000**, *39*, 5306–5317) and compound II of horseradish peroxidase, *D* = 32 cm<sup>-1</sup> (Schultz, C. E.; Rutter, R.; Sage, J. T.; Debrunner, P. G.; Hager, L. P. *Biochemistry*, **1984**, *23*, 4743–4754).  
 (25) The primed coordinate system is defined by the effective *g*-tensor, with the *z'* direction defined to be coincident with the distinct *g*<sub>z,eff</sub> = 2.01 resonance, and *g*<sub>x,eff</sub> = 3.90 and *g*<sub>y,eff</sub> = 4.45. This is distinct from the molecular (unprimed) coordinate system of Chart 1 where *z* is perpendicular to the Fe<sub>2</sub>O<sub>2</sub> plane and the *x*-axis coincides with the Fe–Fe vector.  
 (26) Skulan, A. J.; Hanson, M. A.; Hsu, H. F.; Dong, Y. H.; Que, L.; Solomon, E. I. Submitted for publication in *Inorg. Chem.*  
 (27) Wilkinson, E. C.; Dong, Y. H.; Zang, Y.; Fujii, H.; Fraczkiewicz, R.; Fraczkiewicz, G.; Czernuszewicz, R. S.; Que, L. *J. Am. Chem. Soc.* **1998**, *120*, 955–962.  
 (28) Ghosh, A.; Almlof, J.; Que, L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 770–772.  
 (29) Zheng, H.; Yoo, S. J.; Münck, E.; Que, L. *J. Am. Chem. Soc.* **2000**, *122*, 3789–3790.  
 (30) Kim, C.; Dong, Y. H.; Que, L. *J. Am. Chem. Soc.* **1997**, *119*, 3635–3636.  
 (31) The reported reactivity studies were performed on the [Fe<sub>2</sub>O<sub>2</sub>(TPA)<sub>2</sub>]<sup>3+</sup> complex.

followed by either oxo transfer or a second hydrogen atom abstraction by a second dimer molecule to generate either the alcohol or alkene product.

The present study utilizes a variety of spectroscopic techniques in conjunction with density functional calculations to determine the molecular origins of the physical properties of the  $S = 3/2$ , valence delocalized  $\text{Fe}_2(\text{III,IV})$  bis- $\mu$ -oxo core. Our previous analysis connecting the magnetic and molecular coordinate systems<sup>26</sup> permits use of low-temperature MCD and variable temperature-variable field (VTVH) MCD to determine the polarizations of electronic transitions and allows experimental calibration of density functional calculations. These observations are further supplemented by the results of resonance Raman profile studies which identify excited-state distortions of the  $\text{Fe}_2\text{O}_2$  core. Resonance Raman spectra and normal coordinate analysis (NCA) allow the degree of bond asymmetry in the  $\text{Fe}_2\text{O}_2$  core to be established and compared with density functional calculations to determine the nature of bonding within the core. Combining these probes of the electronic and geometric structure of the  $\text{Fe}_2\text{O}_2$  core allows identification of the superexchange pathways that cause valence delocalization, the geometric factors that result in the distorted,  $C_{2h}$  “diamond core” geometry and its effects on the electronic properties of this site. The nature of this geometric and electronic structure is combined with frontier molecular orbital theory (FMO) to identify likely reaction trajectories and the electronic factors which give rise to its observed reactivity. The electronic structure determined for the  $\text{Fe}_2\text{O}_2$  core is correlated to those of the high-valent protein intermediates **X** and **Q** observed in non-heme iron enzymes.

## 2. Experimental Section

**2.1. Sample Preparation.** Green crystals of the complex  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2](\text{ClO}_4)_3$ , where 5- $\text{Et}_3\text{-TPA}$  = tris(5-ethyl-2-pyridylmethyl)-amine, were prepared as described previously.<sup>22</sup> The complex is thermally unstable at room temperature and was maintained below  $-70^\circ\text{C}$ .

**2.2. UV-vis/MCD Spectroscopy.** Variable-temperature absorption spectra were measured on a Cary 17 double-beam spectrometer with attached Janis Super Vari-Temp liquid helium cryostat. Magnetic circular dichroism (MCD) spectra and VTVH data were collected using CD spectrophotometers incorporating an Oxford Instruments SM4-7T magnetocryostat. Two overlapping wavelength regions on two separate CD spectrophotometers were used: JASCO J200 with liquid  $\text{N}_2$  cooled InSb detector for 2500–600 nm and JASCO J500 with extended S20 photomultiplier tube detector for 850–300 nm. Mulls were prepared in a glovebag under an  $\text{N}_2$  atmosphere at  $4^\circ\text{C}$  by grinding with a cooled mortar and pestle. The fine powder was suspended in Nujol mulling agent and spread between quartz disks. The sample was stored in liquid  $\text{N}_2$  once prepared.

**2.3. Resonance Raman.** Excitation for resonance Raman (rR) spectra was provided by a Coherent I90C-K  $\text{Kr}^+$  and Innova Sabre 24/7  $\text{Ar}^+$  continuous wave ion lasers. Spectra were collected using a series of lines between 752 and 413 nm and incident power in the 5–20 mW range. The sample was placed in an air-driven NMR spinner with cooled ( $\sim 120\text{ K}$ )  $\text{N}_2$  gas flow, arranged in a  $\sim 135^\circ$  backscattering geometry and a polarization scrambler in front of the spectrograph entrance slits. Spectra were collected using a Princeton Instruments ST-135 back-illuminated CCD detector on a Spex 1877 CP triple monochromator with 1200, 1800, and 2400 grooves/nm holographic spectrograph gratings. Samples were prepared by grinding with a cooled mortar and pestle in a glovebag under an  $\text{N}_2$  atmosphere at  $4^\circ\text{C}$ . Similarly ground  $\text{Na}_2\text{SO}_4$  was added and mixed thoroughly before being placed in a

quartz EPR tube. Baseline spectra were collected using ground, activated charcoal in a similar quartz EPR tube.

Normal coordinate analyses (NCA) were performed using the QCPE computer program 576 by M. R. Peterson and D. F. McIntoch, which solves the secular equation  $\mathbf{FG} - \mathbf{E} = 0$  via Miyazawa's diagonalization procedure using a general valence force field.<sup>32–34</sup> Force constants were refined with the nonlinear optimization routine of the simplex algorithm. The  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2]^{3+}$  cation was modeled in the NCA calculations using the “distorted geometry optimized” structure determined via DFT calculations (see section 2.4) with tertiary amine ligands replaced by  $^{25}\text{N}$  and pyridines by  $^{50}\text{N}$ . Models using four ( $\text{Fe}_2\text{O}_2$ ) and eight ( $\text{Fe}_2\text{O}_2^{25}\text{N}_2^{50}\text{N}_2(\text{eq})$ ) atoms were utilized in the NCA calculations to determine the influence of the exogenous ligands upon modal frequencies.

**2.4. Density Functional Calculations.** Electronic structure calculations were performed on an IBM 3BT-RS/6000 computer using version 2.01 of the Amsterdam Density Functional program of Baerends et al.<sup>35,36</sup> The initial structure was obtained from the crystal structure coordinates with nitrogen donors replaced by amines ( $\text{NH}_3$ ). Each atom was described using a triple- $\zeta$  basis set (ADF basis set IV) with a 1s frozen core for oxygen and nitrogen and 2p frozen core for iron. All calculations were performed using the local density approximation of Vosko, Wilk, and Nusair for exchange and correlation<sup>37</sup> and the nonlocal gradient corrections of Becke and Perdew.<sup>38,39</sup> The crystal structure coordinates were successively optimized using the algorithm of Versluis and Ziegler<sup>40</sup> with only the exogenous nitrogen coordinates frozen, then with only the  $\text{Fe}_2\text{O}_2$  core coordinates frozen to create a partially optimized structure which maintains core asymmetry imposed by the ligand. This “distorted geometry optimized” structure is the one described in the discussion unless otherwise noted. Additional Slater-type transition state calculations were performed on this structure to determine single-determinant excited configurational energies.<sup>41</sup> Graphical output of computational results was generated with the Cerius<sup>2</sup> software program developed by Molecular Simulations, Inc.

## 3. Results

**3.1. Absorption and MCD Spectra.** The solid-state mull absorption spectrum of  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2](\text{ClO}_4)_3$  at 5 K is shown in Figure 1a. It consists of a broad absorption envelope with maxima at  $16100\text{ cm}^{-1}$  ( $\epsilon = 3850\text{ M}^{-1}\text{ cm}^{-1}$ ) and  $26700\text{ cm}^{-1}$  ( $\epsilon = 8650\text{ M}^{-1}\text{ cm}^{-1}$ ). The 5 K, 7 T solid-state mull MCD spectrum resolves 13 individual features in the region from 300 to 2150 nm ( $4150\text{--}32500\text{ cm}^{-1}$ ), which are simultaneously Gaussian fit with the absorption data (Table 1). These show C-Term temperature dependence and an alternating sign ( $\pm$ ) with energy (Figure 1b). The ratio of MCD intensity to absorption intensity (C/D) is diagnostic of electronic transition character with a large C/D ratio indicating a large metal-based contribution to the orbitals involved in the transition (d-d transitions), and a small C/D ratio identifying ligand-centered transitions (charge transfer (CT) transitions).<sup>42</sup> The plot of C/D ratio in Figure 1c allows the identification of three regions in

(32) Woodward, L. A. *Introduction to the Theory of Molecular Vibrations and Vibrational Spectroscopy*; Clarendon Press: Oxford, 1972.

(33) Wilson, E. B. J.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; Dover Publications: New York, 1980.

(34) Miyazawa, T. *J. Chem. Phys.* **1958**, *29*, 246.

(35) Baerends, E. J.; Ellis, D. E.; Ros, P. *J. Chem. Phys.* **1973**, *2*, 42.

(36) te Velde, G.; Baerends, E. *J. Int. J. Comput. Phys.* **1992**, *99*, 84.

(37) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

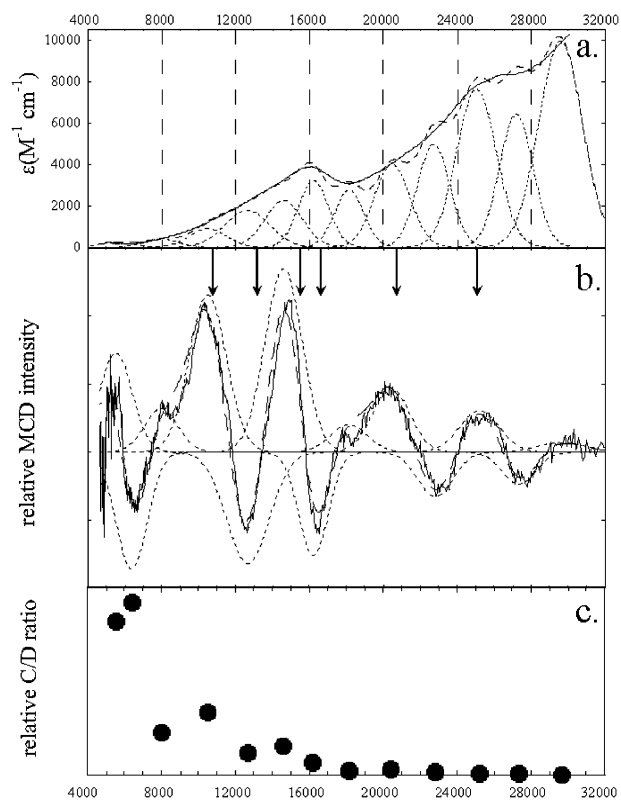
(38) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524.

(39) Perdew, J. P. *J. Chem. Phys.* **1986**, *33*, 8822.

(40) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322–328.

(41) Slater, J. C. *The Calculation of Molecular Orbitals*; John Wiley & Sons: New York, 1979.

(42) Solomon, E. I.; Pavel, E. G.; Loeb, K. E.; Campochiaro, C. *Coord. Chem. Rev.* **1995**, *144*, 369–460.



**Figure 1.** (a) Absorption spectrum of Fe<sub>2</sub>O<sub>2</sub>(5-Et-TPA)<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub> with Gaussian fitting. (b) MCD spectrum with Gaussian fitting and arrows showing the wavelengths at which VTVH data was taken (arbitrary units). (c) C/D ratio of MCD to absorption intensity (arbitrary units).

**Table 1.** Electronic Transition Energies, MCD and Absorption Gaussian Fit Intensities, C/D Ratio, and Transition Polarizations Determined by VTVH Simulations<sup>a</sup>

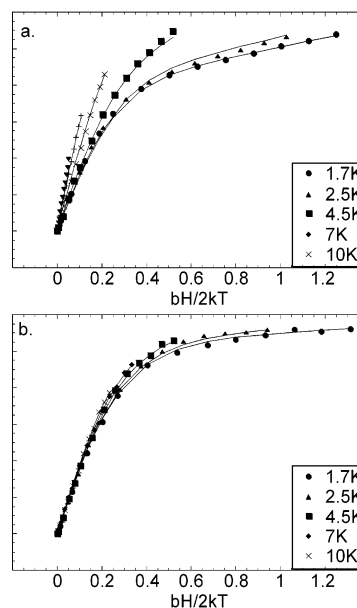
energy (cm <sup>-1</sup> )	MCD intensity	abs. intensity	C/D ratio	polarization
5516	156.5	242	0.2463	
6373	174.8	240	0.2768	
7981	68.4	385	0.0675	
10490	232.0	884	0.0997	y, z
12670	163.5	1778	0.0349	x
14600	266.3	2247	0.0450	y, z
16210	161.2	3217	0.0190	x
18140	44.8	2726	0.0062	
20410	93.7	4214	0.0085	y, z
22810	68.3	4965	0.0052	
25210	59.3	7633	0.0030	y, z
27340	49.3	6433	0.0029	
29640	13.7	9736	0.0005	

<sup>a</sup> Polarizations are given in terms of the molecular coordinate system.

the UV–vis spectrum: strong MCD intensity, weak absorption intensity (4000–10000 cm<sup>-1</sup>); strong MCD intensity, medium absorption intensity (12500–17000 cm<sup>-1</sup>); and weak MCD intensity, strong absorption intensity (17000–30000 cm<sup>-1</sup>) indicating that there are three different types of transitions observed in the electronic spectrum between 4000 and 30000 cm<sup>-1</sup>.

### 3.2. Variable Temperature–Variable Field (VTVH) MCD.

It is possible to determine the polarizations of an electronic transition in randomly oriented samples based upon the shape and nesting of its magnetic saturation curves.<sup>43</sup> VTVH MCD saturation data were collected for the six wavelengths indicated



**Figure 2.** (a) VTVH data with simulation for 13123 cm<sup>-1</sup> that show nested saturation behavior. (b) VTVH data with simulation for 10776 cm<sup>-1</sup> that show unnested saturation behavior.

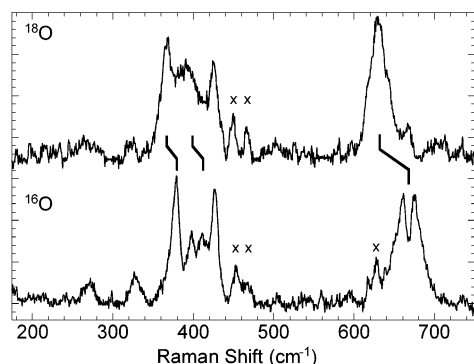
by arrows in Figure 1b. Two types of behavior were observed. Two of the excitation energies studied (13125 and 16665 cm<sup>-1</sup>) showed highly nested VTVH curves (Figure 2a and Supporting Information) while the others showed very little nesting, with the isotherms essentially overlaying each other (Figure 2b and Supporting Information).

To determine the polarizations of the MCD transition at each VTVH wavelength, these data were simulated using eq 1<sup>43</sup>

$$\frac{\Delta\epsilon_{av}}{E} = -\frac{\gamma}{4\pi} \int_{\theta} \int_{\phi} \tanh\left(\frac{g\beta_B B}{2kT}\right) \frac{\sin\theta}{g} (l_x^2 g_x M_{yz}^{eff} + l_y^2 g_y M_{xz}^{eff} + l_z^2 g_z M_{xy}^{eff}) d\theta d\phi \quad (1)$$

where  $g = 2.0023$ ,  $\beta_B$  is the Bohr magneton,  $B$  is the magnetic field,  $l_i$  is the angular momentum operator along axis  $i$ ,  $g_i$  is the  $g$  value along axis  $i$ , and  $M_{ij}^{eff}$  is the effective MCD transition dipole moment, and the expression is integrated over  $\theta$  and  $\phi$  to account for orientational averaging in a powder sample as opposed to a single-crystal measurement.  $M_{ij}^{eff} = m_i^{AJ} m_j^{AK} - L_k \Delta_{KJ}^{-1}$ , where the transition from ground-state A to excited-state J is  $i$  polarized and the transition from A to excited-state K is  $j$  polarized,  $L_k$  represents the spin–orbit coupling moment in the  $k$  direction, and  $\Delta_{KJ}$  is the energy separation between the two excited states. Individual transition polarizations are projected from the calculated  $M_{xy}$ ,  $M_{xz}$ , and  $M_{yz}$  values. Variable temperature EPR and Mössbauer studies have previously measured the molecular zero-field splitting (ZFS),  $D$ , to be  $+35 \pm 15$  cm<sup>-1</sup>.<sup>22</sup> VTVH simulations using this broad range of experimental ZFS values ( $+20 < D < +50$  cm<sup>-1</sup>) resulted in markedly different behaviors. This was most evident for the nested VTVH curves. The best fits to the nested VTVH data were obtained when a zero-field splitting of  $+38 \pm 3$  cm<sup>-1</sup> was used. It was observed that nesting behavior was only reproduced by  $x$ -polarized (i.e., Fe–Fe) simulations, while both  $z$ - and  $y$ -polarizations gave similar fits to unnested VTVH data as the  $g_{z,eff}$  and  $g_{y,eff}$  values are very similar (3.90 and 4.45,

(43) Neese, F.; Solomon, E. I. *Inorg. Chem.* **1999**, *38*, 1847–1865.



**Figure 3.** Raman effect spectra of  $\text{Fe}_2\text{O}_2(5\text{-Et-TPA})_2(\text{ClO}_4)_3$  (647 nm laser excitation). “x” indicates peaks from the  $\text{Na}_2\text{SO}_4$  internal calibrant. The shift in the  $379\text{ cm}^{-1}$  peak upon  $^{18}\text{O}$  substitution is due to a Fermi resonance effect unique to this compound.  $\text{Fe}_2\text{O}_2(\text{R-TPA})_2(\text{ClO}_4)_3$  molecules with differing alkyl substituents do not show this shift.<sup>27</sup>

**Table 2.** Resonance Raman Data for  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2](\text{ClO}_4)_3$

$^{16}\text{O}$ (5-Et <sub>3</sub> -TPA)	$^{18}\text{O}$ (5-Et <sub>3</sub> -TPA)	$\Delta(^{16}\text{O}\text{-}^{18}\text{O})$ range <sup>a</sup>	$\Delta(^{54}\text{Fe}\text{-}^{58}\text{Fe})$ range <sup>a</sup>
666 <sup>b</sup>	631	26–38	2.5–3.7
426	426	0.5–8	6
411		13–18	6.2
397	391	6	4
379	368	0–11	2
328	323	–2 to 0	4
269	265	–1 to 1	0

<sup>a</sup>Ranges of isotope shifts observed in alkyl-substituted  $\text{Fe}_2\text{O}_2(\text{R-TPA})_2(\text{ClO}_4)_3$  analogues. R = 5-Et<sub>3</sub>–, H–, 5-Me<sub>3</sub>–, 5-Me–, and 3-Me<sub>3</sub>–. <sup>b</sup>666  $\text{cm}^{-1}$  is the average energy of the two peaks of the Fermi doublet.

respectively). Table 1 lists the polarizations of the best-fit simulations for each transition in the molecular coordinate system.

**3.3. Raman Spectroscopy.** The resonance Raman spectrum of this molecule has two distinct regions of interest: an intense doublet feature at  $666\text{ cm}^{-1}$  and a group of four modes in the  $380\text{--}425\text{ cm}^{-1}$  region (Figure 3). This behavior is duplicated in three analogous molecules with alkyl substituted pyridine ligands.<sup>27</sup> Upon  $^{18}\text{O}$  substitution, the  $666\text{ cm}^{-1}$  feature and one of the lower energy modes ( $411\text{ cm}^{-1}$ ) shift to lower energy by 31 and  $15\text{ cm}^{-1}$ , respectively, indicating significant oxygen character in these modes. Since the lower energy mode is unresolved in the  $^{18}\text{O}$  spectrum of  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2](\text{ClO}_4)_3$ , the spectra of the closely related alkyl-substituted complexes (where the ethyl substituent has been replaced with a methyl group or hydrogen)<sup>27</sup> are also considered (Table 2). In addition to the  $^{16}\text{O}$  and  $^{18}\text{O}$  isotopomers, the  $^{54}\text{Fe}$ ,  $^{58}\text{Fe}$ , and  $^{15}\text{N}_{\text{amine}}$  isotopomers of the 5-Me<sub>3</sub>-TPA and TPA complexes have been studied, generating a large body of data for analysis.<sup>27</sup>

The doublet observed at  $666\text{ cm}^{-1}$  in the  $^{16}\text{O}$  Raman spectrum of  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2]^{3+}$  has been previously assigned as a Fermi doublet as it is replaced by a single peak upon  $^{18}\text{O}$  substitution.<sup>27</sup> This indicates that there is one mode which is resonance enhanced and of interest in determining the nature of the excited state distortion and another of the same symmetry which coincidentally has a similar energy in the  $^{16}\text{O}$  spectrum. The unmixed modal energies can be determined by solving the interaction matrix,  $M$ , between the two modes. This can be modeled by a  $2 \times 2$  matrix consisting of the preinteraction energies ( $E_i^0$ ) as diagonal elements and the interaction element,  $H_{ab}$ , as the off-diagonal elements.<sup>33</sup>

$$M = \begin{bmatrix} E_a^0 & H_{ab} \\ H_{ab} & E_b^0 \end{bmatrix}$$

The mixed wave functions will be given by

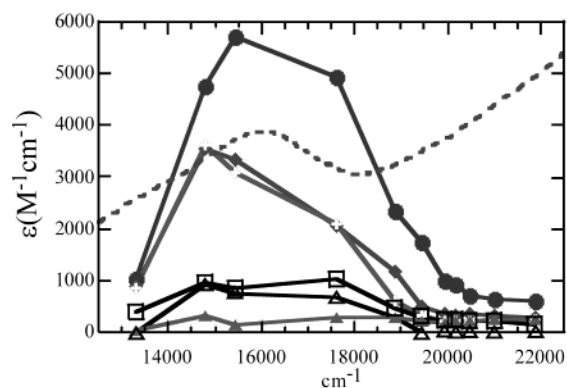
$$\psi_a^{\text{mix}} = \frac{1}{((c_a)^2 + (c_b)^2)^{1/2}} (c_a \psi_a^0 + c_b \psi_b^0)$$

$$\psi_b^{\text{mix}} = \frac{1}{((c_a)^2 + (c_b)^2)^{1/2}} (c_b \psi_a^0 - c_a \psi_b^0)$$

and will be eigenfunctions of matrix  $M$  (with limiting cases:  $c_a = c_b$  if totally mixed and  $c_b = 0$  if noninteracting). The mixed modal energies and intensities are known for the two isotopomers allowing the unmixed energies and intensities to be calculated. This gives the energies of the nonenhanced mode as  $665$  and  $666\text{ cm}^{-1}$  for the  $^{16}\text{O}$  and  $^{18}\text{O}$  form, showing that this mode has minimal oxygen character. The enhanced mode energies are  $666$  and  $640\text{ cm}^{-1}$  for  $^{16}\text{O}$  and  $^{18}\text{O}$ , indicating an isotope shift,<sup>16,18</sup>  $\Delta = 26\text{ cm}^{-1}$ , which is significantly smaller than the  $31\text{ cm}^{-1}$  shift obtained by taking the difference between the mean of the  $^{16}\text{O}$  doublet and the observed  $^{18}\text{O}$  peak. This difference will be of importance to the normal coordinate analysis (see section 4.1). The adjusted oxygen and iron isotope shifts of these molecules are given in Table 2.

Each of the oxygen and iron isotope sensitive modes listed in Table 2 ( $666$ ,  $425$ ,  $411$ ,  $396$ ,  $374\text{ cm}^{-1}$ ) are observed to possess similar resonance Raman enhancement profiles in the region  $13000\text{--}22000\text{ cm}^{-1}$  (Figure 4). Above  $22000\text{ cm}^{-1}$ , even with low laser power and low temperature ( $77\text{ K}$ ), the sample was observed to discolor, indicating decomposition. This prevents the profile from being obtained in this region, although it can be reported that additional resonance intensity of the  $666\text{ cm}^{-1}$  mode is observed in this region. On the basis of isotopic shift data, the two strongly oxygen isotope sensitive bands ( $666$  and  $411\text{ cm}^{-1}$ ) are assigned as Fe–O stretching modes while those with little oxygen isotope sensitivity but significant iron isotope sensitivity ( $425$ ,  $396$ ,  $374\text{ cm}^{-1}$ ) are assigned as Fe–N stretching modes in agreement with previous analysis.<sup>27</sup>

**3.4. Electronic Structure Calculations.** To complement the range of spectroscopies used, spin unrestricted density functional calculations were performed on the single determinant,  $S = 3/2$  ground state of the valence-delocalized model  $[\text{Fe}_2\text{O}_2(\text{NH}_3)_6]^{3+}$  (see Supporting Information for model coordinates). Broken symmetry calculations did not lower the energy of the system or lead to localization. The atomic coordinates used in the model were obtained by freezing the position of the nitrogen ligands in the geometry observed in the crystal structure of  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2](\text{ClO}_4)_3$  and allowing the core oxygens to structurally optimize. This simulates the electronic distortion imposed on the  $\text{Fe}_2\text{O}_2$  core by the constrained 5-Et<sub>3</sub>-TPA ligand, resulting in a DFT optimized geometry that retains the  $C_{2h}$  distortion in the diamond core. This geometry was then reoptimized with the  $\text{Fe}_2\text{O}_2$  core coordinates frozen while floating the positions of the terminal nitrogen ligands. The final geometry was of  $C_{2h}$  symmetry ( $r(\text{Fe}\text{--O}_{\text{short}}) = 1.79\text{ \AA}$  and  $r(\text{Fe}\text{--O}_{\text{long}}) = 1.86\text{ \AA}$ ) with the equatorial nitrogens in the  $\text{Fe}_2\text{O}_2$  plane of inequivalent length ( $r(\text{Fe}\text{--N}_{\text{short}}) = 1.94\text{ \AA}$  and  $r(\text{Fe}\text{--N}_{\text{long}}) = 2.17\text{ \AA}$ ) and the four axial nitrogen distances of equal length ( $r(\text{Fe}\text{--N}_{\text{ax}}) = 2.17\text{ \AA}$ ). The optimized atomic positions differed from those of

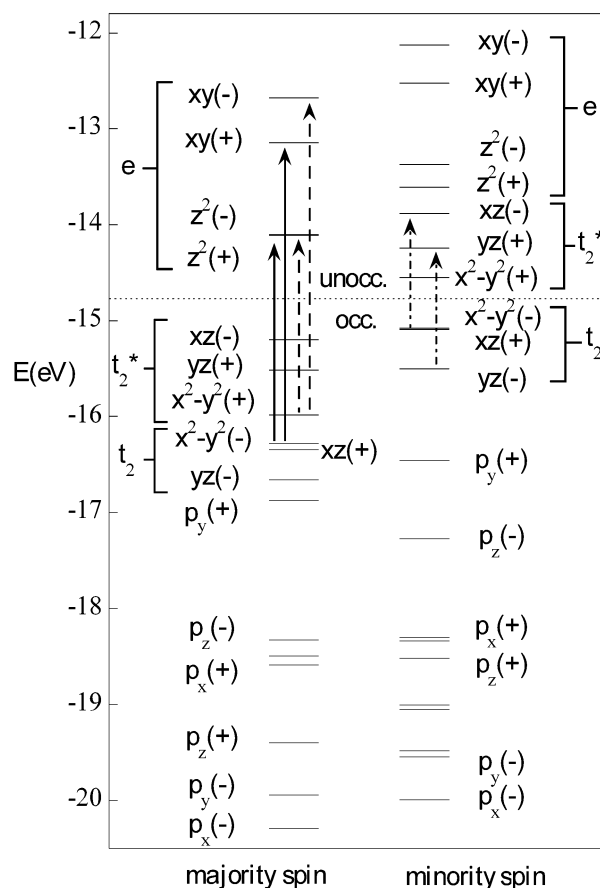


**Figure 4.** Resonance Raman profile of Fe<sub>2</sub>O<sub>2</sub>(5-Et-TPA)<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub>. The absorption spectrum is included as the dashed line, with the profiles of 666 cm<sup>-1</sup> (filled circle), 426 cm<sup>-1</sup> (filled diamond), 411 cm<sup>-1</sup> (empty triangle), 379 cm<sup>-1</sup> (empty cross), 328 cm<sup>-1</sup> (empty square), and 269 cm<sup>-1</sup> (filled triangle) superimposed.

the crystal structure by 0.08 Å for  $r(\text{Fe}-\text{N}_{\text{short}})$ , 0.12 Å for  $r(\text{Fe}-\text{N}_{\text{long}})$  and 0.12 Å for  $r(\text{Fe}-\text{N}_{\text{ax}})$ .

This procedure accounted for both the asymmetry imposed by the exogenous ligand and the differences between the metrics of the crystal structure and those of the lowest energy DFT structure. Comparison of the orbital energy splitting between the “constrained optimized” and crystal structure geometries showed a very similar orbital pattern, as anticipated from the small geometrical changes between the two structures. The greatest change in orbital energies between calculations of the crystal structure geometry and “constrained optimized” geometry is that the high-lying  $xy(-)$   $\sigma^*$  orbital is 2000 cm<sup>-1</sup> higher in energy in the geometry optimized calculation. This is due to the O–O distance decreasing from 2.499 to 2.228 Å upon geometry optimization and indicates some O–O interaction in the geometry-optimized calculations. Full geometry optimization of the [Fe<sub>2</sub>O<sub>2</sub>(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> model results in  $D_{2h}$  symmetry with four equal iron–oxo distances ( $r(\text{Fe}-\text{O}) = 1.807$  Å) (coordinates in Supporting Information). This suggests that the core asymmetry observed derives from the constrained polydentate exogenous ligand, rather than an intrinsic property of the Fe<sub>2</sub>O<sub>2</sub> unit.

The spectroscopically interesting region of the energy level diagram is shown in Figure 5 with energies and compositions of the orbitals given in Table 3. The d-orbital manifold is split into three regions: three doubly (both majority and minority spin) occupied “ $t_2$ ” orbitals, three singly (majority spin) occupied “ $t_2^*$ ” (Figure 6) orbitals, and four unoccupied “e” orbitals.<sup>44</sup> This ligand field splitting between the  $t_2/t_2^*$ <sup>45</sup> and e sets of orbitals is typical of a distorted octahedral geometry for the individual iron atoms. Note that the labels “ $t_2$ ” and “ $t_2^*$ ” differentiate the lower energy, doubly occupied orbitals ( $t_2$ ) from the higher energy, singly occupied orbitals ( $t_2^*$ ) which are most strongly antibonding with the oxo bridges. The four highest energy  $t_2/t_2^*$  orbitals have  $\pi^*$  overlap with the bridging oxo ligands, while for the remaining two these bonding interactions



**Figure 5.** Energy level diagram obtained from a DFT calculation on the restricted geometry optimized structure of Fe<sub>2</sub>O<sub>2</sub>(NH<sub>3</sub>)<sub>6</sub>. Solid arrows show the  $x^2 - y^2(-) \rightarrow z^2(+)$  and  $xy(+)$  transitions, dashed arrows show the  $x^2 - y^2(+)$  and  $xy(-)$  transitions and the dot-dashed arrows show the  $xz(+)$  and  $yz(-) \rightarrow yz(+)$  transitions as discussed in section 4.3.

**Table 3.** Percentage Contributions to Molecular Orbitals of the Geometry Optimized Model<sup>a</sup>

MO label	MO distribution			major orbital contributions
	% Fe	% oxo	% NH <sub>3</sub>	
$xy(+)$	59	24	16	55% Fe $d_{x^2-y^2}$ , 23% O $p_x$
$xy(-)$	60	27	13	59% Fe $d_{x^2-y^2}$ , 1% Fe $d_{xy}$ , 26% O $p_y$
$z^2(-)$	64	8	27	61% Fe $d_{z^2}$ , 7% O $p_x$ , 1% O $p_y$
$z^2(+)$	64	8	27	52% Fe $d_{z^2}$ , 8% Fe $d_{xy}$ , 8% O $p_y$
$xz(-)$	60	31	9	60% Fe $d_{xz}$ , 31% O $p_z$
$yz(+)$	61	38	1	61% Fe $d_{yz}$ , 2% Fe $d_{xz}$ , 38% O $p_z$
$x^2 - y^2(+)$	73	18	8	62% Fe $d_{xy}$ , 11% Fe $d_{z^2}$ , 18% O $p_y$
$x^2 - y^2(-)$	77	17	5	76% Fe $d_{xy}$ , 9% O $p_x$ , 9% O $p_y$
$xz(+)$	89	1	10	87% Fe $d_{xz}$
$yz(-)$	97	1	2	97% Fe $d_{yz}$
O( $p_y^*$ )	20	60	20	11% Fe $d_{xy}$ , 8% Fe $d_{x^2-y^2}$ , 60% O $p_y$
O( $p_z^*$ )	37	60	2	37% Fe $d_{yz}$ , 60% O $p_z$
O( $p_x$ )	14	39	46	8% Fe $d_{xy}$ , 38% O $p_x$

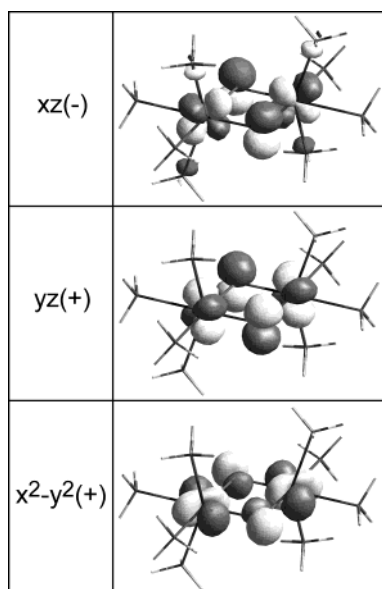
<sup>a</sup> Only majority spin-orbitals are shown as the corresponding minority spin-orbitals differ by <10%. Dashed lines separate doubly occupied (bottom), singly occupied (middle), and unoccupied (top) orbitals.

are symmetry forbidden. The four “e” orbitals;  $z^2(+)$ ,  $z^2(-)$ ,  $xy(+)$ , and  $xy(-)$ ,<sup>46</sup> have  $\sigma^*$  overlap with the ligands ( $xy$  is in

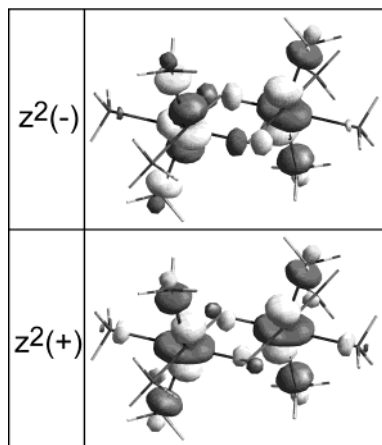
(44) 90% probability density pictures of the full d-manifold are included:  $xy(\pm)$ , Supporting Information Figure 5;  $z^2(\pm)$ , Figure 7;  $t_2^*$ , Figure 6;  $t_2$ , Supporting Information Figure 6. Note that the short Fe–O bonds are at the bottom left and top right of these figures.

(45) The notation “ $t_2/t_2^*$ ” indicates that we are considering the members of both the  $t_2$  and  $t_2^*$  sets of orbitals. Similarly “ $t_2/t_2^* \rightarrow e^*$ ” indicates a transition from a member of either the  $t_2$  or  $t_2^*$  sets of orbitals to a member of the e set of orbitals.

(46) The (+) and (–) notation refers to relative phases of orbitals in the (x, y, z) molecular coordinate system. For the Fe-based orbitals, (+) also indicates gerade inversion symmetry, while (–) is ungerade. For the oxo-based orbitals,  $p_y(-)$  corresponds to the  $\sigma$ -bonding orbital of molecular O<sub>2</sub>,  $p_y(+)$  is  $\sigma^*$ ,  $p_x(+)$  is in the Fe<sub>2</sub>O<sub>2</sub> plane  $\pi$ -orbital,  $p_x(-)$  is  $\pi^*$ ,  $p_z(+)$  is the out-of-plane  $\pi$ -orbital, and  $p_z(-)$  is  $\pi^*$ . This nomenclature does not imply an oxo–oxo overlap at  $r(\text{O}-\text{O}) = 2.499$  Å.



**Figure 6.** Singly occupied  $d_{\pi}$  ( $t_2^*$ ) molecular orbitals identified from density functional theory.



**Figure 7.** Unoccupied majority-spin  $d_{\sigma}$  (e)  $z^2(+)$  and  $z^2(-)$  orbitals

the e set of orbitals as the molecular coordinate system is oriented with the  $x$ -axis bisecting the O–Fe–O angle). The  $xy(\pm)$  orbitals are at a higher energy than the  $z^2(\pm)$  orbitals due to better  $\sigma$ -overlap with the strong oxo donor ligands. The two  $z^2$  orbitals (Figure 7) indicate that the  $\sigma$ -bonding within the  $\text{Fe}_2\text{O}_2$  core is asymmetric, with the oxo p-orbitals rotated by  $22^\circ$  from  $p_x$  ( $z^2(+)$ ) and  $19^\circ$  from  $p_y$  ( $z^2(-)$ ) toward the short Fe–O bond. This asymmetry (distortion from  $D_{2h}$ ) in an unoccupied pair of antibonding orbitals indicates the existence of a corresponding occupied pair of bonding orbitals with similar asymmetry, resulting in inequivalent Fe–O bonds.

A large splitting is found between the  $xz(+)$  and  $xz(-)$  orbitals and between  $yz(+)$  and  $yz(-)$  in the  $t_2/t_2^*$  set of orbitals.  $xz(-)$  and  $yz(+)$  are at high energy due to strong overlap with the two out-of-plane oxo  $p_z$  ligand orbitals (Figure 6) while  $yz(-)$  ( $a_u$  symmetry) and  $xz(+)$  ( $b_g$  symmetry) are at low energy and nonbonding with the oxo atoms as the oxo p-orbital combinations in  $C_{2h}$  symmetry are of either  $b_u$  or  $a_g$  symmetry. Between these are the  $x^2 - y^2(+)$  and  $x^2 - y^2(-)$  orbitals which are less split ( $4300\text{ cm}^{-1}$ ) as these both have in-plane overlap with oxo  $p_y$  and mixed  $p_y/p_x$  orbitals, respectively. The  $x^2 - y^2(-)$  is at lower energy (and hence, doubly occupied) as it has an

additional stabilizing  $\sigma$ -bonding overlap due to the mixed  $p_y/p_x$  oxo contribution arising from the alternating short and long Fe–O bonds of the  $C_{2h}$  distorted  $\text{Fe}_2\text{O}_2$  core.

Immediately below the d-manifold are the six filled oxo 2p orbitals formed from  $\pm$  combinations of the three p-orbitals on each oxo ligand. If bonding consisted of only iron–oxo interactions, the oxo manifold would be the reverse of the iron d-manifold, with the pseudo- $\sigma$  overlapping oxo SALCs (symmetry adapted linear combinations),  $p_y(\pm)$  and  $p_x(\pm)$  at lower energy than the  $\pi$ -overlapping combinations;  $p_z(\pm)$ . However, the highest energy oxo orbital is  $p_y(+)$ . It is located less than  $1800\text{ cm}^{-1}$  below the lowest  $t_2^*$  orbital and far separated ( $11900\text{ cm}^{-1}$ ) from the next oxo orbital indicating that the calculation reflects an interaction between the two oxygen ligands.<sup>47</sup> However, this  $2.5\text{ \AA}$  separation is too long for significant 2p overlap,<sup>48</sup> indicating that the energy of the  $p_y(+)$  orbital is overestimated due to this added interaction. The next oxo-based orbital,  $p_z(-)$ , is  $\pi$ -bonding to the iron  $d_{yz}$  orbitals, while  $p_z(+)$  is slightly lower in energy due to stronger  $\pi$ -bonding overlap with the iron  $d_{xz}$  orbitals. Between these is found the  $p_x(+)$  orbital, which has weak interactions with iron  $z^2(-)$ , while  $p_y(-)$  ( $-$ ) is more stable due to both  $\sigma$ -overlap with the iron  $z^2(+)$  and  $\pi$ -overlap with  $x^2 - y^2(+)$ . The most stable oxo orbital,  $p_x(-)$ , has strong  $\sigma$ -overlap with the iron  $xy(+)$  orbital. Thus, the oxo p-manifold indicates the interplay of two effects; a dominant iron–oxo bonding perturbed by a weak oxo–oxo interaction that is overestimated by the BP86 DFT calculation.

#### 4. Analysis

**4.1. Normal Coordinate Analysis/Force Constant Determination.** Vibrational spectroscopy is highly sensitive to the geometry and bond strengths of a molecule.<sup>33</sup> Two modes are observed to be strongly oxygen isotope sensitive in the resonance Raman spectrum of each of the five previously studied  $\text{Fe}_2\text{O}_2\text{L}_2$  complexes and the 5-Et<sub>3</sub>-TPA complex: one at  $666\text{ cm}^{-1}$  ( $^{16,18}\Delta = 25\text{ cm}^{-1}$ ) and another at  $\sim 410\text{ cm}^{-1}$  ( $^{16,18}\Delta = 15\text{ cm}^{-1}$ ).<sup>27</sup> As described in depth in the Supporting Information, these are assigned as the  $a_{1g}$  and  $b_{1g}$  modes, respectively in  $D_{2h}$ , the latter becoming  $a_g$  in the  $C_{2h}$  symmetry of the rhombic core. This allows mixing of the  $a_{1g}$  ( $D_{2h}$ ) with the  $b_{1g}$  ( $D_{2h}$ ) that derives from the inequivalence of the Fe–O<sub>long</sub> and Fe–O<sub>short</sub> bonds.

Normal coordinate analysis (NCA) is used to determine the relative strength of Fe–O stretching force constants. This analysis gave stretching force constants of  $1.66$  and  $2.72\text{ mdyn/\AA}$  for  $k(\text{Fe–O}_{\text{long}})$  and  $(\text{Fe–O}_{\text{short}})$ , respectively (summarized in Table 4, with the simulation  $f$ -matrix, force constants, and model coordinates in Supporting Information).<sup>49</sup> Table 4 shows that a four-atom model reproduces the isotopic variation of the two strongly oxygen isotope sensitive modes (the modal atomic displacement vectors are shown in Figure 8). The simulation overestimates the isotopic shifts, but this is expected as the four-

(47) A DFT calculation of molecular  $\text{O}_2$  at  $r(\text{O–O}) = 2.499\text{ \AA}$  anticipates the  $3\sigma_g^+ \rightarrow 3\sigma_u^+$  splitting to be  $11500\text{ cm}^{-1}$ .

(48) Ohanian, H. C. *Principles of Quantum Mechanics*; Prentice-Hall: Englewood Cliffs, NJ, 1990.

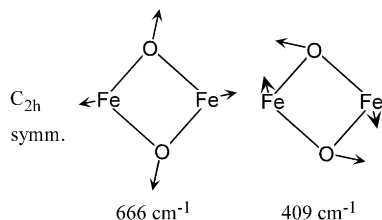
(49) The magnitudes of  $F$ -matrix off-diagonal elements used in the NCA simulations were chosen based on the  $F$ -matrix of the Fe(III)–TPA alkylperoxo monomer (Lehnert, N.; Ho, R. Y. N.; Que, L.; Solomon, E. I. *J. Am. Chem. Soc.* **2001**, *123*, 8271). It is also noted that the NCA solution is not unique and can be achieved by a range of diagonal Fe–O stretching force constants and off-diagonal Fe–O/Fe–O off-diagonal elements. This gives a 35% difference between the two force constants with a str–str interaction of  $0.30\text{ mdyn/\AA}$ , while they differed by 15% with a str–str interaction of  $0.45\text{ mdyn/\AA}$ .



**Table 4.** Comparison of Experimental and Normal Coordinate Analysis Simulated Raman Frequencies for the Fe<sub>2</sub>O<sub>2</sub> and Fe<sub>2</sub>O<sub>2</sub>N(eq)<sub>4</sub> Models<sup>a</sup>

species	Fe <sub>2</sub> O <sub>2</sub> (5-Me <sub>3</sub> -TPA) <sub>2</sub>	Fe <sub>2</sub> O <sub>2</sub> NCA
<sup>16</sup> O <sup>16</sup> O	666	671
<sup>16</sup> O <sup>18</sup> O	(646) <sup>a</sup>	647
<sup>18</sup> O <sup>18</sup> O	640	638
<sup>16</sup> O <sup>16</sup> O	409	410
<sup>16</sup> O <sup>18</sup> O	402	400
<sup>18</sup> O <sup>18</sup> O	394	392

<sup>a</sup> Value estimated from scaling observed Fe<sub>2</sub>O<sub>2</sub>(TPA)<sub>2</sub> peak energies: <sup>16</sup>O<sup>16</sup>O = 666 cm<sup>-1</sup>, <sup>16</sup>O<sup>18</sup>O = 644 cm<sup>-1</sup>, <sup>18</sup>O<sup>18</sup>O = 638 cm<sup>-1</sup>.<sup>27</sup>

**Figure 8.** Stretching vibrational modes of the Fe<sub>2</sub>O<sub>2</sub> core simulated via simultaneously fitted normal coordinate analysis.

atom model requires the 666 and 409 cm<sup>-1</sup> modes to be exclusively due to motion of the iron and oxygen atoms. Any mixing of endogenous Fe–N ligand motion into the experimental Fe<sub>2</sub>O<sub>2</sub> core modes will decrease the fraction of oxygen motion in the mode and, in turn, decrease the isotopic shift.<sup>50</sup>

The magnitude of a stretching force constant is related bond lengths via the empirical relationship commonly referred to as Badger's rule.<sup>51,52</sup> This relationship can be extended to correlate stretching force constant to bond strength, as described in the Supporting Information. Using the NCA Fe–O stretching force constants, the effective bond orders for the short and long Fe–O bonds in the Fe<sub>2</sub>O<sub>2</sub> diamond core are estimated as 1.25 and 1.0, respectively, reflecting the geometric distortion from *D*<sub>2h</sub> symmetry in the diamond core.

**4.2. Excited-State Geometry.** Quantitative analysis of the resonance Raman profile data involves correlating the resonance intensities to the distortions along the normal modes.<sup>33,53</sup> The relative dimensionless excited-state distortion, Δ<sub>κ</sub>, can be determined from the preresonance ratio

$$\frac{I_k}{I_{k'}} = \frac{\Delta_k^2 \nu_k^2}{\Delta_{k'}^2 \nu_{k'}^2} \quad (2)$$

where *I<sub>k</sub>* is the integrated intensity and *ν<sub>k</sub>* is the modal frequency. The relative modal distortions are listed in Table 5. This shows that the excited-state distortion is projected onto a number of vibrational modes, which have been assigned to both iron–oxygen and iron–nitrogen stretching motion. If the electronic transitions in the 13000–21000 cm<sup>-1</sup> region were iron–oxo CT in nature, electron density would move from a filled iron–

**Table 5.** Relative Distortions of Resonance Raman Enhanced Normal Modes of Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub><sup>a</sup>

<i>ν</i> (cm <sup>-1</sup> )	666	426	411	397	378	326
Δ(rel.)	1.00	1.10	0.54	0.57	1.20	0.72

<sup>a</sup> Excitation wavelength = 647 nm.

oxo bonding orbital to its corresponding antibonding orbital as overlap between the ground- and excited-state wave functions is required for absorption intensity. The resulting excited-state geometric distortion would be a lengthening of the iron–oxo bond and would dominantly resonance enhance those modes that vibrate along this bond.

Alternatively, transitions between states in the d-manifold (*t<sub>2</sub>*/\* → *e*) would be *d<sub>π\*</sub>* to *d<sub>σ\*</sub>* in nature. This bonding change would weaken all ligand–metal bonds and result in resonance enhancement of a number of iron–oxo (666, 411 cm<sup>-1</sup>) and iron–nitrogen (426, 397, 378 cm<sup>-1</sup>) based vibrational modes<sup>27</sup> as is observed experimentally. This indicates that the three electronic transitions identified in the simultaneous Gaussian fitting of the absorption and MCD spectra at 14600, 16210, and 18140 cm<sup>-1</sup> involves metal-based (ie *d* → *d*) electronic transitions, consistent with the C/D ratio of MCD to absorption intensity (see section 3.1).

The loss of resonance intensity at high excitation energy (20000–22000 cm<sup>-1</sup>) in all modes is unusual as this region has considerable absorption intensity. This may be due to a resonance interference effect, but photodecomposition of the sample for excitation energies greater than 22 000 cm<sup>-1</sup> prevents this from being evaluated experimentally.

**4.3. Electronic Spectral Assignments: Comparison to BP86 DFT Calculations.** Three regions have been identified in the electronic spectrum from 5000 to 32000 cm<sup>-1</sup> based upon relative C/D ratios (Figure 1). The two lower energy regions (4000–10000 cm<sup>-1</sup>) and (12500–17000 cm<sup>-1</sup>) are metal based and the highest energy region (17000–30000 cm<sup>-1</sup>) is CT in nature. The distortions obtained from the resonance Raman profile also indicate that the 12500–17000 cm<sup>-1</sup> region is metal based as they involve elongation along both iron–oxo and iron–nitrogen bonds. The polarizations of a number of transitions have been obtained from MCD VTVH saturation data and have been related to the molecular coordinate system. These provide a rigorous basis for spectral assignments. The relationship between transition polarizations and their orbital origin is given in the Supporting Information.

The molecular orbital scheme in Figure 5 identifies three types of electronic transitions; *t<sub>2</sub>* → *t<sub>2</sub>*\*, *t<sub>2</sub>*/*t<sub>2</sub>*\* → *e*, and oxo → Fe CT. These are qualitatively correlated with the three regions identified in the absorption and MCD spectra with *t<sub>2</sub>* → *t<sub>2</sub>*\* at lowest energy, *t<sub>2</sub>*/*t<sub>2</sub>*\* → *e* at intermediate energy, and oxo → Fe CT at highest energy. Group theory allows only three transitions of the *t<sub>2</sub>* → *t<sub>2</sub>*\* type: *xz*(+) → *xz*(-), *yz*(-) → *yz*(+), and *x*<sup>2</sup> - *y*<sup>2</sup>(-) → *x*<sup>2</sup> - *y*<sup>2</sup>(+). These are expected to have weak absorption and strong MCD intensity as they are metal-based (*x*-polarized) transitions.<sup>54</sup> The first two are predicted to have similar energies, while the last is expected to be at much lower energy. There are two major transitions in the lowest energy region of the absorption spectrum with weak absorption and strong MCD intensity, 5520 and 6380 cm<sup>-1</sup>. These are assigned to *xz*(+) → *xz*(-) and *yz*(-) → *yz*(+), while *x*<sup>2</sup> - *y*<sup>2</sup>(-) → *x*<sup>2</sup> - *y*<sup>2</sup>(+) is

(50) Additional resonance enhanced vibrations in the 430–250 cm<sup>-1</sup> region show small oxygen isotope shifts (Table 2) and have been previously assigned as Fe–N stretches of the exogenous ligands with some admixture of Fe<sub>2</sub>O<sub>2</sub> core stretching. Qualitative simulations on an Fe<sub>2</sub>O<sub>2</sub>N<sub>4</sub> model (including the equatorial nitrogens) reproduce this behavior, with Δ(<sup>16</sup>O<sup>16</sup>O – <sup>18</sup>O<sup>18</sup>O) = 2 and 1 cm<sup>-1</sup> for the Fe–N<sub>am</sub> and Fe–N<sub>py</sub> stretching modes, respectively, and a similar decrease in the oxygen isotope shift of the Fe–O stretching modes.

(51) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128–131.

(52) Herschbach, D. R.; Laurie, V. W. *J. Chem. Phys.* **1961**, *35*, 458–463.

(53) Henson, M. J.; Mukherjee, P.; Root, D. E.; Stack, T. D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **1999**, *121*, 10332–10345.

(54) Wong, P.; Schatz, P. N. *Prog. Inorg. Chem.* **1981**, *28*, 369.

**Table 6.** Comparison of Calculated and Experimental Electronic Transition Energies and Intensities<sup>a</sup>

transition type	transition	$E_{\text{calc}}$ (cm <sup>-1</sup> )	int <sub>calc</sub>	pol <sub>calc</sub>	$E_{\text{expt}}$ (cm <sup>-1</sup> )	int <sub>expt</sub>	pol <sub>expt</sub>
$t_2 \rightarrow t_2^*$	$yz(-) \rightarrow yz(+)$	9700	1230	x	5516	242	
$t_2 \rightarrow t_2^*$	$xz(+) \rightarrow xz(-)$	10300	1260	x	6373	240	
$t_2 \rightarrow e$	$x^2 - y^2(-) \rightarrow xy(+)$	23590	1560	y	10490	884	(y,z)
$t_2 \rightarrow e$	$x^2 - y^2(-) \rightarrow z^2(+)$	13320	1300	x	12670	1778	x
$t_2^* \rightarrow e$	$x^2 - y^2(+) \rightarrow xy(-)$	20930	1840	y	14600	2247	(y,z)
$t_2^* \rightarrow e$	$x^2 - y^2(+) \rightarrow z^2(-)$	14800	1610	x	16210	3217	x
oxo $\rightarrow$ $t_2$	$p_y \rightarrow x^2 - y^2(+)$	14880	4070	y	>17000		

<sup>a</sup> Calculated intensities are scaled to the experimental values.

predicted to be below 5000 cm<sup>-1</sup>, the detection limit of our MCD spectrometer.

The transitions in the 12500–17000 cm<sup>-1</sup> region will have either dominant metal–metal overlap (the *x*-polarized 12670 and 16210 cm<sup>-1</sup> transitions) or oxo–oxo overlap (the *y*-polarized 10490 and 14600 cm<sup>-1</sup> transitions). These transitions alternate in MCD sign and have similar C-term intensities (Figure 1b and Table 1), suggesting a pseudo-A intensity mechanism.<sup>55,56</sup> This mechanism requires two perpendicularly polarized electric-dipole-allowed transitions from a common ground state (e.g.  $\langle A|x|J\rangle \neq 0$  and  $\langle A|y|K\rangle \neq 0$ ) whose excited states are able to spin–orbit couple via a component of spin angular momentum perpendicular to the transition dipole polarizations (e.g.,  $\langle J|L_z|K\rangle \neq 0$ ). Second-order perturbation theory then requires the two transitions  $A \rightarrow J$  and  $A \rightarrow K$  to be of opposite sign and the same magnitude. A pair of  $t_2 \rightarrow e$  transitions,  $x^2 - y^2(-) \rightarrow z^2(+)$  and  $xy(+)$ , and a pair of  $t_2^* \rightarrow e$  transitions,  $x^2 - y^2(+) \rightarrow z^2(-)$  and  $xy(-)$  (refer to Table 3 for orbital compositions), fulfill the strict requirements of this model. The two pairs differ only by their inversion symmetries, with similar orbital contributions, indicating that they should have similar MCD intensities. The  $x^2 - y^2(+) \rightarrow z^2(-)$  transition is metal–metal (*x*) polarized due to significant mixing of  $x^2 - y^2(-)$  into the excited state.<sup>57</sup> The  $x^2 - y^2(+) \rightarrow xy(-)$  transition is oxo–oxo (*y*) polarized due to overlap of oxo- $p_y$  orbitals. The second pair of transitions differs only in their inversion symmetries, leading to the same polarizations for each transition and the same origin of spin–orbit mixing. This leads to the four transitions in the 12500–17000 cm<sup>-1</sup> region being assigned to  $x^2 - y^2(-) \rightarrow z^2(+)$ ,  $x^2 - y^2(-) \rightarrow xy(+)$ ,  $x^2 - y^2(+) \rightarrow z^2(-)$ , and  $x^2 - y^2(+) \rightarrow xy(-)$ .

The highest energy region of the electronic spectra is dominated by CT transitions as indicated by their small C/D ratio (Figure 1c). Two transitions are observed to not be metal–metal (*y,z*) polarized, indicating that at least two of the transitions are due to either oxo–iron or nitrogen–iron CT transitions. There are a large number of calculated transitions in this region from each of the six oxo *p*-orbital SALCs to the *d*-manifold. These include the excitation from the isolated, high-energy,  $p_y$ - $(+)$  into the  $x^2 - y^2(+)$   $t_2^*$  orbital. It is predicted by the calculation to be at much lower energy (overlapping the  $t_2^* \rightarrow t_2$  or  $t_2^*/t_2 \rightarrow e$  regions) than the other CT transitions, which is not observed experimentally, as the electronic spectrum is split into discrete regions containing transitions of similar origin. This

reflects the overestimation of the O–O interaction in the DFT calculation (see section 3.4).

As presented in the Supporting Information, these experimental electronic spectral assignments were compared to those predicted by density functional theory. This reinforces the observation from the EPR superhyperfine broadening and magnetic tensor analyses<sup>26</sup> that the  $t_2/t_2^*$  splitting is overestimated in the calculation as the experimental  $t_2 \rightarrow t_2^*$  transition energy is ~60% of the calculated value (agreeing well with the 55% covalency scaling required in simulations of the EPR superhyperfine broadening data).<sup>26</sup>

## 5. Discussion

### 5.1. Geometric and Electronic Structure of the Fe<sub>2</sub>O<sub>2</sub> Diamond Core.

We have observed that a fully geometry optimized Fe<sub>2</sub>O<sub>2</sub> core has *D*<sub>2h</sub> symmetry but that this symmetry is reduced to *C*<sub>2h</sub> in the presence of inequivalent equatorial nitrogen donors. This inequivalence arises both from the steric constraints of 5-Et<sub>3</sub>-TPA and from the chemical nature of the nitrogen donors, tertiary amine and alkyl-substituted pyridine, resulting in unequal Fe–N bond lengths,  $r(\text{Fe–N}_{\text{am}}) = 2.049$  Å vs  $r(\text{Fe–N}_{\text{eq}}) = 2.025$  Å (*N*<sub>eq</sub> refers to the equatorial pyridine ligand). As a result, the oxo ligand trans to the long Fe–N<sub>am</sub> bond can more easily donate charge to the iron, resulting in a shorter Fe–O bond relative to the oxo bond trans to the short Fe–N<sub>eq</sub> bond.

DFT calculations identify the magnitude of Fe–O bond strength asymmetry in the  $S = 3/2$ , valence delocalized Fe<sub>2</sub>O<sub>2</sub> core. The iron–oxo bonds consist of a fraction (~0.375) of a  $\pi$ -bond (from three half-filled,  $\pi$ -antibonding orbitals spread over four iron–oxo bonds) and a  $\sigma$ -bond. The  $\sigma$ -bond is generated by two unoccupied  $x^2 - y^2$  orbitals contributing strong  $\sigma$ -bonds, while the unoccupied pair of  $z^2$  orbitals only contributes weakly to bonding as reflected by their small oxo contributions relative to the  $x^2 - y^2$  orbitals (Figure 7 and Table 3). This sum (two strong plus two weak  $\sigma$  bonds) is distributed over the four Fe–O bonds, resulting in a single  $\sigma$  bond. In the distorted diamond core, the  $\pi$ -overlapping SOMOs are symmetric with respect to metal–oxo bonding (Figure 6), while the unoccupied  $\sigma$ -molecular orbitals have some asymmetry (Figure 7). This derives from contributions from both oxo  $p_x$  and  $p_y$ , resulting in a rotated pair of oxo *p*-orbitals which point along the shorter iron–oxo bond (Figure 7). This deviation from *D*<sub>2h</sub> symmetry for the unoccupied orbitals indicates that there is a corresponding set of bonding orbitals with similar asymmetry, reflecting asymmetry in the bonding of the Fe<sub>2</sub>O<sub>2</sub> core.

For small deviations from *D*<sub>2h</sub>, the core  $\sigma$ -bonding is well described by the *xy* orbital, whose lobes are directed along the two Fe–O vectors. At large deviations, with one Fe–O bond

(55) Solomon, E. I.; Hanson, M. A. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; John Wiley & Sons: New York, 1999; Vol. 2, pp 1–130.

(56) Peipho, S. B.; Schatz, P. N. *Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism*; John Wiley & Sons: New York, 1983.

(57) This is not a consequence of the *C*<sub>2h</sub> core distortion as  $x^2 - y^2(-)$  and  $z^2(-)$  are both of *A*<sub>1g</sub> symmetry under *D*<sub>2h</sub>.

much stronger than the other, there will be a rotation of the molecular coordinate system, with the  $z^2$  orbital becoming collinear with the stronger Fe–O bond, resulting in alternating single and double bonds within the Fe<sub>2</sub>O<sub>2</sub> core. Previous literature descriptions of the high-valent Fe<sub>2</sub>O<sub>2</sub> core proposed for intermediate **Q** of MMO range from an electronically symmetric rhombus<sup>58–60</sup> to a dimer of ferryl units (for the Fe<sub>2</sub>-(4,4) case) resulting in alternating single and double bonds (asymmetric).<sup>3,61</sup> DFT calculations indicate that the core asymmetry of the [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> molecule is not large enough to result in rotation of the molecular coordinate system (to having  $z^2$  along the stronger Fe–O bond) as illustrated by the unoccupied  $\sigma$ -antibonding contours in Figure 7. Thus the bonding within the Fe<sub>2</sub>O<sub>2</sub> diamond core is calculated to be nearer to the symmetric limit.

The limited difference in bond order predicted by the DFT calculation can be estimated by the angular overlap model (AOM)<sup>62–64</sup> and tested by experiment. AOM indicates that the short Fe–O bond is ~15% stronger than the long Fe–O bond. From resonance Raman data, NCA analysis of the oxygen isotope sensitive normal modes have identified differences between the stretching force constants of the long and short Fe–O bonds ( $k_{\text{str}}(\text{Fe}-\text{O}_{\text{long}}) = 1.66$  and  $k_{\text{str}}(\text{Fe}-\text{O}_{\text{short}}) = 2.72$  mdyn/Å). These can be correlated with the stretching force constants and bond orders of other iron–oxo species to estimate the relative Fe–O bond strengths. This gives bond orders of 1.25 and 1.0 for Fe–O<sub>short</sub> and Fe–O<sub>long</sub>, respectively, consistent with the AOM values. Thus, the electronic asymmetry in the Fe<sub>2</sub>O<sub>2</sub> core is limited, deriving from inequivalence of equatorial Fe–N bonds. Importantly, the  $t_2^*$  valence orbitals important for the unique spectral properties and reactivity (see section 5.3) of this core are not affected by this asymmetry.

**5.2. Valence Delocalization.** Valence delocalization in mixed-valent binuclear systems can arise from direct metal–metal interactions and/or superexchange pathways involving bridging ligands. Both resonance Raman spectroscopy and the experimentally calibrated calculated splitting of the  $t_2/t_2^*$  manifold allow the relative importance of these two interactions to be evaluated.

A-term resonance Raman enhancement occurs for totally symmetric modes whose motion has a nonzero projection onto electronic excited-state distortions. No oxygen isotope sensitive modes are observed below 250 cm<sup>-1</sup>, while accordion modes are typically found in the 100–125 cm<sup>-1</sup> region.<sup>53,65</sup> In the Fe<sub>2</sub>-(OH)<sub>3</sub><sup>65</sup> core a low-energy core mode (124 cm<sup>-1</sup>) is resonance enhanced and has been assigned to the totally symmetric accordion motion. This is a bending motion which results in a large change in the metal–metal distance while keeping the

metal-bridging ligand bond lengths constant. Resonance enhancement of this mode in Fe<sub>2</sub>(OH)<sub>3</sub> indicates that the primary bonding change between the ground and excited state is between the two metals, indicating a strong metal–metal interaction. For the Fe<sub>2</sub>O<sub>2</sub> complexes studied here, the  $t_2^* \rightarrow e$  transitions would be expected to distort along this coordinate if direct metal–metal overlap occurs as the donor orbital is Fe–Fe  $\pi$ -bonding (Figure 6) while the acceptor orbital has a  $\sigma^*$  Fe–Fe orientation ( $z^2(-)$ , Figure 7). The absence of the accordion mode in the resonance Raman spectra of Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub><sup>3+</sup> indicates that there is no significant metal–metal interaction influencing the bonding in the core.

This is supported by the ligand field splitting of the  $t_2/t_2^*$  manifold predicted by DFT calculations; all three of the lower energy  $t_2$  orbitals have antibonding iron–iron overlap ( $yz(-)$ ;  $\delta^*$ ,  $xz(+)$ ;  $\pi^*$ ,  $x^2 - y^2(-)$ ;  $\sigma^*$ ) while the higher energy  $t_2^*$  orbitals have bonding metal–metal overlap (Figures 5 and 6). The opposite energy order would be observed if metal–metal bonding was a dominant feature of the Fe<sub>2</sub>O<sub>2</sub> core. The superexchange contributions to valence delocalization can be identified in the SOMOs. Each of the SOMOs has significant oxo contributions that are oriented for  $\pi$ -overlap with the iron d-orbitals (Figure 6). This overlap constitutes a series of strong superexchange pathways by which electron density can be delocalized over the Fe<sub>2</sub>O<sub>2</sub> core. This results in a spin density of 30–35% on each iron atom in each of the three SOMOs that is further stabilized by electron exchange to form the observed  $S = 3/2$  spin-delocalized ground state.

This DFT description is probed by ground-state magnetic data, particularly by the previously analyzed superhyperfine tensor and its anisotropy.<sup>26</sup> The presence of significant oxo character in the three SOMOs is identified by the broadening of the  $g_{\text{eff}} = 3.90$  feature upon <sup>17</sup>O substitution. This anisotropy in the  $g_z$  direction (perpendicular to the Fe<sub>2</sub>O<sub>2</sub> plane) is shown by the calculations to be due to the  $t_2^*$   $yz(+)$  and  $xz(-)$  orbitals (Figure 6) which contain large oxo  $p_z$  contributions. These orbitals are activated for hydrogen atom abstraction by their low energy and strong oxo content.

**5.3. Reactivity.** The [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>]<sup>3+</sup> ion is observed to either hydroxylate or desaturate cumene via a 2:1 [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>]<sup>3+</sup>/cumene stoichiometry.<sup>30,31</sup> The first reaction step is a hydrogen atom abstraction from the cumene  $\alpha$ -carbon to generate a cumene radical which reacts with the second [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>]<sup>3+</sup> molecule to generate either  $\alpha$ -methyl styrene or cumyl alcohol. We can apply our electronic structure description of [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>]<sup>3+</sup> to investigate the hydrogen atom abstraction step from cumene.<sup>66</sup>

The frontier molecular orbital (FMO) formalism identifies the key contributors to intermolecular reactivity.<sup>67–69</sup> These are the net atomic charges and the energies and overlaps of the electron donor and acceptor orbitals. The bridging oxo and cumene  $\alpha$ -H atoms which bond during the hydrogen atom abstraction step have favorable charges, with the  $\alpha$ -H having a

- (58) Gherman, B. F.; Dunitz, B. D.; Whittington, D. A.; Lippard, S. J.; Friesner, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 3836–3837.  
 (59) Dunitz, B. D.; Beachy, M. D.; Cao, Y. X.; Whittington, D. A.; Lippard, S. J.; Friesner, R. A. *J. Am. Chem. Soc.* **2000**, *122*, 2828–2839.  
 (60) Torrent, M.; Musaev, D. G.; Basch, H.; Morokuma, K. *J. Comput. Chem.* **2002**, *23*, 59–76.  
 (61) Siegbahn, P. E. M.; Crabtree, R. H.; Nordlund, P. *J. Biol. Inorg. Chem.* **1998**, *3*, 314–317.  
 (62) Companion, A. L.; Komarynsky, M. A. *J. Chem. Educ.* **1964**, *41*, 257–264.  
 (63) Solomon, E. I.; Lever, A. B. P. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; John Wiley & Sons: New York, 1999; Vol. 1, pp 1–92.  
 (64) Antibonding overlap between unoccupied Fe d-orbitals and oxo p-orbitals was used as an estimate of bond strength in the corresponding filled bonding orbitals, with the approximation;  $\pi$ -bond = 0.75  $\sigma$ -bond.  
 (65) Gamelin, D. R.; Bominaar, E. L.; Mathoniere, C.; Kirk, M. L.; Wiegardt, K.; Girerd, J. J.; Solomon, E. I. *Inorg. Chem.* **1996**, *35*, 4323–4335.

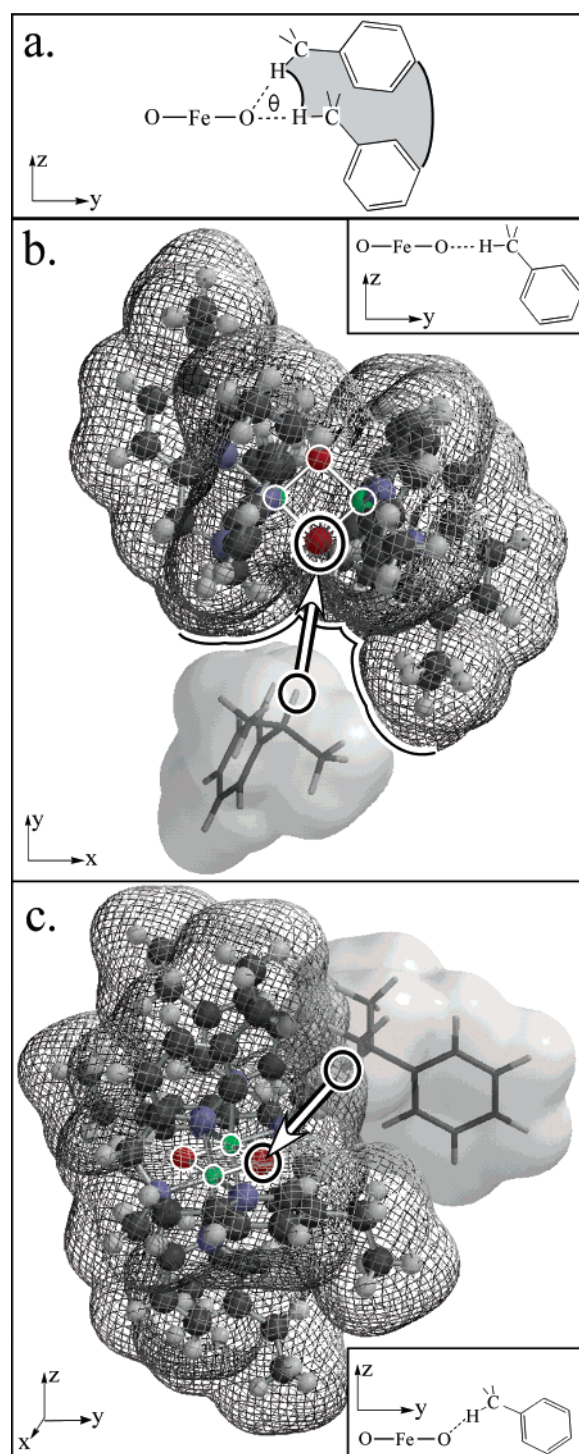
- (66) A hydride transfer mechanism is not considered because radical trapping of a cumylperoxy species is observed when oxidation of cumene by the dimer is performed aerobically and the observation of formation of the phenoxy radical of 2,4-di-*tert*-butylphenol upon mixing with the dimer. Both of these observations indicate that a hydrogen atom abstraction step begins the oxidation process. (Kim, C.; Dong, Y. H.; Que, L. *J. Am. Chem. Soc.* **1997**, *119*, 3635–3636.)  
 (67) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223–228.  
 (68) Salem, L. *J. Am. Chem. Soc.* **1986**, *90*, 543–552.  
 (69) Salem, L. *J. Am. Chem. Soc.* **1986**, *90*, 553–559.

weak positive dipole and the oxo having a calculated negative charge similar to that of the bridging oxo in  $[\text{Cu}_2\text{O}_2]^{2+}$  which also performs H-atom abstraction.<sup>70</sup> The donor orbital of cumene is the  $\sigma$ -bonding orbital of the  $\alpha$ -C–H bond. Our studies have identified the acceptor orbitals to be the three  $t_2^*$  SOMO orbitals, which are separated by less than  $5000\text{ cm}^{-1}$ . The orbital overlap term depends on both the oxygen orbital coefficient and the orientation of the oxo contribution to the molecular orbitals involved in the reaction. The  $x^2 - y^2(+)$  is oriented with its oxo p-lobes in the y-direction (along the O–O vector), while for both  $yz(+)$  and  $xz(-)$  the oxo  $p_z$ -orbitals are oriented out of the  $\text{Fe}_2\text{O}_2$  plane (Figure 6). Further, the  $yz(+)$  and  $xz(-)$  are calculated to have much greater oxo  $p_z$  character than the  $x^2 - y^2(+)$  oxo  $p_y$  contribution (38% and 31% vs 18%) making substrate approach from out of the  $\text{Fe}_2\text{O}_2$  plane more favorable than approach along the O–O vector.

To determine the ability of substrate to approach and overlap with these  $t_2^*$  orbitals, molecular mechanics (pm3(tm)) calculations were performed to identify the reaction coordinate involving the least steric interference from the endogenous 5-Et<sub>3</sub>-TPA ligand while allowing greatest overlap between the cumene  $\alpha$ -C–H orbital and the relevant oxo p-orbital.<sup>71</sup> The lowest energy approach of cumene to  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2]^{3+}$  consists of a family of orientations with the  $\alpha$ -H in the y–z plane of the molecular coordinate system and the plane of the phenyl ring within  $\sim 10^\circ$  of the y–z plane. The phenyl ring orientation is chosen to minimize the interaction of the cumene phenyl and  $\beta$ -methyl groups with the endogenous 5-Et<sub>3</sub>-TPA ligands. The O–( $\alpha$ -H) vector and the molecular y-axis can adopt a range of values, with  $-55^\circ > \theta > 55^\circ$ , as shown in Figure 9a, with a linear O–O–( $\alpha$ -H) defined to be  $0^\circ$ . Figure 9a shows the range of substrate approaches traced between the  $\theta = 0^\circ$  and  $55^\circ$  configurations, with Figure 9b and Figure 9c showing the 90% electron density surfaces of the cumene and  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2]^{3+}$  in the  $0^\circ$  and  $50^\circ$  configurations, respectively.

Approach with the cumene  $\alpha$ -C–H bond in the  $\text{Fe}_2\text{O}_2$  plane ( $\theta = 0^\circ$ ) is hindered by the presence of the equatorial ethyl-substituted pyridine ligand and the tertiary amine (highlighted by dark line in Figure 9b). This reaction coordinate is further limited by the low  $< 18\%$  oxo  $p_y$  contribution which is only present in one  $t_2^*$  orbital (the  $x^2 - y^2(+)$ ). As the O–O–( $\alpha$ -H) angle is increased from linear ( $\theta = 0^\circ$ ), the steric interaction decreases, minimizing at  $50^\circ$  (Figure 9c). The steric contribution to the system energy at  $\theta = 50^\circ$  was half that at  $0^\circ$ . Importantly, this approach affords good overlap with the more highly covalent  $yz(+)$  and  $xz(-)$  oxo  $p_z$ -orbitals (38% and 31% respectively).<sup>72</sup>

Hence, the best approach geometry to the bridging oxo is with the O–( $\alpha$ -H) vector rotated  $\sim 50^\circ$  from the molecular y-axis (O–O vector) as this simultaneously minimizes the steric

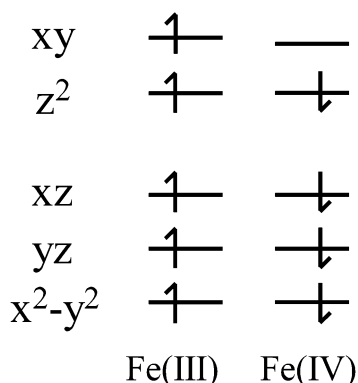


**Figure 9.** Calculated pm3(tm) cumene approach trajectories. (a) Range of cumene approach angles in the y–z plane (Fe is out of this plane but included for perspective), shown for  $0^\circ < \theta < 55^\circ$ . (b) pm3(tm) calculated 90% electron potential energy surfaces for cumene approach with  $\theta = 0^\circ$ . (c) pm3(tm) calculated 90% electron potential energy surfaces for cumene approach with  $\theta = 50^\circ$ . The arrow is the  $\alpha$ -H–oxo vector and circles highlight the cumene  $\alpha$ -H and the atoms of the  $\text{Fe}_2\text{O}_2$  core for clarity.

interaction energy while allowing good overlap with the highly covalent SOMOs,  $yz(+)$  and  $xz(-)$ . This reaction is driven by having low energy  $t_2^*$  acceptor orbitals with significant oxo character perpendicular to the  $\text{Fe}_2\text{O}_2$  plane providing good overlap with the cumene C– $\alpha$ -H donor orbital in an orientation compatible with the steric constraints of the 5-Et<sub>3</sub>-TPA ligand.

(70) Chen, P.; Solomon, E. I. *J. Inorg. Biochem.* **2002**, *88*, 368–374.

(71) The 90% electron density surfaces were calculated for cumene and  $[\text{Fe}_2\text{O}_2(5\text{-Et}_3\text{-TPA})_2]^{3+}$  to determine possible directions of approach for cumene to the sterically hindered  $\text{Fe}_2\text{O}_2$  core. Single point enthalpy of formation values was calculated for a variety of orientations using a 3.2 Å  $\alpha$ -C–bridging oxo distance to gauge the effect of the steric bulk upon substrate approach. This distance is greater than the 2.55 Å (Basch, H.; Musaev, D. G.; Mogi, K.; Morokuma, K. *J. Phys. Chem. B* **2001**, *105*, 4770–4770. Musaev, D. G.; Basch, H.; Morokuma, K. *J. Am. Chem. Soc.* **2002**, *124*, 4135–4148.)  $\rightarrow$  2.70 Å (Siegbahn, P. E. M. *Inorg. Chem.* **1999**, *38*, 2880–2889.)  $\alpha$ -C–bridging oxo distance proposed for the transition state of the putative hydrogen atom abstraction step in MMO, but using  $r(\alpha\text{-C–O}) = 2.6$  Å led to ligand–substrate approaches of less than the combined van der Waals radii. Thus, the longer distance was used to identify steric barriers.



**Figure 10.** d-manifold orbital occupation for intermediate **X** of RR.

The reactive nature of the d-orbitals to H-atom abstraction by the oxo bridge is thus due to the strong oxo-iron donor interaction within the diamond core.

**5.4. Relation to Protein Intermediates. 5.4.1. Ribonucleotide Reductase (RR).** The activated oxygen intermediate **X** of class I ribonucleotide reductase has been identified to contain an Fe<sub>2</sub>(III,IV) center with bridging oxygen donors.<sup>17–20</sup> Among the possible geometries are the bis-μ-oxo or μ-oxo-μ-1,1-carboxylato core. This enzyme intermediate differs from the [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>]<sup>3+</sup> model in its spin state and charge distribution as each iron is high spin and AF coupled to produce a  $S = 1/2$ , valence-localized ground state, while the model complex has two low-spin irons generating a  $S = 3/2$ , valence-delocalized ground state.

Changing from low-spin iron to high-spin iron in the Fe<sub>2</sub>(III,IV) bis-μ-oxo core results in electrons being redistributed among the 10 d-orbitals (Figure 10). The ligand-field splitting pattern of the  $S = 3/2$  d-manifold, indicates that the low-spin core has four unfilled σ-orbitals and three half-filled π-orbitals, while the high-spin analogue has one unfilled and three half-filled σ-orbitals and six half-filled π-orbitals.<sup>73</sup> Therefore, going to high spin results in some σ-bonding being lost (and replaced by π-bonding), resulting in a net weakening of the bonding within the Fe<sub>2</sub>O<sub>2</sub> core. The weaker iron-oxo bonds of the high-spin isomer would also be longer than those of the low-spin complex. This predicted weakening of the bonding within the Fe<sub>2</sub>O<sub>2</sub> core is consistent with results for the high-spin [Fe<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O)(6-Me<sub>3</sub>-TPA)<sub>2</sub>]<sup>3+</sup> species for which the Fe<sup>III</sup>-O-Fe<sup>IV</sup>=O core is formed.<sup>29,74</sup> This molecule consists of two AF-coupled high-spin iron ions which generate a  $S = 1/2$  ground state, as

observed in **X**. This observation is also consistent with ENDOR analysis which favors a mono-oxo bridge with a terminal oxo/hydroxo/water ligand structure for **X**.<sup>19,20</sup>

The high-spin complex would be expected to be antiferromagnetically (AF) coupled. This can be seen by comparing the exchange pathways of the high-spin bis-μ-oxo, d<sup>4</sup>d<sup>5</sup> Fe<sub>2</sub>(III,IV) complex to those of high-spin bis-μ-oxo, d<sup>4</sup>d<sup>4</sup> Mn<sub>2</sub>(III,III), which has strong AF coupling with  $2J = -201 \text{ cm}^{-1}$  ( $H = -2J S_1 \cdot S_2$ ).<sup>75,76</sup> The change in the d-manifold electron population between Mn<sub>2</sub>(III,III) and Fe<sub>2</sub>(III,IV) is the addition of one electron to the in-plane σ\* xy orbital. This results in the replacement of one ferromagnetic (F) pathway with an AF pathway and Fe<sub>2</sub>(III,IV) having an additional AF contribution to  $J$  relative to Mn<sub>2</sub>(III,III). Thus, a high-spin Fe<sub>2</sub>(III,IV) bis-μ-oxo or structurally related dimer is expected to display AF coupling and a  $S = 1/2$  ground state as observed experimentally in **X**.

Valence delocalization in the  $S = 3/2$  complex is due to the three strong oxo-π superexchange pathways (Figure 6). The ability of a complex to maintain delocalization and avoid vibronic trapping increases with the splitting between the singly occupied d-orbital (+) and (−) combinations. In the  $S = 3/2$  complex, the calculated splittings between the x<sup>2</sup> - y<sup>2</sup>(±), xz(±), and yz(±) molecular orbitals are 3320, 9460, and 9670 cm<sup>-1</sup>, respectively, providing a large contribution to resonance delocalization. For the high-spin case, the three π pathways are lost, being replaced by one xy σ pathway<sup>77</sup> resulting in a much smaller barrier to vibronic trapping. Additionally, vibronic trapping will be much greater for the high-spin Fe<sub>2</sub>(III,IV) as the electron being delocalized is in a σ\* rather than a π\* d-orbital. This leads to a much larger geometric distortion with electron delocalization, further stabilizing the valence-localized structure.

This analysis indicates that decreasing the t<sub>2</sub>/e ligand field splitting of the two irons in the  $S = 3/2$  dimer to generate two high-spin metal ions is expected to change Fe<sub>2</sub>O<sub>2</sub> core bonding and spin topology to form a valence localized, AF-coupled  $S = 1/2$  core, the magnetic signature observed for intermediate **X** of RR.

**5.4.2. Methane Monooxygenase (MMO).** Intermediate **Q** of MMO is proposed to consist of a bis-μ-oxo Fe<sub>2</sub>(IV,IV) AF coupled,  $S = 0$  core based on EXAFS and Mössbauer data.<sup>3,15,16</sup> Oxidation of the [Fe<sub>2</sub>O<sub>2</sub>(5-Et<sub>3</sub>-TPA)<sub>2</sub>]<sup>3+</sup> ion will generate an Fe<sub>2</sub>(IV,IV) center with one less electron in the t<sub>2</sub>\* set of orbitals. This will also increase Z<sub>eff</sub>, resulting in shorter Fe-O bonds and larger ligand-field splitting within the d-manifold. This will have a small effect upon the splitting within the t<sub>2</sub>\* set leading to the prediction that this core would display a  $S = 1$  ground state, in contrast with the experimentally observed spin  $S = 0$  of **Q**.<sup>78</sup> However, the high-spin bis-μ-oxo Fe<sub>2</sub>(IV,IV) dimer, the one-electron oxidized form of the high-spin Fe<sub>2</sub>(III,IV) in Figure

(72) An additional orientation with the cumene phenyl ring between two adjacent 5-Et<sub>3</sub>-TPA pyridines was also found (figure in Supporting Information). In this conformation,  $\theta = 40^\circ$ , with the cumene α-H displaced slightly from the y - z plane. The steric energy was similar to that of the configuration with  $\theta = 50^\circ$  and the cumene phenyl in the y - z plane (Figure 9c). However, this was only possible with the pyridine ethyl substituents rotated away from the cumene. In solution these are able to freely rotate, periodically blocking this cleft and hindering the approach of the cumene α-H to the Fe<sub>2</sub>O<sub>2</sub> core.

(73) This corresponds to <sup>8</sup>/<sub>2</sub>σ bonds and <sup>3</sup>/<sub>2</sub>π bonds distributed over the four Fe-O bonds for the low-spin complex, and a net <sup>5</sup>/<sub>2</sub>σ and <sup>9</sup>/<sub>2</sub>π for the high-spin analogue.

(74) Both the high-spin and low-spin states can be accessed in mononuclear peroxo-Fe(III)-TPA complexes by varying the position of alkyl substituents on the TPA ligand, resulting in small changes in the Fe-N(TPA) bond lengths. (Zang, Y.; Kim, J.; Dong, Y. H.; Wilkinson, E. C.; Appelman, E. H.; Que, L. *J. Am. Chem. Soc.* **1997**, *119*, 4197–4205.) The bonding in such complexes is dominated by the iron-peroxo interaction. (Lehnert, N.; Ho, R. Y. N.; Que, L.; Solomon, E. I. *J. Am. Chem. Soc.* **2001**, *123*, 8271–8290. Lehnert, N.; Ho, R. Y. N.; Que, L.; Solomon, E. I. *J. Am. Chem. Soc.* **2001**, *123*, 12802–12816.) This indicates that small changes in the substituted TPA ligand can change the spin state without changing the dominant contributors to the electronic structure of the complex.

(75) Glerup, J.; Goodson, P. A.; Hazell, A.; Hazell, R.; Hodgson, D. J.; McKenzie, C. J.; Michelsen, K.; Rychlewski, U.; Toftlund, H. *Inorg. Chem.* **1994**, *33*, 4105–4111.

(76) Exchange between two SOMOs with orbital overlap produces an AF contribution to  $J$ , exchange between a SOMO and an unoccupied molecular orbital results in a ferromagnetic (F) contribution to  $J$ , and that pairs of unoccupied orbitals do not contribute to exchange. (Goodenough, J. B. *Phys. Rev.* **1955**, *79*, 564. Kanamori, J. *J. Phys. Chem. Solids* **1959**, *10*, 87.) These contributions are summed over the 25 orbital pathways ( $5 \times 5$  combinations of d-orbitals) to generate the observed ground-state spin ladder.

(77) The xy(±) pair are split by 3450 cm<sup>-1</sup> in the valence-delocalized  $S = 3/2$  calculation.

10, is expected to have a  $S = 0$  ground state. It is isoelectronic with both the bis- $\mu$ -oxo  $\text{Mn}_2(\text{III},\text{III})$  and mono- $\mu$ -oxo  $\text{Mn}_2(\text{III},\text{III})$  structures. The former exhibits strong AF exchange coupling ( $2J = -201 \text{ cm}^{-1}$  [ $H = -2J S_1 \cdot S_2$ ])<sup>75</sup> while the latter shows weak coupling (both AF and F) for complexes whose metal–metal separation is consistent with the EXAFS metal–metal distance observed for **Q**.<sup>79</sup> **Q** has large exchange coupling, with only a lower limit established ( $-J > 30 \text{ cm}^{-1}$ ), consistent with the doubly bridged structure.

The FMO contribution to reactivity of the high-spin bis- $\mu$ -oxo  $\text{Fe}_2(\text{IV},\text{IV})$  dimer is anticipated to be quite different from that of the  $S = 3/2$  complex. The acceptor orbitals on the  $S = 3/2$  complex for hydrogen atom abstraction are the oxo  $p_z$  orbitals mixed into  $xz(-)$  and  $yz(+)$  ( $z$  is perpendicular to the  $\text{Fe}_2\text{O}_2$  plane (Figure 6)). In the high-spin  $\text{Fe}_2(\text{IV},\text{IV})$  case, H atom abstraction will place an electron in a presently unoccupied  $xy$  orbital, which will bond with the oxo ligand via in-plane  $p$ -orbitals (Supporting Information Figure 5). Thus, the FMO-predicted most favored approach trajectory would be from within the  $\text{Fe}_2\text{O}_2$  plane, in contrast with the predicted trajectory in Figure 9 for the first hydrogen atom abstraction step of the  $S = 3/2$  complex but consistent with calculated H-atom reaction coordinate of **Q** with substrate.<sup>58,59,61,80</sup>

## 6. Summary

The combination of varied spectroscopic methods and density functional calculations has allowed the molecular origins of the unique electronic and geometric features of the  $\text{Fe}_2\text{O}_2$  diamond core to be determined. The  $C_{2h}$  distortion of the core is due to the effects of the sterically constrained endogenous ligands and results in a small (20%) difference in bond strength between adjacent Fe–O bonds. This results in a limited perturbation of the electronic structure of the  $\text{Fe}_2\text{O}_2$  core, whose valence

delocalization is dominated by the three singly occupied  $\pi^*$  metal-based orbitals. These SOMOs are also key to the observed reactivity of this complex as they overlap with the substrate C–H bonding orbital during the initial hydrogen atom abstraction step. FMO theory has indicated that the best trajectory for reactivity is with the substrate approaching from  $\sim 50^\circ$  out of the  $\text{Fe}_2\text{O}_2$  plane, which allows favorable overlap with the unpaired oxo  $p_z$  density. Extension of the electronic structure description of the  $S = 3/2$  complex to the high-valent enzyme intermediates **X** and **Q** showed that the transition from low spin to high spin anticipates valence localization and AF coupling in these intermediates as observed experimentally. This leads to a large change in bonding which affects superexchange pathways through the bis- $\mu$ -oxo bridge and valence orbitals on the oxo ligands available for hydrogen atom abstraction.

**Acknowledgment.** The authors thank Drs. Frank Neese, Nicolai Lehnert, and Robert K. Szilagy for their advice and observations during this study. Professor Daniel Gamelin is recognized for initiating this study. This work was supported by grants from the NSF Biophysics Program (9816051 to E.I.S.) and the National Institutes of Health (GM-38767 to LQ). A.J.S. was supported by a predoctoral fellowship from the NSF.

**Supporting Information Available:** Coordinates,  $F$ -matrices, and force constants for the  $\text{Fe}_2\text{O}_2$  and  $\text{Fe}_2\text{O}_2\text{N}_2$  NCA models, VTVH MCD simulations and polarizations for 928, 646, 482, and 399 nm, coordinates of DFT fully geometry optimized and “constrained” geometry optimized structures, majority spin–orbital contours of the  $xy(\pm)$  and  $t_2$  orbitals, normal coordinate analysis (NCA) results discussion, electronic absorption group theory, DFT-calculated transition energies and oscillator strengths discussion, and alternate H-atom abstraction approach geometry from pm3-tm calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA021137N

(78) The oxidation of the  $S = 3/2$  core will result in the elimination of a strong superexchange pathway by removing a  $t_2^*$  electron.

(79) Brunold, T. C.; Gamelin, D. R.; Solomon, E. I. *J. Am. Chem. Soc.* **2000**, *122*, 8511–8523.

(80) Siegbahn, P. E. M. *Inorg. Chem.* **1999**, *38*, 2880–2889.