

Characterization of Two Distinct Adducts in the Reaction of a Nonheme Diiron(II) Complex with O₂

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Two [Fe^{II}₂(N-EtHPTB)(μ-O₂X)]²⁺ complexes, where N-EtHPTB is the anion of *N,N,N',N'*-tetrakis(2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane and O₂X is O₂PPh₂ (**1**·O₂PPh₂) or O₂AsMe₂ (**1**·O₂AsMe₂), have been synthesized. Their crystal structures both show interiron distances of 3.54 Å that arise from a (μ-alkoxo)diiron(II) core supported by an O₂X bridge. These diiron(II) complexes react with O₂ at low temperatures in MeCN (−40 °C) and CH₂Cl₂ (−60 °C) to form long-lived O₂ adducts that are best described as (μ-η¹:η¹-peroxo)diiron(III) species (**2**·O₂X) with ν_{O–O} ~ 850 cm^{−1}. Upon warming to −30 °C, **2**·O₂PPh₂ converts irreversibly to a second (μ-η¹:η¹-peroxo)diiron(III) intermediate (**3**·O₂PPh₂) with ν_{O–O} ~ 900 cm^{−1}, a value which matches that reported for [Fe₂(N-EtHPTB)(O₂)(O₂CPh)]²⁺ (**3**·O₂CPh) (Dong et al. *J. Am. Chem. Soc.* **1993**, *115*, 1851–1859). Mössbauer spectra of **2**·O₂PPh₂ and **3**·O₂PPh₂ indicate that the iron centers within each species are antiferromagnetically coupled with *J* ~ 60 cm^{−1}, while extended X-ray absorption fine structure analysis reveals interiron distances of 3.25 and 3.47 Å for **2**·O₂PPh₂ and **3**·O₂PPh₂, respectively. A similarly short interiron distance (3.27 Å) is found for **2**·O₂AsMe₂. The shorter interiron distance associated with **2**·O₂PPh₂ and **2**·O₂AsMe₂ is proposed to derive from a triply bridged diiron(III) species with alkoxo (from N-EtHPTB), 1,2-peroxo, and 1,3-O₂X bridges, while the longer distance associated with **3**·O₂PPh₂ results from the shift of the O₂PPh₂ bridge to a terminal position on one iron. The differences in ν_{O–O} are also consistent with the different interiron distances. It is suggested that the O···O bite distance of the O₂X moiety affects the thermal stability of **2**·O₂X, with the O₂X having the largest bite distance (O₂AsMe₂) favoring the **2**·O₂X adduct and the O₂X having the smallest bite distance (O₂CPh) favoring the **3**·O₂X adduct. Interestingly, neither **3**·O₂AsMe₂ nor the benzoate analog of **2**·O₂X (**2**·O₂Bz) are observed.

Introduction

Over the past 20 years, a growing family of oxygen-activating, nonheme diiron enzymes has been revealed and cataloged.^{1–8} Most notably, this group includes soluble methane monooxygenase, the R2 subunit of class I ribonucleotide reductases, toluene and *o*-xylene monooxygenases,

phenol hydroxylase, and stearyl acyl carrier protein Δ⁹-desaturase. The catalytic cycles of several of these enzymes include peroxide-bridged diiron(III) intermediates that are stable enough to be detected and characterized.^{9–16} The precise role of the peroxide moieties commonly observed in biological reactions remains poorly understood, in spite of the existence of a fairly large body of work describing them.

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To complement these biological studies, a variety of biomimetic diiron complexes has been synthesized and characterized.^{17–26} Using synthetic compounds, it is also not unusual to observe peroxide-bridged diiron(III) species, especially in carboxylate-bridged complexes, wherein a common motif is a (μ - η^1 : η^1 -peroxy)diiron(III) moiety.

It is curious that nature evolved mechanisms that include quasi-stable peroxide intermediates as steps along catalytic pathways. The growing number of trapped and characterized synthetic analogs to these peroxo moieties indicates that this inherent stability is not limited to biological systems.^{17–21} Carboxylates are most often used as bridges supporting the (μ -peroxy)diiron(III) species, with only two papers reporting (μ -peroxy)diiron(III) complexes with noncarboxylate bridges.^{27,28} To investigate how substitution of the carboxylate bridge would affect the properties of the (μ -peroxy)diiron(III) unit, we synthesized and crystallized two diiron(II) complexes using the ligand N-EtHPTB (anion of *N,N,N',N'*-tetrakis(2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane), wherein the benzoate bridge of $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2\text{CPh})]^{2+}$ ($\mathbf{1}\cdot\text{O}_2\text{CPh}$), a complex first reported in 1990 by Ménage et al.,²⁹ is replaced with diphenylphosphinate ($\mathbf{1}\cdot\text{O}_2\text{PPh}_2$) or dimethylarsinate ($\mathbf{1}\cdot\text{O}_2\text{AsMe}_2$). Reaction of these new species with O_2 produces (μ - η^1 : η^1 -peroxy)diiron(III) moieties that exhibit surprising behaviors. In this paper, we report the crystallographic details of the precursor diiron(II) complexes and the spectroscopic characterization of their dioxygen adducts.

Experimental Section

Materials and Syntheses. All reagents and solvents were purchased from commercial sources and were used as received, unless noted otherwise. The $^{18}\text{O}_2$ (97%) and the $^{16}\text{O}_2/^{16}\text{O}^{18}\text{O}/^{18}\text{O}_2$ mixture (1:2:1) were purchased from Cambridge Isotope Laboratories, Inc., Andover, Massachusetts. The ligand N-EtHPTB was synthesized using a published procedure.³⁰ Solvents were dried according to published procedures and distilled under Ar prior to use.³¹ Preparation and handling of air-sensitive materials were carried out under

an inert atmosphere by using either standard Schlenk and vacuum-line techniques or a glovebox. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia.

$\mathbf{1}\cdot\text{O}_2\text{PPh}_2$. N-EtHPTB (181 mg, 0.250 mmol) was dissolved in MeOH (~10 mL) along with Et_3N (0.19 mL, 1.4 mmol). Diphenylphosphinic acid (54.5 mg, 0.250 mmol) was added and allowed to dissolve. $\text{Fe}(\text{OTf})_2\cdot 2\text{MeCN}$ ³² (238 mg, 0.546 mmol) was added, producing a yellow solution. After 5 min, NaBPh_4 (180 mg, 0.526 mmol) was added, resulting in immediate precipitation of a white powder. The solid was filtered and dried in vacuo. Recrystallization from MeCN and Et_2O produced colorless crystals, some suitable for X-ray diffraction structural analysis. Yield: 341 mg (79%). Anal. for $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2\text{PPh}_2)](\text{BPh}_4)_2$ and calcd for $\text{C}_{105}\text{H}_{102}\text{B}_2\text{Fe}_2\text{N}_{11}\text{O}_3\text{P}$: C, 72.89; H, 5.94; N, 8.90%. Found: C, 72.87; H, 5.97; N, 8.84%.

$\mathbf{1}\cdot\text{O}_2\text{AsMe}_2$. N-EtHPTB (146.3 mg, 0.202 mmol) was dissolved in MeOH (~10 mL) along with Et_3N (0.141 mL, 1.01 mmol). Dimethylarsinic acid (30.0 mg, 0.217 mmol) was added and allowed to dissolve. $\text{Fe}(\text{OTf})_2\cdot 2\text{MeCN}$ ³² (182.7 mg, 0.419 mmol) was added, producing a yellow solution. After 5 min, NaBPh_4 (212.8 mg, 0.622 mmol) was added, resulting in immediate precipitation of a white powder. The solid was filtered and dried in vacuo. Recrystallization from MeCN and Et_2O produced pale yellow crystals, some suitable for X-ray diffraction structural analysis. Yield: 270 mg (93%). Anal. for $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2\text{AsMe}_2)](\text{BPh}_4)(\text{OTf})$ and calcd for $\text{C}_{70}\text{H}_{75}\text{AsBF}_3\text{Fe}_2\text{N}_{10}\text{O}_6\text{S}$: C, 58.43; H, 5.25; N, 9.73%. Found: C, 58.62; H, 4.97; N, 9.74%.

$\mathbf{1}\cdot\text{O}_2\text{CPh}$. N-EtHPTB (107.6 mg, 0.149 mmol) was dissolved in MeOH (~10 mL) along with Et_3N (0.11 mL, 0.82 mmol). Sodium benzoate (23.1 mg, 0.160 mmol) was added and allowed to dissolve. $\text{Fe}(\text{OTf})_2\cdot 2\text{MeCN}$ (144.4 mg, 0.331 mmol) was added, producing a yellow solution. After 5 min, NaBPh_4 (119 mg, 0.348 mmol) was added, resulting in immediate precipitation of a white powder. The solid was filtered and dried in vacuo. Recrystallization from MeCN and Et_2O produced pale yellow-green crystals. Yield: 132 mg (71%). Anal. for $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2\text{CPh})(\text{OTf})_2]$ and calcd for $\text{C}_{52}\text{H}_{54}\text{F}_6\text{Fe}_2\text{N}_{10}\text{O}_9\text{S}_2$: C, 49.85; H, 4.34; N, 11.18%. Found: C, 49.70; H, 4.38; N, 10.72%.

Physical Methods. UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Resonance Raman spectra were collected on an ACTON AM-506M3 monochromator with a Princeton LN/CCD data collection system using a Spectra-Physics Model 2060 krypton laser. Low-temperature spectra of the peroxo intermediates in CH_2Cl_2 and MeCN were obtained at 77 K using a 135° backscattering geometry. Samples were frozen onto a gold-plated copper coldfinger in thermal contact with a Dewar flask containing liquid nitrogen. Raman frequencies were referenced to the features of indene. Slits were set for a band-pass of 4 cm^{-1} for all spectra. Mössbauer spectra were recorded with two spectrometers, using Janis Research Super-Vari-temp dewars that allowed studies in applied magnetic fields up to 8.0 T in the temperature range from 1.5 to 200 K. Mössbauer spectral simulations were performed using the WMOSS software package (WEB Research, Edina, MN). Isomer shifts are quoted relative to Fe metal at 298 K.

X-Ray Diffraction Crystallography. X-ray diffraction data were collected on a Bruker SMART platform CCD diffractometer at 173(2) K.³³ Preliminary sets of cell constants were calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The data collection was carried out using Mo $\text{K}\alpha$ radiation (graphite monochromator). Randomly oriented regions of reciprocal space were surveyed to the extent of one sphere and to a

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Table 1. Crystal Data and Structure Refinement for $1 \cdot O_2PPh_2(BPh_4)_2 \cdot MeCN$ and $1 \cdot O_2AsMe_2(BPh_4)(OTf) \cdot MeCN$

	$1 \cdot O_2PPh_2(BPh_4)_2 \cdot MeCN$	$1 \cdot O_2AsMe_2(BPh_4)(OTf) \cdot MeCN$
empirical formula	$C_{105}H_{102}B_2Fe_2N_{11}O_3P$	$C_{72}H_{78}BF_3Fe_2N_{11}O_6S$
fw	1730.27	1479.94
T (K)	173(2)	173(2)
Mo $K\alpha$ λ , Å	0.71073	0.71073
space group	$P2_1/c$	$P2_1/c$
a (Å)	18.937(4)	16.1151(12)
b (Å)	23.855(5)	15.6370(12)
c (Å)	21.817(5)	28.473(2)
α (deg)	90	90
β (deg)	114.903(4)	103.4900(10)
γ (deg)	90	90
V (Å ³)	8940(3)	6977.0(9)
Z	4	4
ρ (calcd), Mg/m ³	1.286	1.409
abs coeff (mm ⁻¹)	0.402	0.985
$R1^a$	0.0492	0.0338
$wR2^b$	0.0957	0.0798

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR2 = \frac{[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}}{\sum |F_o|}$$

resolution of 0.84 Å. The intensity data were corrected for absorption and decay using SADABS.³⁴ Final cell constants were calculated after integration with SAINT.³⁵ The structures were solved and refined using SHELXL-97.³⁶ The space group $P2_1/c$ was determined on the basis of systematic absences and intensity statistics. Direct-methods solutions were calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Brief crystal data and intensity collection parameters for the crystalline complexes are shown in Table 1. Complete crystallographic details, atomic coordinates, anisotropic thermal parameters, and fixed hydrogen atom coordinates are given in the Supporting Information.

X-Ray Absorption Spectroscopy. X-ray absorption spectroscopy (XAS) data were collected on beamline 9-3 at Stanford Synchrotron Radiation Lightsource (SSRL) of the SLAC National Accelerator Laboratory and on beamline X3B at the National Synchrotron Lightsource of Brookhaven National Laboratory (NSLS). At SSRL, the synchrotron ring SPEAR was operated at 3.0 eV and a 50–100 mA beam current. Energy resolution of the focused incoming X-rays was achieved using a Si(220) double-crystal monochromator, which was then detuned to 50% of maximal flux to attenuate second harmonic X-rays. At NSLS, the synchrotron ring was operated at 2.8 GeV and a 100–300 mA beam current, and a Si(111) double-crystal monochromator was used. Fluorescence data were collected over the energy range of 6.8–8.0 keV using a 30-element Ge detector (SSRL) or 13-element Ge detector (NSLS). The beam spot size on samples was 5 mm (horizontal) \times 1 mm (vertical). A total of 13 scans were collected for $2 \cdot O_2AsMe_2$ at NSLS (55 min/scan), and 14 scans were collected for $2 \cdot O_2PPh_2$ and $3 \cdot O_2PPh_2$ at SSRL (25 min/scan). All spectra were referenced against an iron foil.

Pre-edge quantification was carried out with the SSEXAFS program using a standard procedure.³⁷ Standard procedures

were used to reduce, average, and process the raw data using the EXAFSPAK package,³⁸ which was also used for X-ray absorption fine structure (EXAFS) fitting. Theoretical EXAFS amplitude and phase functions were calculated using the FEFF package (version 8.4). The input models for FEFF calculations are shown in Figures S1 and S2 (Supporting Information). The parameters r and σ^2 were floated, while n was kept fixed for each fit and systematically varied in integer steps between fits. The scale factor was fixed at 0.9, and the threshold energy (E_0) was varied but maintained at a common value for all shells. The goodness of fit was determined using eq 1:

$$F = \sqrt{\sum k^6 (\chi_{exp} - \chi_{calcd})^2 / N} \quad (1)$$

where N is the number of data points.³⁹

Results

Several diiron enzymes activate O_2 via $(\mu-\eta^1:\eta^1$ -peroxy)diiron(III) intermediates.^{9–14,16} In order to better understand the behavior of these biological moieties, we synthesized two diiron(II) complexes and characterized their O_2 adducts. Combining 2 equiv of $Fe(OTf)_2 \cdot 2MeCN$ with 1 equiv of the ligand N-EtHPTB followed by the addition of 1 equiv of either diphenylphosphinic acid or dimethylarsinic acid afforded complexes with the general formulation $[Fe_2(N-EtHPTB)(O_2X)](Y)_2$ (cation = $1 \cdot O_2X$ where $O_2X = O_2PPh_2$ or O_2AsMe_2 and $Y =$ counteranions). Recrystallization of these compounds from MeCN and diethyl ether produced crystals suitable for X-ray diffraction structural analysis (Table 1). In solution, these complexes reacted with dioxygen at low temperatures, producing intermediates that were characterized using UV–vis, resonance Raman, Mössbauer, and X-ray absorption spectroscopies.

X-Ray Crystallography. The results from analysis of the $1 \cdot O_2PPh_2$ and $1 \cdot O_2AsMe_2$ structures are compared in Table 2 with information from the previously published crystal structure of $1 \cdot O_2CPh$.^{29,40} Figure 1 shows an ORTEP view of $1 \cdot O_2PPh_2$ with the hydrogen atoms removed as well as a cartoon of the general structure

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Table 2. Selected Interatom Distances and Bond Angles for $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2\text{X})]^{2+}$

	$1 \cdot \text{O}_2\text{PPh}_2$	$1 \cdot \text{O}_2\text{AsMe}_2$	$1 \cdot \text{O}_2\text{CPh}^a$
τ_{ave}	0.77	0.81	0.93
Interatom Distances (Å)			
Fe1–O1	2.004(2)	2.0145(13)	1.976(5)
Fe2–O1	1.992(2)	2.0037(14)	1.964(5)
Fe1–N1	2.294(3)	2.3366(16)	2.316(6)
Fe2–N2	2.352(3)	2.3892(16)	2.280(7)
Fe1–O2	2.008(2)	1.9825(14)	2.057(5)
Fe2–O3	2.021(2)	1.9863(14)	2.019(6)
Fe1–N3	2.086(3)	2.1372(17)	2.064(6)
Fe1–N5	2.115(3)	2.1023(18)	2.069(6)
Fe2–N7	2.075(3)	2.1088(17)	2.080(6)
Fe2–N9	2.098(3)	2.0759(17)	2.064(6)
P1/C44/As1–O2	1.514(2)	1.6740(15)	1.264(9)
P1/C44/As1–O3	1.512(2)	1.6776(14)	1.253(9)
Fe1···Fe2	3.5405(10)	3.5357(5)	3.4749(31)
O2···O3	2.5600(32)	2.7991(21)	2.2251(74)

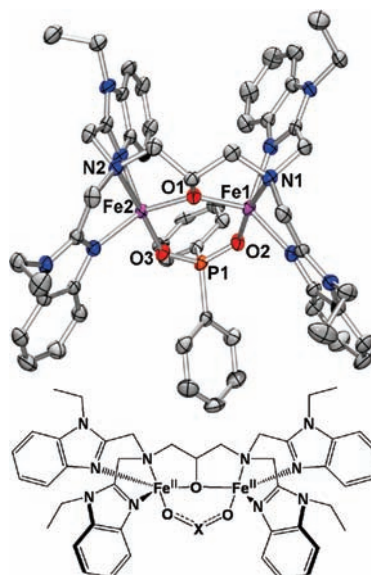
Bond Angles (deg)

Fe1–O1–Fe2	124.76(11)	123.27(6)	123.8(2)
O1–Fe1–O2	105.55(9)	105.77(6)	98.6(2)
O1–Fe2–O3	99.44(9)	107.92(6)	101.5(2)
Fe1–O2–P1/C44/As1	132.01(14)	127.24(8)	136.4(5)
Fe2–O3–P1/C44/As1	138.88(15)	128.15(8)	133.9(5)
O2–P1/C44/As1–O3	115.59(13)	113.26(7)	124.2(7)

^a Data for $1 \cdot \text{O}_2\text{CPh}$ were re-refined using full-matrix least squares on F^2 , and atoms were renamed to match the labeling scheme of $1 \cdot \text{O}_2\text{PPh}_2$ and $1 \cdot \text{O}_2\text{AsMe}_2$. The new solution was deposited directly with the Cambridge Crystallographic Data Centre (deposition number CCDC 731669). Values in the table represent recalculated distances and angles.

shared by all three cations. In each complex, both metal atoms are five-coordinate iron(II) and form a six-membered ring along with three atoms of the bridging moiety and the ligand alkoxide oxygen. Other similarities include distorted trigonal-bipyramidal iron centers, the axial positions of which are occupied by amine nitrogen atoms and bridging moiety oxygen atoms. The equatorial sites are occupied by benzimidazole nitrogen atoms and the alkoxide oxygen atom. For the most part, the interatomic distances and angles do not significantly fluctuate between species. However, variations of note include the O–C–O, O–P–O, and O–As–O angles formed by the three-atom linkers between the iron atoms, with values of 113.26(7) ($1 \cdot \text{O}_2\text{AsMe}_2$), 115.59(13) ($1 \cdot \text{O}_2\text{PPh}_2$), and 124.2(7)° ($1 \cdot \text{O}_2\text{CPh}$), and the geometry about the iron atoms, with average τ values⁴¹ of 0.81 ($1 \cdot \text{O}_2\text{AsMe}_2$), 0.77 ($1 \cdot \text{O}_2\text{PPh}_2$), and 0.93 ($1 \cdot \text{O}_2\text{CPh}$).

Clearly, the differences observed between the three-atom linker angles in each complex result from the different hybridization of the central atom. The central carbon atom in the benzoate bridge is sp^2 -hybridized, producing an angle 3° greater than the ideal 120° predicted for trigonal-planar geometry. As the benzoate oxygen atoms bind to the iron atoms, they must spread apart to accommodate the interiron distance (3.4749(31) Å), producing an O–C–O angle of 124.2(7)°. The same effect is observed in the diphenylphosphinate- and dimethylarsinate-bridged complexes, where the central atom in each three-atom linker is sp^3 -hybridized. However, instead of producing angles of

**Figure 1.** Crystal structure of the cation $1 \cdot \text{O}_2\text{PPh}_2$ (50% ellipsoids) with hydrogen atoms removed. Generic cartoon of $1 \cdot \text{O}_2\text{X}$: $\text{O}_2\text{X} = \text{O}_2\text{AsMe}_2$ ($1 \cdot \text{O}_2\text{AsMe}_2$), O_2PPh_2 ($1 \cdot \text{O}_2\text{PPh}_2$), O_2CPh ($1 \cdot \text{O}_2\text{CPh}$).

109.5°, the ligated oxygen atoms are forced apart to accommodate the interiron distances of 3.5357(5) ($1 \cdot \text{O}_2\text{AsMe}_2$) and 3.5405(10) ($1 \cdot \text{O}_2\text{PPh}_2$) Å, producing respective O–As–O and O–P–O angles of 113.26(7) and 115.59(13)°.

Interestingly, the interiron distances found in $1 \cdot \text{O}_2\text{AsMe}_2$ and $1 \cdot \text{O}_2\text{PPh}_2$ are greater than that found in $1 \cdot \text{O}_2\text{CPh}$, in spite of the fact that the former complexes produce sharper angles with their three-atom linkers. Examination of the bond lengths between the oxygen atoms and the central atom in the three-atom linker of each complex reveals a trend with distances in $1 \cdot \text{O}_2\text{AsMe}_2$ being ~0.16 Å longer than those in $1 \cdot \text{O}_2\text{PPh}_2$, which in turn contains distances ~0.25 Å longer than those found in $1 \cdot \text{O}_2\text{CPh}$. The longer As–O and P–O bond lengths found in $1 \cdot \text{O}_2\text{AsMe}_2$ and $1 \cdot \text{O}_2\text{PPh}_2$ result in significantly increased O···O bite distances of 2.7991(21) ($1 \cdot \text{O}_2\text{AsMe}_2$) and 2.5600(32) Å ($1 \cdot \text{O}_2\text{PPh}_2$) versus 2.2251(74) Å ($1 \cdot \text{O}_2\text{CPh}$). This shorter distance in $1 \cdot \text{O}_2\text{CPh}$ is reflected in a shorter interiron distance, in spite of the fact that the three-atom linker has a wider angle than the linkers in either $1 \cdot \text{O}_2\text{PPh}_2$ or $1 \cdot \text{O}_2\text{AsMe}_2$.

UV–Vis Spectroscopy. The UV–vis spectrum of $1 \cdot \text{O}_2\text{PPh}_2$ in CH_2Cl_2 has no notable features except for a UV tail and an extremely weak absorbance maximum around 1000 nm (Figure 2, inset). Bubbling dioxygen through this solution at –80 °C elicits an intense green-blue color (Figure 2, solid green line) with absorption maxima at 368 and 678 nm ($2 \cdot \text{O}_2\text{PPh}_2$). Upon warming to –30 °C, the green-blue solution becomes deep blue over an 8 min period (Figure 2, dotted blue line). The absorption maximum at 368 nm shifts to 344 nm while gaining intensity. The maximum at 678 nm shifts to 621 nm with a concomitant loss of intensity, and a new shoulder appears at 509 nm (Figure S3, Supporting Information). The complex spectral changes and the lack of true isosbestic points suggest the appearance of more than one species during this time period. Further warming

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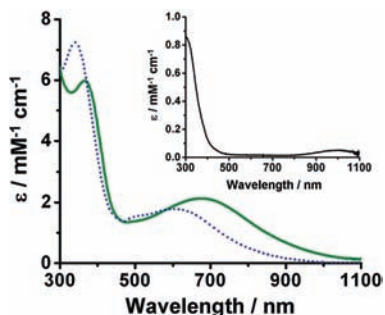


Figure 2. UV-vis spectra of $1\cdot\text{O}_2\text{PPh}_2$ (inset), $2\cdot\text{O}_2\text{PPh}_2$ (solid green line), and mostly $3\cdot\text{O}_2\text{PPh}_2$ (dotted blue line) in CH_2Cl_2 .

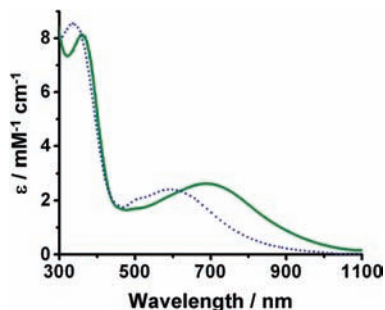


Figure 3. UV-vis spectra recorded at $-40\text{ }^\circ\text{C}$ in MeCN for $2\cdot\text{O}_2\text{PPh}_2$ (solid green) and $3\cdot\text{O}_2\text{PPh}_2$ (dotted blue).

to room temperature produces the final product, a yellow solution ($4\cdot\text{O}_2\text{PPh}_2$) with no remarkable absorption features in the visible spectrum.

Oxygenation of $1\cdot\text{O}_2\text{PPh}_2$ in MeCN at $-40\text{ }^\circ\text{C}$ produces a green-blue solution ($\lambda_{\text{max}} = 686\text{ nm}$) with spectroscopic characteristics (Figure 3, solid green line) similar to those of $2\cdot\text{O}_2\text{PPh}_2$ in CH_2Cl_2 at $-80\text{ }^\circ\text{C}$. However, in contrast to complications observed when warming the latter, warming the MeCN solution to $-30\text{ }^\circ\text{C}$ and maintaining that temperature for 15 min results in clean conversion to a deep blue solution ($3\cdot\text{O}_2\text{PPh}_2$) with a visible absorption maximum at 590 nm (Figure 3, dotted blue line), corresponding to the 588 nm peak observed upon oxygenation of $1\cdot\text{O}_2\text{CPh}$.²⁹ Unlike the reaction in CH_2Cl_2 , conversion from $2\cdot\text{O}_2\text{PPh}_2$ to $3\cdot\text{O}_2\text{PPh}_2$ in MeCN produces true isobestic points at 363 and 618 nm (Figure S4, Supporting Information). Warming to room temperature causes $3\cdot\text{O}_2\text{PPh}_2$ to decay to the final product, a yellow solution ($4\cdot\text{O}_2\text{PPh}_2$) with no remarkable absorption features in the visible spectrum.

Oxygenation of $1\cdot\text{O}_2\text{AsMe}_2$ in MeCN at $-40\text{ }^\circ\text{C}$ changes the almost colorless solution to a deep green-blue color with UV-vis absorption maxima at 348 and 632 nm (Figure S5, Supporting Information) associated with $2\cdot\text{O}_2\text{AsMe}_2$. It exhibits UV-vis absorption features analogous to those of $2\cdot\text{O}_2\text{PPh}_2$, but the similarity ends there. Instead of converting to a different species when warmed to $-30\text{ }^\circ\text{C}$, $2\cdot\text{O}_2\text{AsMe}_2$ is stable for more than an hour, at which point observation was aborted. Warming this solution to $0\text{ }^\circ\text{C}$ leads to slow decay with $\sim 25\%$ loss of intensity at 632 nm over a 4 h period. Gradual blue-shifting of the absorbance maxima in conjunction with the presence of time traces that cannot be fit to first-order decay rates leads us to hypothesize that the system passes through an unobserved intermediate ($3\cdot\text{O}_2\text{AsMe}_2$) comparable to

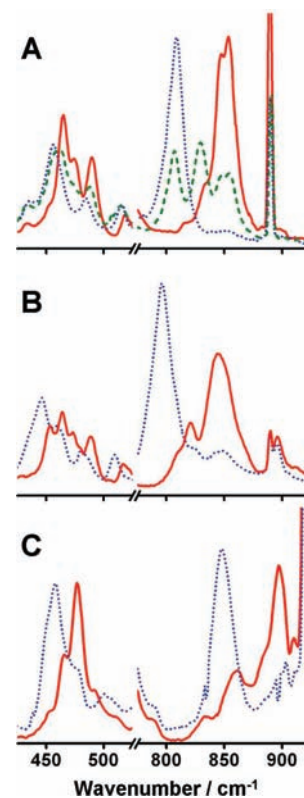


Figure 4. Resonance Raman spectra of frozen solutions of $2\cdot\text{O}_2\text{PPh}_2$ in CH_2Cl_2 (A), $2\cdot\text{O}_2\text{AsMe}_2$ in CH_2Cl_2 (B), and $3\cdot\text{O}_2\text{PPh}_2$ in MeCN (C). Solid red = $^{16}\text{O}_2$. Dotted blue = $^{18}\text{O}_2$. Dashed green = mixed O_2 .

$3\cdot\text{O}_2\text{PPh}_2$ prior to complete decay to the yellow product ($4\cdot\text{O}_2\text{AsMe}_2$).

Resonance Raman Spectroscopy. Resonance Raman (rR) spectroscopy is a particularly effective technique for examining vibrational transitions in complexes that have strong chromophores. In light of this fact, rR spectra of $2\cdot\text{O}_2\text{AsMe}_2$, $2\cdot\text{O}_2\text{PPh}_2$, and $3\cdot\text{O}_2\text{PPh}_2$ were collected, analyzed, and compared with spectra presented in earlier reports^{21,26,40,42–46} in an attempt to gain insight into their individual molecular structures.

The rR spectrum of $2\cdot\text{O}_2\text{PPh}_2$ in frozen CH_2Cl_2 using $^{16}\text{O}_2$ and 647.1 nm excitation shows two intense peaks at 845 and 853 cm^{-1} in addition to three peaks at 465, 475, and 490 cm^{-1} (Figure 4A, solid red line). These features suggest the presence of an iron(III)-peroxo chromophore. With the use of $^{18}\text{O}_2$ (Figure 4A, dotted blue line), the peaks at 845 and 853 cm^{-1} shift to a single peak at 807 cm^{-1} . This shift of 42 cm^{-1} is in agreement with the change predicted for an O–O oscillator by application of Hooke's law, thereby assigning the peaks at 845 and

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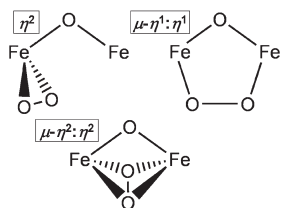


Figure 5. Possible O₂ coordination modes in Fe₂O₂-alkoxo core.

853 cm⁻¹ as a Fermi doublet of ν_{O-O}. Additionally, with the use of ¹⁸O₂, the peaks at 465, 475, and 490 cm⁻¹ are replaced with peaks at 455 and 484 cm⁻¹. Again, using Hooke's law, we can assign the peaks at 465 and 475 cm⁻¹ to a Fermi doublet representing ν_{Fe-O}, which collapses to a single peak at 455 cm⁻¹ upon ¹⁸O substitution. The peak at 490 cm⁻¹ clearly shifts to lower energy in the ¹⁸O isotopomer, but the change of only 6 cm⁻¹ and the relative weakness of the signal lead us to suspect that this peak arises from a ligand vibration coupled to the Fe-O stretch.

Repeating this experiment using a mixture of ¹⁶O₂, ¹⁸O₂, and ¹⁶O¹⁸O (Figure 4A, dashed green line) allowed us to gain insight into the peroxo binding mode. While the ν_{Fe-O} region is not well-resolved, the ν_{O-O} region clearly shows peaks at 806, 829, 845, and 853 cm⁻¹, corresponding to features arising from the ¹⁸O-¹⁸O, ¹⁶O-¹⁸O, and ¹⁶O-¹⁶O isotopomers, respectively. The peak at 829 cm⁻¹ is assigned to ν_{16O-18O} by comparison with the spectra obtained from the ¹⁶O₂ and ¹⁸O₂ isotopomers. The appearance of only a single peak between 806 and 845 cm⁻¹ with a line width comparable to those of the ν_{16O-16O} and ν_{18O-18O} peaks indicates that the dioxygen moiety is symmetrically ligated. Three possible symmetric coordination modes are shown in Figure 5.

The rR spectrum of 3·O₂PPh₂ generated by using ¹⁶O₂ in MeCN shows peaks at 477 and 897 cm⁻¹ (Figure 4C, solid red line), corresponding to ν_{Fe-O} and ν_{O-O}, respectively. Using ¹⁸O₂ to generate the sample respectively shifts these peaks to 458 and 848 cm⁻¹ (Figure 4C, dotted blue line), confirming the assignments. Similar results are obtained for 3·O₂PPh₂ generated in CH₂Cl₂ (Figure S6, Supporting Information), but the samples were contaminated with residual 2·O₂PPh₂ due to incomplete conversion, preventing precise assignment of ν_{Fe-O}.

Raman spectra of 2·O₂AsMe₂ (Figure 4B) generated in CH₂Cl₂ using either ¹⁶O₂ (solid red line) or ¹⁸O₂ (dotted blue line) reveal peaks assigned to ν_{O-O} at 845 and 796 cm⁻¹, respectively. The peak at 464 cm⁻¹ in the ¹⁶O₂ spectrum shifts to 443 cm⁻¹ upon ¹⁸O₂ substitution and is assigned to ν_{Fe-O}.

From an examination of the rR data summarized in Table 3, we see that ν_{O-O} can be used to group the oxygenated intermediates into two categories. Raman shifts near 850 cm⁻¹ are characteristic of the first category, which includes the 2·O₂X species. The second category consists of complexes that exhibit ν_{O-O} near 900 cm⁻¹ and includes the 3·O₂X intermediates. In addition to segregating the intermediates, the ν_{O-O} values ranging from ~850 to 900 cm⁻¹ demonstrate that all of the species in each group are peroxo complexes.

Mössbauer Spectroscopy. Using Mössbauer spectroscopy, we examined 2·O₂PPh₂ and 3·O₂PPh₂ in frozen

CH₂Cl₂ and MeCN solutions. Unfortunately, the chlorine atoms of dichloromethane have a very high extinction coefficient at 14.4 keV, and one can therefore not study samples with a path length of more than 1 mm. However, freezing a 1-mm-thick CH₂Cl₂ solution generates an intolerably uneven sample thickness due to meniscus formation. We found a simple solution to the problem by dripping ca. 80 μL of dichloromethane solution onto a stack of five Fisher-brand paper filter discs stacked into the 1-cm-diameter Mössbauer cup. After freezing, we obtained homogeneous and firmly packed samples.

Figure 6 shows 4.2 K Mössbauer spectra of 2·O₂PPh₂ (A) and 3·O₂PPh₂ (B) in CH₂Cl₂ (black hash marks) and MeCN (solid red lines). In both solvents, 2·O₂PPh₂ exhibits one doublet with quadrupole splitting ΔE_Q = 1.26 mm/s and isomer shift δ = 0.56 mm/s. The CH₂Cl₂ sample contains a high-spin iron(II) contaminant (~15%, arrow), most likely belonging to diiron(II) starting material.

Figure 7 shows 8.0 T spectra of 2·O₂PPh₂ recorded at 4.2 K (A) and 80 K (B,C). The 4.2 K spectrum reveals that the dinuclear complex, as expected, has a ground state with cluster spin S = 0. The variable-temperature spectra, taken at 50 K (not shown) and 80 K were analyzed with a spin-Hamiltonian appropriate for an exchange-coupled dinuclear complex comprising two high-spin (S₁ = S₂ = 5/2) iron(III) ions (eq 2, where all symbols have their conventional meanings). For the iron(III) sites considered here, the zero-field splitting parameters D_{1,2} are generally on the order of 1 cm⁻¹ and can be neglected.

$$\begin{aligned} \hat{H} = & J\hat{S}_1 \cdot \hat{S}_2 \\ & + \sum_{i=1,2} \{ 2\beta\hat{S}_i \cdot \hat{B} + A_o\hat{S}_i \cdot \hat{I}_i - g_n\beta_n\hat{B} \cdot \hat{I}_i + \check{H}_{Q(i)} \} \quad (2) \end{aligned}$$

The determination of J by Mössbauer spectroscopy has been described in the literature.^{47,48} For an external field B = 8.0 T, applied parallel to the observed γ-rays, one compares the effective field at the iron nuclei, B_{eff}(i) = B + B_{int}(i), at 4.2 K and some higher temperature, say 80 K. At 4.2 K, only the S = 0 ground state of the diiron(III) cluster is populated, and thus B_{eff}(i) = B. At 80 K, higher excited states of the spin ladder can become populated (essentially the S = 1 manifold, S₁ + S₂ = S), and in the limit of fast electronic transitions among the thermally populated spin levels, the two iron nuclei experience an internal magnetic field B_{int}(i) = -⟨S_i⟩_{th}A_o(i) / g_nβ_n, where ⟨S_i⟩_{th} is the thermally averaged expectation value of the spin for site i. For nonheme octahedral sites with N/O coordination, we can take A_o(i) = -21 T. The expression for B_{int} is quite simple, because zero-field splittings can be ignored and because the magnetic hyperfine interactions of iron(III) sites are generally isotropic. Figure 8 shows a plot of ⟨S_{1z}⟩_{th} = ⟨S_{2z}⟩_{th} versus J for B = 8.0 T evaluated at T = 8.0 T.

The solid red line in the 4.2 K spectrum of Figure 7A is a simulation assuming that only the S = 0 ground state is

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Table 3. Physical Properties of $2 \cdot \text{O}_2\text{X}$ and $3 \cdot \text{O}_2\text{X}$ Complexes

complex	solvent	λ_{max} (nm) [ε] ($\text{M}^{-1} \text{cm}^{-1}$)	$\nu_{\text{O}-\text{O}}$ (cm^{-1}) [$^{18}\text{O}_2$]	$\nu_{\text{Fe}-\text{O}}$ (cm^{-1}) [$^{18}\text{O}_2$]	J (cm^{-1})	δ (mm/s)	ΔE_{Q} (mm/s)	η^f	Fe...Fe (Å)
$2 \cdot \text{O}_2\text{AsMe}_2$	MeCN	348, 632 [7300, 2100]	845 ^a [796]	464 ^a [443]					3.27
$2 \cdot \text{O}_2\text{PPh}_2$	CH_2Cl_2	368, 678 [6000, 2100]	845, 853 [829], ^b [807]	465, 475 455	57 ± 7	0.56(1)	-1.26(2)	0.4	
$2 \cdot \text{O}_2\text{PPh}_2$	MeCN	358, 686 [7400, 2200]	845, 853 [807]	465, 476 [455]	57 ± 7	0.56(1)	-1.26(2)	0.4	3.25
$2 \cdot \text{O}_2\text{CPh}$	CH_2Cl_2	not observed							
$3 \cdot \text{O}_2\text{AsMe}_2$	MeCN	not observed							
$3 \cdot \text{O}_2\text{PPh}_2^c$	CH_2Cl_2	344, 509, 621 [7200, 1600, 1800]	898 [845]		60 ± 10	0.56(2) 0.54(2)	0.86(5) -0.52(3)	~ 0 ~ 0	
$3 \cdot \text{O}_2\text{PPh}_2^d$	MeCN	338, 509, 590 [8300, 2000, 2300]	897 [848]	477 [458]	60 ± 10	0.53(2)	-1.03(4)	~ 1	3.47
$3 \cdot \text{O}_2\text{CPh}^e$	CH_2Cl_2	588 [1500]	900 [850]	476 [460]					

^a Measured in CH_2Cl_2 . ^b $\nu_{\text{O}-\text{O}}$ from $^{16}\text{O}^{18}\text{O}$. ^c Resonance Raman spectroscopy indicates incomplete conversion; some $2 \cdot \text{O}_2\text{PPh}_2$ remains, probably red-shifting the peroxo-to-metal charge transfer to 621 nm. In addition, an unknown amount of $3 \cdot \text{O}_2\text{PPh}_2$ has decayed to $4 \cdot \text{O}_2\text{PPh}_2$, reducing the measured extinction coefficients. ^d Mössbauer values represent 80% of the total iron. ^e Values from ref 40. $J\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter of the electric field gradient tensor.

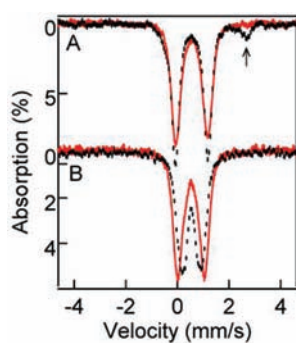


Figure 6. The 4.2 K zero field spectra of $2 \cdot \text{O}_2\text{PPh}_2$ (panel A) in CH_2Cl_2 (black hash marks) and MeCN (solid red line) and $3 \cdot \text{O}_2\text{PPh}_2$ (panel B) in CH_2Cl_2 (black hash marks) and MeCN (solid red line). The high-energy line of a diiron(II) contaminant is marked by an arrow.

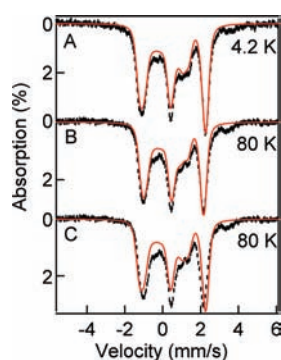


Figure 7. The 8.0 T Mössbauer spectra of $2 \cdot \text{O}_2\text{PPh}_2$ in CH_2Cl_2 recorded at 4.2 K (A) and 80 K (B). The solid red lines are theoretical curves using the parameters listed in Table 3. The data in shown C are the same as in B; the solid red line in C is a simulation obtained by assuming (wrongly) that only the $S = 0$ ground state is occupied at 80 K (two-spin simulation for $J = 1000 \text{ cm}^{-1}$). The solid red line in B was obtained for $J = 57 \text{ cm}^{-1}$ (alternatively, one can simulate the spectrum by assuming a state with $S = 0$ and adjust the applied field to $B = 7.35 \text{ T}$).

populated. The solid red line drawn into the 80 K spectrum of C is the same curve as shown in A. It can be seen that the experimental splitting at 80 K is smaller than expected for a strictly diamagnetic compound. At 80 K, the diiron center is magnetically isotropic, and thus B_{int} is antiparallel ($B_{\text{int}} < 0$) to the applied field.

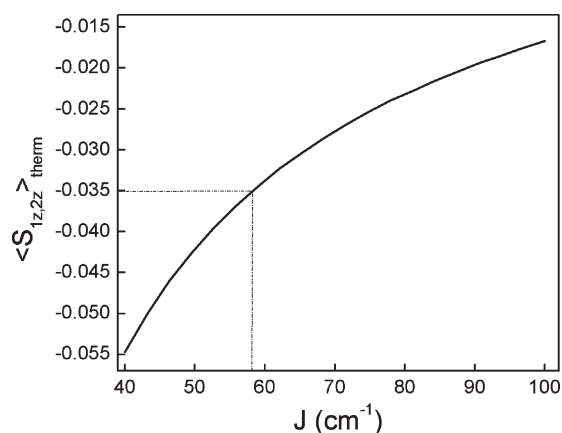


Figure 8. Thermally averaged spin expectation values, $\langle S_{1z} \rangle_{\text{th}} = \langle S_{2z} \rangle_{\text{th}}$, calculated at 80 K for an applied field $B = 8.0 \text{ T}$, for an antiferromagnetically coupled dimer comprising two high-spin ($S_1 = S_2 = 5/2$) iron(III) ions for the Hamiltonian $H = JS_1 \cdot S_2 + 2\beta(S_1 + S_2) \cdot B$. The zero-field splittings of the iron(III) sites are small and can be ignored.

Simulating the 8.0 T spectrum with an “applied” field of 7.35 T yields the solid red line of Figure 7B. Taking $A_0 = -21 \text{ T}$ yields $\langle S_{i,z} \rangle_{\text{th}} = -0.035$ and, thus from the graph of Figure 8, a J value slightly smaller than 60 cm^{-1} . Our best simulations using the full Hamiltonian of eq 2 (the 2Spin option of WMOSS) yielded $J = 57 \pm 7 \text{ cm}^{-1}$ for $2 \cdot \text{O}_2\text{PPh}_2$, taking also into account an 8.0 T spectrum recorded at 50 K (not shown). The same J value was obtained for $2 \cdot \text{O}_2\text{PPh}_2$ in MeCN.

The zero-field spectra of $3 \cdot \text{O}_2\text{PPh}_2$ depend on which solvent is used (Figure 6B). The CH_2Cl_2 spectrum is best represented by assuming two doublets of equal intensity with $\delta(1) = 0.56$ and $\delta(2) = 0.58 \text{ mm/s}$ and $\Delta E_{\text{Q}}(1) = 0.86$ and $\Delta E_{\text{Q}}(2) = -0.52 \text{ mm/s}$. In contrast, the spectrum of the MeCN sample is best represented by one doublet with $\delta = 0.53 \text{ mm/s}$ and $\Delta E_{\text{Q}} = -1.03 \text{ mm/s}$ (representing $\sim 80\%$ of Fe); the remainder may belong to a doublet with $\Delta E_{\text{Q}} \sim -0.90 \text{ mm/s}$ or, alternatively, belong to a distribution of minority species. Analysis of the 8.0 T spectra of $3 \cdot \text{O}_2\text{PPh}_2$ in MeCN, shown in Figure S7 (Supporting Information), again suggests a J value of $\sim 60 \text{ cm}^{-1}$, as do the 8.0 T spectra in CH_2Cl_2 (Figure S8, Supporting Information).

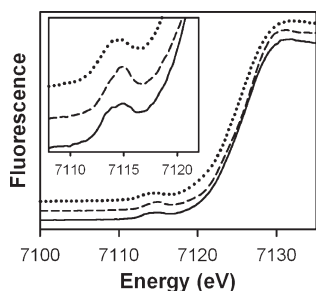


Figure 9. Fe K-edge X-ray absorption spectroscopy near-edge structures (XANES, fluorescence excitation) of $2 \cdot \text{O}_2\text{PPh}_2$ (top), $2 \cdot \text{O}_2\text{AsMe}_2$ (middle), and $3 \cdot \text{O}_2\text{PPh}_2$ (bottom). Inset: Magnified pre-edge absorption peaks.

Table 4. XANES Parameters for Complexes $2 \cdot \text{O}_2\text{PPh}_2$, $2 \cdot \text{O}_2\text{AsMe}_2$, and $3 \cdot \text{O}_2\text{PPh}_2$

complex	E_0 (eV)	$E_{\text{pre-edge}}$ (eV)	pre-edge area	pre-edge width
$2 \cdot \text{O}_2\text{PPh}_2$	7126.2	7114.6	15.8(3)	3.84(6)
$2 \cdot \text{O}_2\text{AsMe}_2$	7125.9	7114.3	15.1(4)	3.66(8)
$3 \cdot \text{O}_2\text{PPh}_2$	7126.3	7114.7	16.1(2)	3.14(4)

The Mössbauer parameters of each characterized complex are summarized in Table 3. We found that, within error, the J values are almost equivalent across the permutations of species and solvents. The same is true of the isomer shifts. However, the quadrupole splitting values determined for this series of complexes range from -1.26 to 0.86 mm/s, and in the case of $3 \cdot \text{O}_2\text{PPh}_2$ in CH_2Cl_2 , the presence of two distinct doublets revealed that the two iron atoms in this complex exist in different environments, a property unique to this species/solvent combination.

X-Ray Absorption Spectroscopy. To date, intermediates $2 \cdot \text{O}_2\text{PPh}_2$, $3 \cdot \text{O}_2\text{PPh}_2$, and $2 \cdot \text{O}_2\text{AsMe}_2$ have not yielded crystals of sufficient quality for X-ray diffraction characterization. To gain further insight into the structures of these complexes, we resorted to XAS, including X-ray absorption near-edge structure (XANES) and EXAFS analyses. Figure 9 shows XANES of $2 \cdot \text{O}_2\text{AsMe}_2$, $2 \cdot \text{O}_2\text{PPh}_2$, and $3 \cdot \text{O}_2\text{PPh}_2$ with parameters shown in Table 4. Edge energies (E_0) assigned to the inflection points of these spectra are ~ 7126 eV, higher than the values typical of diiron(III) clusters containing an oxo bridge (~ 7123 – 7124 eV), including diiron(III) peroxo complexes reported by Fiedler et al.²⁶ Westre et al. reported that (μ -oxo)diiron(III) complexes have edge energies ~ 2 eV lower than those found for (μ -hydroxo)diiron(III) complexes.⁴⁹ Pre-edge peaks observed at ~ 7114 – 7115 eV in our complexes are typical of diiron(III) clusters.^{26,49} It has been shown that an oxo bridge distorts the geometry of a diiron cluster, resulting in a more intense symmetry-forbidden $1s \rightarrow 3d$ transition.⁵⁰ Our measured pre-edge areas of ~ 15 – 16 units are smaller than the ~ 20 units (derived by the same standard method developed by Scarrow et al.)³⁷ found for six-coordinate (μ -oxo)(μ -peroxo)diiron(III) clusters.²⁶ It follows that the higher edge energies and smaller pre-edge areas observed in the XANES parameters of $2 \cdot \text{O}_2\text{AsMe}_2$, $2 \cdot \text{O}_2\text{PPh}_2$, and $3 \cdot \text{O}_2\text{PPh}_2$ are indicative of six-coordinate diiron(III) complexes without oxo bridges.

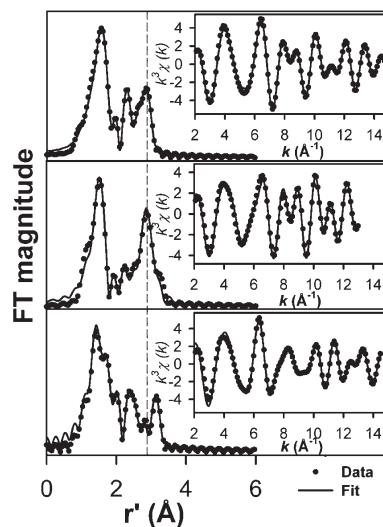


Figure 10. Fourier transforms of the Fourier-filtered Fe K-edge EXAFS data $k^3\chi(k)$ (inset) of $2 \cdot \text{O}_2\text{PPh}_2$ (top), $2 \cdot \text{O}_2\text{AsMe}_2$ (middle), and $3 \cdot \text{O}_2\text{PPh}_2$ (bottom). Experimental data displayed with solid circles (●) and fits with solid lines (—). Back-transformation range ~ 0.7 – 3 Å ($2 \cdot \text{O}_2\text{PPh}_2$) and 0.7 – 3.5 Å ($2 \cdot \text{O}_2\text{AsMe}_2$ and $3 \cdot \text{O}_2\text{PPh}_2$). Fourier transformed range, $k = 2$ – 15 Å⁻¹ ($2 \cdot \text{O}_2\text{PPh}_2$), 2 – 13 Å⁻¹ ($2 \cdot \text{O}_2\text{AsMe}_2$), and 2 – 14.8 Å⁻¹ ($3 \cdot \text{O}_2\text{PPh}_2$). Fit parameters are provided in Table 5 and Table S1 in bold italics.

The Fourier-filtered k^3 -weighted EXAFS data of $2 \cdot \text{O}_2\text{AsMe}_2$, $2 \cdot \text{O}_2\text{PPh}_2$, and $3 \cdot \text{O}_2\text{PPh}_2$ and their corresponding Fourier transforms are presented in Figure 10. Features of $2 \cdot \text{O}_2\text{PPh}_2$ and $2 \cdot \text{O}_2\text{AsMe}_2$ are similar in the range of 2 – 8 Å⁻¹, where scattering from low Z atoms is dominant, but different from those of $3 \cdot \text{O}_2\text{PPh}_2$. This suggests that the first two complexes have similar ligand geometries that differ from that of $3 \cdot \text{O}_2\text{PPh}_2$. In the region beyond 8 Å⁻¹, EXAFS data of $2 \cdot \text{O}_2\text{AsMe}_2$ and $2 \cdot \text{O}_2\text{PPh}_2$ share similar oscillation phases, but $2 \cdot \text{O}_2\text{AsMe}_2$ exhibits a greater amplitude that most probably derives from a larger contribution from the higher Z arsenic scatterer. Consequently, the Fourier transforms of the $2 \cdot \text{O}_2\text{AsMe}_2$ and $2 \cdot \text{O}_2\text{PPh}_2$ data are very similar with inner-shell peaks at $r' = 1.6$ and $r' = 2.0$ Å and outer-shell peaks at $r' = 2.3$ and $r' = 2.8$ Å, although the $r' = 2.8$ Å peak of the $2 \cdot \text{O}_2\text{AsMe}_2$ spectrum is, as expected, much more intense than the corresponding peak observed for $2 \cdot \text{O}_2\text{PPh}_2$.

In the region beyond 8 Å⁻¹, data from $3 \cdot \text{O}_2\text{PPh}_2$ have a different phase and a smaller amplitude than those from $2 \cdot \text{O}_2\text{AsMe}_2$ and $2 \cdot \text{O}_2\text{PPh}_2$. This difference suggests a dissimilar geometry about the iron atoms in $3 \cdot \text{O}_2\text{PPh}_2$ as well as a smaller contribution from high Z atoms. The Fourier transform of the $3 \cdot \text{O}_2\text{PPh}_2$ data shares the same general features as the other two complexes, but with a more complicated inner-shell peak near $r' = 1.6$ Å and an outer-shell peak at $r' = 3.1$ Å instead of an $r' = 2.8$ Å peak.

Table 5 shows some of the progressive fits for the three complexes, with the best fits for each species shown in bold-italics (see Table S1 for all of the fits including all scatterers, Supporting Information). The inner-shell features of the three complexes can best be fitted with a total coordination number of six, with four to five ligands near 2.0 – 2.2 Å and one ligand near 2.3 Å, corresponding to the Fe–N_{amine} bond as observed in the crystal structures of $1 \cdot \text{O}_2\text{PPh}_2$, $1 \cdot \text{O}_2\text{AsMe}_2$, and $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2)(\text{OPPh}_3)_2]^{3+}$.¹⁹ In $3 \cdot \text{O}_2\text{PPh}_2$, a short Fe–O distance of

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Table 5. Selected EXAFS Fitting Results for $2 \cdot \text{O}_2\text{PPh}_2$, $2 \cdot \text{O}_2\text{AsMe}_2$, and $3 \cdot \text{O}_2\text{PPh}_2^a$

complex	fit	Fe–O/N			Fe–O/N			Fe–O/N			Fe···C			Fe···X			F^c	F'^d
		N	R (Å)	σ^2	N	R (Å)	σ^2	N	R (Å)	σ^2	N	R (Å)	σ^2	N	R (Å)	σ^2		
$2 \cdot \text{O}_2\text{PPh}_2$	A	4	1.99	6.14	1	2.29	3.31				5	2.94	10.66	1P	3.12	–0.30	0.488	0.023
	B	4	2.00	6.54	1	2.31	3.64				5	2.99	2.19	5C	2.21	2.26	0.662	0.042
	C	4	2.00	6.69	1	2.31	2.71	1	2.54	0.58	5	2.99	3.55	1Fe	3.28	3.18	0.392	0.018
	D	4	2.00	6.57	1	2.30	1.50	1	2.51	3.00^b	5	2.96	7.95	1Fe	3.25	4.06	0.304	0.013
													1P	3.14	3.00^b			
$2 \cdot \text{O}_2\text{AsMe}_2$	A	5	1.97	10.82	1	2.25	2.19				3	2.93	3.86	1Fe	3.25	0.98	0.611	0.040
	B	5	1.97	10.95	1	2.26	2.85				3	2.90	7.46	1As	3.19	1.94	0.595	0.038
	C	5	1.97	10.66	1	2.25	1.03				3	2.95	1.63	6C	3.28	0.40	0.809	0.079
	D	3	1.97	3.94	2	2.17	4.28	1	2.35	5.35	3	2.94	2.76	1Fe	3.27	1.24	0.381	0.018
	E	3	1.97	3.87	2	2.17	3.82	1	2.36	3.80	3	2.93	5.20	1As	3.21	2.24	0.369	0.019
	F	3	1.97	3.85	2	2.17	3.89	1	2.35	4.24	3	2.92	3.34	1Fe	3.13	19.43	0.344	0.022
													1As	3.21	1.97			
	G	3	1.97	3.84	2	2.17	3.90	1	2.36	4.71	3	2.94	2.22	1Fe	3.27	1.02	0.344	0.022
													1As	3.45	12.71			
$3 \cdot \text{O}_2\text{PPh}_2$	A	4	2.04	5.73	1	2.33	0.48	1	1.88	1.23	4	2.95	2.39	1Fe	3.47	4.59	0.366	0.012
	B	4	2.04	5.74	1	2.33	0.52	1	1.88	1.28	4	2.95	2.30	1P	3.61	1.50	0.452	0.018
	C	4	2.03	5.73	1	2.33	0.67	1	1.88	1.24	4	2.95	2.63	5C	3.50	2.99	0.494	0.021
	D	4	2.04	5.58	1	2.33	0.80	1	1.88	1.12	4	2.95	2.43	1Fe	3.44	3.73	0.332	0.011
													0.5P	3.39	0.69			

^a Resolution ~ 0.12 Å for $2 \cdot \text{O}_2\text{PPh}_2$ and $3 \cdot \text{O}_2\text{PPh}_2$ and ~ 0.14 Å for $2 \cdot \text{O}_2\text{AsMe}_2$; σ^2 = Debye–Waller factor in units of 10^{-3} Å². ^b σ^2 value held fixed during optimization. ^c F = goodness of fit calculated as $F = \sqrt{[\sum k^6(\chi_{\text{exp}} - \chi_{\text{cal}})^2/N]}$, where N = the number of data points.³⁹ ^d $F' = F^2/\nu$, where $\nu = n_{\text{idp}} - n_{\text{var}}$, n_{idp} is the number of independent points in each data set, and n_{var} is the number of variables used in each optimization step. F' is used to indicate the improvement of fit upon the introduction of a shell.³⁹

1.88 Å can be resolved from other Fe–O/N distances and is assigned to the peroxo ligand.^{19–21,26} Interestingly, introduction of a ligand at 2.5 Å to the fit of $2 \cdot \text{O}_2\text{PPh}_2$ data improves the fit quality significantly (fit C, $2 \cdot \text{O}_2\text{PPh}_2$). This same addition does not improve fit qualities for $2 \cdot \text{O}_2\text{AsMe}_2$ and $3 \cdot \text{O}_2\text{PPh}_2$. The $r' = 2.3$ Å peaks of the three complexes correspond to three to five Fe···C paths near 2.95 Å, which arise from carbon atoms adjacent to the ligating nitrogen atoms of the benzimidazole rings of the N-EtHPTB ligand.

The $r' = 2.8$ Å feature of $2 \cdot \text{O}_2\text{PPh}_2$ can be well-simulated with an Fe···Fe distance near 3.25 Å. Attempts to simulate this distance with a single Fe···P path or five Fe···C paths respectively resulted in a negative σ^2 value (fit A, $2 \cdot \text{O}_2\text{PPh}_2$) or a lower fit quality (fit B, $2 \cdot \text{O}_2\text{PPh}_2$), indicating that these paths are not responsible for the $r' = 2.8$ Å peak. However, introducing an Fe···P path at 3.14 Å remarkably improved the fit quality (fit D, $2 \cdot \text{O}_2\text{PPh}_2$), indicating that a phosphorus atom is present at this distance from the iron atoms in $2 \cdot \text{O}_2\text{PPh}_2$. Similarly, including an Fe···P path at 3.23 Å in addition to an Fe···Fe path at 3.30 Å remarkably improved the fits to the EXAFS data for $[\text{Fe}_2(\text{O})(\text{O}_2\text{P}(\text{OPh})_2)_2(\text{HB}(\text{pz})_3)_2]$.⁵¹ The 3.16 Å Fe···P distance found for $2 \cdot \text{O}_2\text{PPh}_2$ is slightly shorter than the average 3.25 Å Fe···P distance seen in the crystal structure of $1 \cdot \text{O}_2\text{PPh}_2$, an observation consistent with the different iron oxidation states of these two complexes.

The intense $r' = 2.8$ Å peak in $2 \cdot \text{O}_2\text{AsMe}_2$ can be simulated equally well with either a 3.27 Å Fe···Fe path or a 3.21 Å Fe···As path with relatively small σ^2 values (fits D and E, $2 \cdot \text{O}_2\text{AsMe}_2$). An attempt to replace the Fe···Fe/As paths with six Fe···C paths yielded poor results (compare fit C to fits A and B, $2 \cdot \text{O}_2\text{AsMe}_2$). Including both the Fe···Fe and the Fe···As paths does

not significantly improve the fit (fits F and G, $2 \cdot \text{O}_2\text{AsMe}_2$). However, we favor the presence of both the 3.27 Å Fe···Fe and 3.21 Å Fe···As paths given the following reasons: (i) $2 \cdot \text{O}_2\text{AsMe}_2$ most likely contains one arsenic and two iron atoms. (ii) Fe···As distances of ~ 3.2 – 3.3 Å have been found in related (μ -alkoxo)(μ -1,3-dimethylarsinato)diiron(III) complexes by both X-ray crystallography and EXAFS.^{27,52,53} (iii) the phase shift and amplitude associated with iron and arsenic scatterers as simulated by FEFF are very similar in the k range used for $2 \cdot \text{O}_2\text{AsMe}_2$; therefore, only one path with a small σ^2 value is sufficient to obtain a good simulation of the data (see Figures S9 and S10 in the Supporting Information for a detailed description). The 3.21 Å Fe···As distance found for $2 \cdot \text{O}_2\text{AsMe}_2$ is slightly shorter than the average 3.28 Å Fe···As distance found in the crystal structure of $1 \cdot \text{O}_2\text{AsMe}_2$. As is the case with the Fe···P distances in $1 \cdot \text{O}_2\text{PPh}_2$ and $2 \cdot \text{O}_2\text{PPh}_2$, this difference is consistent with differences in iron oxidation states. That the 3.21 Å Fe···As distance is slightly longer than the 3.16 Å Fe···P distance found for $2 \cdot \text{O}_2\text{PPh}_2$ comes as no surprise, given that arsenic has a greater atomic radius than phosphorus (respectively, 1.15 and 1.00 Å).⁵⁴

The 3.1 Å feature of $3 \cdot \text{O}_2\text{PPh}_2$ is best fitted with an Fe···Fe path at 3.47 Å (fit A, $3 \cdot \text{O}_2\text{PPh}_2$). Replacing this Fe···Fe path by either one Fe···P path (fit B, $3 \cdot \text{O}_2\text{PPh}_2$) or five Fe···C paths (fit C, $3 \cdot \text{O}_2\text{PPh}_2$) results in significantly lower fit quality. Thus, the $r' = 3.1$ Å feature is attributed to an Fe···Fe path at 3.47 Å. This distance is longer than the Fe···Fe distances found in $2 \cdot \text{O}_2\text{PPh}_2$ and $2 \cdot \text{O}_2\text{AsMe}_2$, consistent with the observed difference in phase shift and the lower amplitude in the k range of 8–13 Å^{–1} for $3 \cdot \text{O}_2\text{PPh}_2$ compared to the other

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two complexes. Adding half an $\text{Fe}\cdots\text{P}$ path to fit A ($3\cdot\text{O}_2\text{PPh}_2$) only increased the fit quality by $\sim 10\%$ (fit D, $3\cdot\text{O}_2\text{PPh}_2$). Therefore, our EXAFS analysis cannot unambiguously establish the presence of a phosphorus atom at this distance from the iron atom.

All of the peroxo intermediates we have characterized above decay upon warming to room temperature to yellow products $4\cdot\text{O}_2\text{X}$, which were only characterized by UV-vis spectroscopy. For these complexes, we suggest a generic formulation of $[\text{Fe}_4(\text{N-EtHPTB})_2(\text{O}_2\text{X})_2(\mu\text{-O})_2]^{4+}$, by analogy to two tetranuclear iron(III) complexes whose crystal structures were reported in 1988.⁵⁵ These structures show two $[\text{Fe}^{\text{III}}_2(\text{HPTB})(\text{O}_2\text{CPh})]^{4+}$ units connected by two oxo groups that bridge between one iron(III) of one unit and the corresponding iron in the other unit. This tetranuclear form was also proposed by Feig et al. as the end product in their mechanistic studies of the reactions of O_2 with $1\cdot\text{O}_2\text{CPh}$ and two sister complexes.⁵⁶ In the absence of crystal structures, we cannot be sure that $4\cdot\text{O}_2\text{PPh}_2$ and $4\cdot\text{O}_2\text{AsMe}_2$ exist as tetra-iron species and leave open the possibility that either complex may in fact remain dinuclear. We also note that the reported tetranuclear structures may form as a result of crystallization conditions and may not reflect the nature of $4\cdot\text{O}_2\text{X}$ in solution.

Discussion

A common step in dioxygen activation by biological diiron(II) systems is the formation of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-peroxo})\text{diiron(III)}$ moieties,^{9–16} which are often stable enough to be trapped and characterized. Synthetic $(\mu\text{-}\eta^1\text{:}\eta^1\text{-peroxo})\text{diiron(III)}$ complexes also exhibit enough stability to allow characterization,^{17,24,26–28} and some in fact have been crystallized.^{18–21} For the purpose of examining the factors affecting the stability of this moiety, we synthesized diiron(II) complexes using the dinucleating ligand N-EtHPTB and diphenylphosphinate or dimethylarsinate in lieu of more frequently employed carboxylate bridges. Solutions of these complexes reacted with dioxygen, forming $(\mu\text{-}\eta^1\text{:}\eta^1\text{-peroxo})\text{diiron(III)}$ moieties, which were examined spectroscopically.

Upon oxygenation, $1\cdot\text{O}_2\text{AsMe}_2$ forms $2\cdot\text{O}_2\text{AsMe}_2$, a metastable green-blue intermediate, before decaying to the yellow iron(III) end product. Complex $1\cdot\text{O}_2\text{PPh}_2$ also forms a green-blue intermediate ($2\cdot\text{O}_2\text{PPh}_2$), but this species converts to a second intermediate ($3\cdot\text{O}_2\text{PPh}_2$), a deep blue species, before decaying to the yellow end product. This second intermediate is reminiscent of $3\cdot\text{O}_2\text{CPh}$, the $(\mu\text{-}\eta^1\text{:}\eta^1\text{-peroxo})\text{diiron(III)}$ intermediate observed upon oxygenation of $1\cdot\text{O}_2\text{CPh}$.²⁹ These results bring up three questions: (i) What is the nature of $2\cdot\text{O}_2\text{X}$ and $3\cdot\text{O}_2\text{X}$? (ii) How does $2\cdot\text{O}_2\text{X}$ convert to $3\cdot\text{O}_2\text{X}$? (iii) Why are $2\cdot\text{O}_2\text{CPh}$ and $3\cdot\text{O}_2\text{AsMe}_2$ not observed?

We first address the identities of $2\cdot\text{O}_2\text{PPh}_2$, $3\cdot\text{O}_2\text{PPh}_2$, and $2\cdot\text{O}_2\text{AsMe}_2$, determination of which rests on evidence gathered from a variety of spectroscopic techniques. Because each of these intermediates has a strong chromophore arising from






	$\nu_{\text{O-O}}$
	721 – 747 cm^{-1}
	747 cm^{-1}
	790 cm^{-1}
	805 – 827 cm^{-1}
	840 – 908 cm^{-1}

Figure 11. Peroxo O–O stretching ranges reported for various dicopper, copper–iron, monoiron, and diiron complexes.

a peroxo ligand-to-metal charge-transfer (LMCT) band, rR spectroscopy is a good place to start, as it serves as an excellent probe of O–O vibrations. The rR spectra of these species exhibit features at $\sim 850\text{--}900\text{ cm}^{-1}$ that are assigned to $\nu_{\text{O-O}}$ on the basis of isotopic substitution studies. Upon ^{18}O substitution, the frequency downshifts observed for peaks around 850 cm^{-1} in the rR spectra of both $2\cdot\text{O}_2\text{PPh}_2$ and $2\cdot\text{O}_2\text{AsMe}_2$ unequivocally indicate the presence of a ligated peroxide moiety. The rR spectrum produced by using an isotopic mixture of O_2 reveals that the peroxide in $2\cdot\text{O}_2\text{PPh}_2$ is symmetrically ligated. Because its Mössbauer spectrum shows equivalent iron(III) atoms, the peroxide must be ligated to the diiron(III) center in either a $\mu\text{-}\eta^1\text{:}\eta^1$ or a $\mu\text{-}\eta^2\text{:}\eta^2$ configuration. No $(\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo})\text{diiron(III)}$ complex has been reported to date, but there are examples of dicopper and heme-copper species containing $(\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo})\text{dimetal}$ cores. Figure 11 shows a trend wherein the O–O stretch increases in frequency as the peroxide moiety moves from $\mu\text{-}\eta^2\text{:}\eta^2$ to $\mu\text{-}\eta^1\text{:}\eta^2$ to η^2 to $\mu\text{-}\eta^1\text{:}\eta^1$ (Figure 11).^{21,26,40,42–46}

Comparing those frequencies to values observed for $2\cdot\text{O}_2\text{PPh}_2$, $2\cdot\text{O}_2\text{AsMe}_2$, and $3\cdot\text{O}_2\text{PPh}_2$ leads us to conclude that the peroxide is ligated in a $\mu\text{-}\eta^1\text{:}\eta^1$ mode in all three complexes, as found in the crystal structure of $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2)(\text{OPPh}_3)_2]^{3+}$.¹⁹ However, the $\sim 50\text{ cm}^{-1}$ disparity observed between the $\nu_{\text{O-O}}$ values of $2\cdot\text{O}_2\text{X}$ and $3\cdot\text{O}_2\text{X}$ raises the interesting question of why they are different.

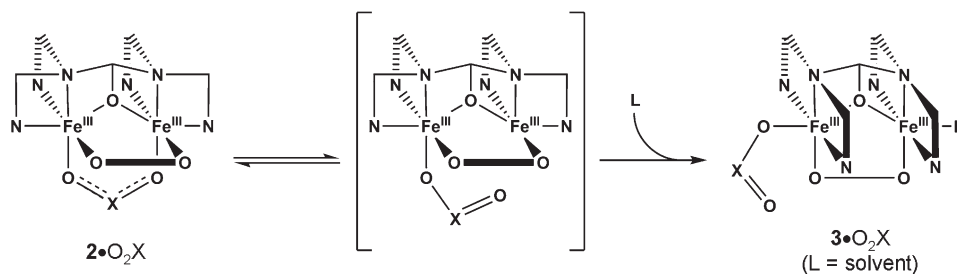
One possible explanation for the difference is a change in the $\text{Fe}\cdots\text{Fe}$ distance. Brunold et al. proposed a mechanical coupling model for understanding $(\mu\text{-}\eta^1\text{:}\eta^1\text{-peroxo})\text{diiron(III)}$ units wherein the stretching frequency of the peroxide bond increases due to increased mechanical coupling to the Fe–O stretch as the Fe–O–O angle opens from 90° .⁵⁷ On the basis of this model, it stands to reason that, as the iron centers move apart, the Fe–O–O angle should increase, thus producing a higher-frequency $\nu_{\text{O-O}}$.⁵⁸ This relationship between $\nu_{\text{O-O}}$ values and $\text{Fe}\cdots\text{Fe}$ distances is supported by a recent publication showing that an increase in the $\text{Fe}\cdots\text{Fe}$

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(58) The Brunold and Solomon model also predicts that, as $\nu_{\text{O-O}}$ increases, $\nu_{\text{Fe-O}}$ will decrease. This predicted trend is consistent with our observations, but we found a decrease of only $\sim 7\text{ cm}^{-1}$ between $2\cdot\text{O}_2\text{PPh}_2$ and $3\cdot\text{O}_2\text{PPh}_2$, which is much smaller than the $\sim 110\text{ cm}^{-1}$ change predicted by the model for an increase in $\nu_{\text{O-O}}$ from ~ 850 to $\sim 900\text{ cm}^{-1}$. The disparity may be due to differences in the Fe–O–O–Fe dihedral angle between our intermediates (0° observed in the $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2)(\text{OPPh}_3)_2]^{3+}$ crystal structure¹⁹) and the complex used in their calculations (52.9°).²⁰ Further theoretical work extending the mechanical coupling model to other diiron- O_2 adducts would be desirable.

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Scheme 1. Conversion of $2 \cdot \text{O}_2\text{X}$ to $3 \cdot \text{O}_2\text{X}$ 

distance can be directly correlated to the increase in the stretching frequency of the peroxide bond in a series of $\text{Fe}_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-O}_2)(\mu\text{-OR})$ complexes.²⁶ Applying this correlation to the values of $\nu_{\text{O-O}}$ observed for $2 \cdot \text{O}_2\text{PPh}_2$, $2 \cdot \text{O}_2\text{AsMe}_2$, and $3 \cdot \text{O}_2\text{PPh}_2$ generates respective $\text{Fe} \cdots \text{Fe}$ distances of 3.16, 3.13, and 3.40 Å, values in reasonable agreement with distances of 3.25, 3.27, and 3.47 Å determined from EXAFS analysis.

On the basis of this information, as well as Mössbauer evidence for equivalent iron atoms in $2 \cdot \text{O}_2\text{PPh}_2$ and the bidentate phosphinate bridge observed in the crystal structure of $1 \cdot \text{O}_2\text{PPh}_2$, we postulate that the diiron(III) center in $2 \cdot \text{O}_2\text{PPh}_2$ is bridged by three groups: the alkoxo oxygen of N-EtHPTB, the 1,2-peroxo moiety, and the phosphinate ligand. The structure of $1 \cdot \text{O}_2\text{PPh}_2$ has one open coordination site on each iron atom, both of which are properly positioned to allow dioxygen to coordinate easily in the 1,2-peroxo bridging mode found in $2 \cdot \text{O}_2\text{PPh}_2$ (Scheme 1). The parallels observed in the UV-vis, rR, Mössbauer, and EXAFS spectra of $2 \cdot \text{O}_2\text{PPh}_2$ and $2 \cdot \text{O}_2\text{AsMe}_2$ indicate that the latter complex is also triply bridged, with the role of the arsenate moiety analogous to that of the phosphinate moiety in $2 \cdot \text{O}_2\text{PPh}_2$.

Complex $2 \cdot \text{O}_2\text{PPh}_2$ is observed to convert to $3 \cdot \text{O}_2\text{PPh}_2$ at temperatures above -40°C . In this conversion, the phosphinate moiety is proposed to shift to a terminal position on one iron, resulting in the larger interiron distance revealed by EXAFS analysis and the increased $\nu_{\text{O-O}}$ seen in the rR spectrum of $3 \cdot \text{O}_2\text{PPh}_2$. On the basis of similar rR data and similar electronic transitions in the visible range, we propose that $3 \cdot \text{O}_2\text{PPh}_2$ and $3 \cdot \text{O}_2\text{CPh}$ share the same basic dibridged structure (Scheme 1). A Hammett study of $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2)(\text{O}_2\text{X})]^{2+}$ (O_2X = substituted benzoate) showed a correlation between σ values of the benzoate substituent and the lifetimes of the peroxo intermediates, with electron-withdrawing substituents increasing $t_{1/2}$.¹⁹ This effect indicates that the benzoate remains coordinated to the diiron(III) unit in a MeCN solution of $3 \cdot \text{O}_2\text{CPh}$ at -10°C . Since this 1996 report, we have noted the similarity of the resonance Raman data from $3 \cdot \text{O}_2\text{CPh}$ with those collected after adding OPPh_3 ^{26,40} and deduce that the benzoate moiety in $3 \cdot \text{O}_2\text{CPh}$ must occupy a terminal position. While this conclusion is at odds with the bridging configuration proposed by the authors who originally characterized this peroxo complex,^{29,40} they had the benefits of neither the mechanical coupling model of Brunold et al.⁵⁷ nor a comparison of the $\nu_{\text{O-O}}$ values of $3 \cdot \text{O}_2\text{CPh}$ and its OPPh_3 adduct.²⁶ The unchanged $\nu_{\text{O-O}}$ value recorded after OPPh_3 ligation indicates that the $\text{Fe} \cdots \text{Fe}$ distance is comparable in the two complexes. The interiron distance of 3.47 Å measured in $3 \cdot \text{O}_2\text{PPh}_2$ closely matches the interiron distance of 3.462 Å reported¹⁹ in the crystal structure of $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2)-$

$(\text{OPPh}_3)_2]^{3+}$, suggesting that, in $3 \cdot \text{O}_2\text{PPh}_2$, the phosphinate becomes a terminal ligand on one iron, thereby opening up a coordination site on the other (Scheme 1). In acetonitrile, this site is most likely occupied by solvent, making both iron centers six-coordinate and indistinguishable by Mössbauer spectroscopy. However, in CH_2Cl_2 , the available coordination site cannot be filled by the noncoordinating solvent or the BPh_4 counterion. This produces a complex in which one iron atom is six-coordinate and the other is five-coordinate, a condition reflected by the presence of two quadrupole doublets in the Mössbauer spectrum (Figure 6 and Table 3).

During conversion from $2 \cdot \text{O}_2\text{PPh}_2$ to $3 \cdot \text{O}_2\text{PPh}_2$ at -30°C , the peroxo-to-iron(III) charge-transfer band blue-shifts 96 nm in MeCN and 57 nm in CH_2Cl_2 (Table 3). It is not clear why such large blue-shifts occur. An obvious difference between the proposed structures of $2 \cdot \text{O}_2\text{X}$ and $3 \cdot \text{O}_2\text{X}$ (Scheme 1) is the binding site of the peroxide. In $2 \cdot \text{O}_2\text{X}$, it is cis to the N-EtHPTB amine nitrogen atoms, while in $3 \cdot \text{O}_2\text{X}$, it is trans to those atoms. There is also a difference in the Fe-O-O angles due to different $\text{Fe} \cdots \text{Fe}$ distances in each intermediate. Because the degree of peroxide and iron orbital mixing affects the energy required for a LMCT, any changes in the iron coordination sphere, especially changes involving the peroxide, can produce changes in the visible absorbance spectrum. The smaller shift observed in CH_2Cl_2 may be partially accounted for by incomplete conversion to $3 \cdot \text{O}_2\text{PPh}_2$, but we must also consider the presence of one five-coordinate iron center as another factor that can affect the λ_{max} (Scheme 1, $3 \cdot \text{O}_2\text{X}$).

The mechanism proposed in Scheme 1 would require the N3 ligand set on either end of the 2-hydroxypropane ligand backbone to rearrange from a facial to a meridional configuration during conversion from $2 \cdot \text{O}_2\text{PPh}_2$ to $3 \cdot \text{O}_2\text{PPh}_2$. Our hypothetical structure of $2 \cdot \text{O}_2\text{PPh}_2$ is based on the crystal structure of $1 \cdot \text{O}_2\text{PPh}_2$ (Figure 1), which clearly shows an open coordination site on each iron atom cis to its respective amine nitrogen. Dioxygen binding to these sites would be expected to be facile, and the resulting peroxo complex would have a geometry similar to that of the simplified cartoon representing $2 \cdot \text{O}_2\text{X}$ shown in Scheme 1, with the N3 ligand sets configured facially. The proposed structure of $3 \cdot \text{O}_2\text{PPh}_2$ is based on the crystal structure of $[\text{Fe}_2(\text{N-EtHPTB})(\text{O}_2)(\text{OPPh}_3)_2]^{3+}$, in which both N3 ligand sets of the dinucleating N-EtHPTB ligand adopt meridional configurations and both OPPh_3 ligands coordinate trans to the alkoxo bridge.¹⁹ In addition to N-ligand rearrangement, conversion of $2 \cdot \text{O}_2\text{X}$ to $3 \cdot \text{O}_2\text{X}$ also requires the bridging oxyanion in the initial species to move to a terminal position in the second species. Shifting O_2X to a monodentate coordination mode forms the unobserved species shown in the center of Scheme 1, which can revert to $2 \cdot \text{O}_2\text{X}$ or irreversibly rearrange to form $3 \cdot \text{O}_2\text{X}$.

In both MeCN and CH₂Cl₂ at -30 °C, we observe significant conversion of 2·O₂PPh₂ to 3·O₂PPh₂, indicating that the latter is thermodynamically favored at this temperature. In contrast, no buildup of 3·O₂AsMe₂ is observed at any temperature, so 2·O₂AsMe₂ must be the more favored form. In the case of O₂X = benzoate, however, the equilibrium shifts in the opposite direction, and only 3·O₂CPh has been reported. Also, 2·O₂CPh has not been observed despite the fact that the reaction of 1·O₂CPh with O₂ has been investigated in various solvents and solvent combinations at low temperatures,^{29,40} including one study by stopped-flow methods in propionitrile at -75 °C.⁵⁹

The distinct preferences of the different O₂X moieties for 2·O₂X versus 3·O₂X suggest that the nature of the O₂X bridge in 2·O₂X affects the equilibrium associated with the conversion of 2·O₂X to 3·O₂X. Clearly, arsenate favors 2 and benzoate favors 3, while phosphinate is intermediate between the two. A comparison of the pK_a values of the corresponding conjugate acids (HO₂AsMe₂, 6.27;^{60,61} HO₂PPh₂, 2.32;⁶² HO₂CPh, 4.19⁶³) does not reveal a trend that matches our observations. However, an examination of the respective bite distances of the bridging oxyanions in each of the diiron(II) precursors shows that the lifetime of 2·O₂X increases with a larger O···O distance (namely, 2.23 Å for O₂CPh, 2.56 Å for O₂PPh₂, and 2.80 Å for O₂AsMe₂, as deduced from the structures of the three 1·O₂X complexes). We speculate that the bigger O···O bite distance imposes less strain on the bicyclic moiety (Figure 12) and results in the more stable, triply bridged core of 2·O₂AsMe₂. On the other hand, the smaller bite distance of the benzoate bridge makes it difficult to span an Fe···Fe distance of ca. 3.2 Å expected for 2·O₂CPh and leads to facile conversion of the benzoate bridge to a terminal ligand and formation of 3·O₂CPh.

This movement of an O₂X ligand from a bridging to a terminal position corresponds to a phenomenon of some importance in diiron enzymes, referred to as a carboxylate shift.⁶⁴ For soluble methane monooxygenase, toluene monooxygenase, and ribonucleotide reductase, one of the conserved glutamate residues (E243, E231, and E238, respectively) of the common diiron active site alternates between terminal and μ-1,1 or μ-1,3 coordination modes in the diiron(III) and diiron(II) forms.^{65–69} These carboxylate

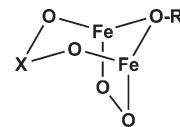


Figure 12. Generic representation of the bicyclic diiron core proposed for 2·O₂X.

shifts alter the interiron distance in each active site and may affect the ability of each diiron site to activate O₂. When O₂ is activated, the iron–iron distance can change by as much as 1.5 Å from the diiron(II) starting point to the diiron(IV) state associated with methane oxidizing intermediate Q,³ so the number and the nature of bridging ligands are of vital importance for controlling oxygen activation. While this current work does not directly address the question of how to facilitate O–O bond cleavage at a diiron center, it does shed light on the ability of O₂X ligands to tune interiron distances by changing coordination modes. We have demonstrated that moving an O₂X ligand from a μ-1,3 to a terminal coordination mode changes the interiron distance of an alkoxide-bridged (μ-η¹:η¹-peroxo)diiron(III) complex by ~0.2 Å. This means relatively minor ligand rearrangements can produce substantial changes in interiron distances, which in turn, affect the stability of the O–O bond.

In summary, we have synthesized two new diiron(II) complexes and investigated their reaction with oxygen, producing (μ-η¹:η¹-peroxo)diiron(III) species. By varying the central atom of a three-atom chain bridging the iron atoms, we were able to produce and stabilize a peroxo moiety previously unobserved when using N-EtHPTB as a ligand (Scheme 1). Under the right conditions, the diphenylphosphinate-bridged form of this peroxo moiety converts to a second peroxo-containing species, akin to other peroxo complexes previously formed using this ligand. Although (μ-η¹:η¹-peroxo)diiron(III) complexes of N-EtHPTB and other ligands have been studied for years, this conversion of one peroxo species to another is reported here for the first time; we suspect that it takes place upon oxygenation of all previously reported, three-atom bridged, diiron(II) N-EtHPTB complexes, albeit often so rapidly that it has never been observed. Further experiments are underway to confirm this hypothesis.

Supporting Information Available: Crystallographic data for 1·O₂PPh₂ and 1·O₂AsMe₂. UV–vis, resonance Raman and Mössbauer spectra. Complete EXAFS fitting results, including FEFF models. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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