Diiron Complexes of 1,8-Naphthyridine-Based Dinucleating Ligands as Models for Hemerythrin

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Abstract: The hydroxo-bridged diiron(II) compounds $[Fe_2(BPEAN)(\mu\text{-}OH)(OTf)](OTf)_2$ (**1**) and $[Fe_2(BEPEAN)(\mu\text{-}OH)](OTf)_3$ (**2**) were prepared by using 1,8-naphthyridine-based dinucleating ligands BPEAN and BEPEAN, where BPEAN = 2,7-bis{bis[2-(2-pyridyl)ethyl]aminomethyl}-1,8-naphthyridine and BEPEAN = 2,7-bis{bis[2-(2-(5-ethyl)pyridyl)ethyl]aminomethyl}-1,8-naphthyridine. When compound **2** was treated with excess 30% aqueous H_2O_2 in acetonitrile at −40 °C, a red-brown species (**3**) was produced. The UV−vis spectrum of **3** exhibited an absorption maximum at 505 nm (ϵ = 1500 M^{-1} cm^{-1}), close to that observed for oxyHr. Resonance Raman experiments revealed an isotope-sensitive O−O stretching band at 868 cm^{-1}. When a mixture of 1:1 H_2O_2/D_2O_2 (25% in 1:1 H_2O/D_2O) was used to generate **3**, a broader Raman band centered at 870 cm^{-1} appeared, indicating the peroxide group to be protonated. The ^1H ENDOR spectrum of **3**, cryoreduced to the diiron(II,III) state, showed a signal with $A \approx 12$ MHz that disappeared when D_2O_2 in D_2O was used to generate **3**, providing further evidence for the presence of a hydroperoxide ligand bound to iron. The EPR spectrum of the cryoreduced sample revealed that **3** has a (μ-oxo)diiron(III) core, a conclusion supported by Mössbauer spectroscopy. The Mössbauer spectrum exhibited the unusual quadrupole splitting values that are characteristic of the diiron(III) center of oxyHr. Thus, all spectroscopic properties of **3** are consistent with it being a hydroperoxo-bound (μ-oxo)diiron(III) complex. The hydroperoxide ligand is more resistant to deprotonation than in mononuclear iron(III) analogues, which may reflect the presence of a hydrogen bond between the hydroperoxide and bridging oxide groups. At room temperature, acetonitrile/water solutions of **3** decayed to iron(II) species, releasing the iron-bound hydroperoxide group to form O_2.

Introduction

Carboxylate-bridged diiron centers in several metalloproteins perform some of the more interesting O_2 activation functions in biology.[1−4] A bis(μ-carboxylato)(μ-oxo/hydroxo)diiron center in the dioxygen transport protein hemerythrin (Hr) reversibly binds O_2.[5] Two physiologically relevant forms of hemerythrin have been characterized. Reduced deoxyHr has a diiron(II) center bridged by two carboxylate groups from protein side chain residues and a hydroxide group (Figure 1). One iron is six-coordinate with three terminal His ligands whereas the other iron is five-coordinate with two such His ligands.[6] The resulting asymmetric diiron(II) center is well engineered by nature for reversible O_2 binding.

When an O_2 molecule reacts with deoxyHr, two electrons transfer from the diiron(II) center to dioxygen, affording a hydroperoxide diiron(III) core (oxyHr).[5−8] The peroxide ligand binds in a terminal site to the iron atom that is five-coordinate in deoxyHr. The proton of the hydroxide bridge in deoxyHr transfers to the peroxide ligand to form a terminally bound hydroperoxide,[5,7,8] stabilized by hydrogen bonding to the bridging oxide ligand that results (Figure 1). Such an O_2-derived ligand terminally bound to one iron atom was identified in the

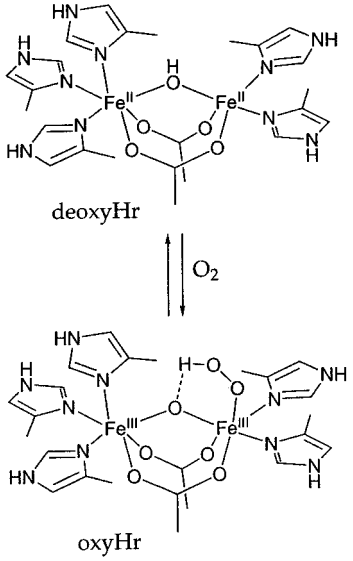

Figure 1. Postulated reversible O_2 binding in hemerythrin.

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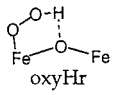
Table 1. Summary of Spectroscopic Data for Hydroperoxide-Bound Diiron(III) Species

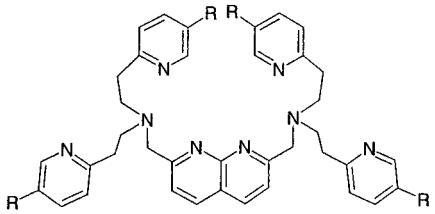
	UV-vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}))	Resonance Raman (cm^{-1})		Mössbauer (mm/s)		ref.
		$\nu_{O\text{-}OH}$ ($^{18}O_2H$)	$\nu_{O\text{-}OD}$	δ	ΔE_Q	
 oxyHr	330 (6800) 500 (2200)	844 (798)	848	0.51, 0.52	1.96, 0.95	9-14
O_2 adduct of $[Fe_2(\mu\text{-OH})(\mu\text{-}Ph_4DBA)(TMEDA)_2\text{-}(OTf)]$	470 (2600)	843 (797)		0.50[a]	1.48[a]	17
3	505 (1500)	868 (828)	871	0.51, 0.50	1.78, 1.11	this work

[a] Values of δ_{av} and ΔE_{Qav} were reported.

X-ray crystal structure of oxyHr.[6] The peroxidic nature of this ligand was revealed by several experiments. There is an intense absorption band centered at 500 nm (ϵ = 2200 M^{-1} cm^{-1}), indicative of a peroxoiron(III) charge-transfer transition for oxyHr.[9,10] The resonance Raman spectrum displays a sharp band around 844 cm^{-1} which shifts to 798 cm^{-1} when $^{18}O_2$ is used to generate oxyHr.[11] Mössbauer data are consistent with high-spin iron(III) centers (δ_1 = 0.51 mm/s, $\Delta E_{Q1} \approx$ 1.96 mm/s; δ_2 = 0.52 mm/s, $\Delta E_{Q2} \approx$ 0.95 mm/s), and differ significantly from the iron(II) parameters in deoxyHr (δ = 1.14 mm/s, $\Delta E_Q \approx$ 2.76 mm/s).[12]

Shifts of 2−4 cm^{-1} in the O−O stretching frequency of oxyHr occurred when the resonance Raman spectrum was recorded in D_2O,[13,14] which was taken as support for protonation of the peroxide ligand. Resonance Raman studies of the symmetric Fe−O−Fe vibration in various forms of hemerythrin revealed a perturbation in the Fe−O stretch, suggesting the existence of the hydrogen bond from the terminal hydroperoxide to the bridging oxide.[13,15,16] The presence of such a putative hydrogen bond between the hydroperoxide and the bridging oxide in oxyHr has not yet been encountered in synthetic model compounds, nor has a functional model that binds O_2 reversibly like the protein been obtained.

Recent work from our laboratory has afforded a model in which the O_2-binding step in hemerythrin was reproduced by using a new dinucleating dicarboxylate ligand, dibenzofuran-4,6-bis(diphenylacetate) (Ph_4DBA).[17] A peroxodiiron(III) species formed in the reaction of a hydroxo-bridged, coordinatively unsaturated diiron(II) precursor $[Fe_2(\mu\text{-OH})(\mu\text{-}Ph_4DBA)(TMEDA)_2(OTf)]$ with O_2 at −78 °C. The spectroscopic properties of this species matched well those of oxyHr (Table 1). Mössbauer spectroscopic data suggested the presence of a (μ-oxo)diiron(III) core in the oxidized species, implying that the proton had migrated from the bridging hydroxide group. A terminally bound hydroperoxide group may have formed, but its existence could not be determined. Although unstable upon standing at −78 °C, this compound is the only example reported to date that models the hydroperoxodiiron(III) active site of oxyHr.



BPEAN R = H
BEPEAN R = Et

Figure 2. Schematic representation of BPEAN and BEPEAN ligands.

As described elsewhere, we have developed chemistry to prepare multidentate dinucleating ligands using 1,8-naphthyridine as a bridging unit.[18] The 1,8-naphthyridine molecule can coordinate two metal ions in a syn,syn bidentate fashion just like a bridging carboxylate, a frequently encountered dinucleating ligand in biological systems. In the present paper we describe the synthesis and characterization of the hydroxo-bridged diiron(II) compounds $[Fe_2(BPEAN)(\mu\text{-OH})(OTf)](OTf)_2$ (**1**) and $[Fe_2(BEPEAN)(\mu\text{-OH})](OTf)_3$ (**2**), which contain the dinucleating ligands BPEAN and BEPEAN,[19] where BPEAN = 2,7-bis{bis[2-(2-pyridyl)ethyl]aminomethyl}-1,8-naphthyridine and BEPEAN = 2,7-bis{bis[2-(2-(5-ethyl)pyridyl)ethyl]-aminomethyl}-1,8-naphthyridine (Figure 2). When **2** is treated with excess 30% aqueous H_2O_2 in acetonitrile at −40 °C, a hydroperoxodiiron(III) compound (**3**) forms, the spectroscopic properties and reactivity studies of which are presented.

Experimental Section

General Procedures and Methods. All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Diethyl ether was purified by passage through an activated Al_2O_3 column under nitrogen. Dichloromethane, acetonitrile, and propionitrile were distilled from CaH_2 under nitrogen. Fourier transform infrared spectra were recorded on a Bio-Rad FTS135 instrument. UV−vis spectra were recorded on a Varian 1-E spectrophotometer. Mössbauer spectra were recorded on an MS1 spectrometer (WEB Research Co.) with a ^{57}Co source in a Rh matrix maintained at

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room temperature in the Massachusetts Institute of Technology Department of Chemistry Instrumentation Facility. The cryogenic reduction and subsequent EPR and ^{1}H ENDOR experiments were performed at Northwestern University. The BPEAN and BEPEAN ligands were synthesized as reported elsewhere,[19] and $Fe(OTf)_2{\cdot}2CH_3CN_3$ was obtained by following a known procedure.[20] All air-sensitive manipulations were carried out either in a nitrogen-filled Vacuum Atmospheres drybox or by standard Schlenk line techniques.

[Fe$_2$(BPEAN)(μ-OH)(OTf)](OTf)$_2$ (1). A portion of BPEAN (92 mg, 0.151 mmol) in acetonitrile (2 mL) was added to a solution of $Fe(OTf)_2{\cdot}2CH_3CN_3$ (125 mg, 0.302 mmol) in acetonitrile (2 mL). The solution was stirred for 10 min, and Bu_3N (36 μL, 0.151 mmol) was added. To this solution under N_2 atmosphere was added H_2O (3 μL), and the solution was stirred for 15 min. The color of the solution turned red. The solvent was removed under vacuum and the residue dissolved in CH_2Cl_2 (4 mL). To this solution was added Et_2O until it turned cloudy. Precipitates were filtered off, and pink-red crystals suitable for X-ray crystallography were obtained after the solution was stored at −30 °C for 24 h (71 mg, 40%). FTIR (KBr, cm^{-1}): 3477 (br), 3080 (m), 2961 (m), 2876 (w), 1605 (s), 1570 (w), 1556 (w), 1517 (w), 1490 (m), 1440 (m), 1305 (m), 1280 (s), 1260 (s), 1214 (s), 1155 (s), 1035 (s), 955 (w), 869 (w), 792 (m), 765 (m), 638 (s). UV−vis (MeCN, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 510 (680). Anal. Calcd for **1**, $C_{41}H_{41}N_8O_{10}S_3F_9Fe_2$: C, 41.57; H, 3.49; N, 9.46. Found: C, 41.58; H, 3.54; N, 9.68.

[Fe$_2$(BEPEAN)(μ-OH)](OTf)$_3$ (2). A portion of BEPEAN (100 mg, 0.139 mmol) in acetonitrile (2 mL) was added to a solution of $Fe(OTf)_2{\cdot}2CH_3CN_3$ (114 mg, 0.278 mmol) in acetonitrile (2 mL). The solution was stirred for 10 min, and Bu_3N (33 μL, 0.139 mmol) was added. To this solution under N_2 atmosphere was added H_2O (3 μL), and the mixture was allowed to stir for 15 min. The color of the solution turned red, the solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2 (4 mL) and filtered. The filtrate was evaporated to dryness under vacuum, and the residue was dissolved in propionitrile. Pink-red crystals were obtained by diffusion of Et_2O into this propionitrile solution (89 mg, 49%). FTIR (KBr, cm^{-1}): 3470 (br), 3068 (m), 2970 (s), 2936 (s), 2877 (s), 1611 (s), 1571 (m), 1554 (w), 1499 (m), 1459 (m), 1438 (m), 1405 (w), 1259 (s), 1160 (s), 1089 (w), 1030 (s), 952 (w), 875 (m), 844 (s), 795 (m), 757 (m), 638 (s). UV−vis (MeCN, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 510 (640). Anal. Calcd for **2**, $C_{49}H_{57}N_8O_{10}S_3F_9Fe_2$: C, 45.38; H, 4.43; N, 8.64. Found: C, 45.82; H, 4.67; N, 8.39.

X-ray Crystallographic Studies. X-ray crystallographic studies were carried out on a Bruker (former Siemens) CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) controlled by a Pentium-based PC running the SMART software package.[21] Single crystals were mounted at room temperature on the ends of quartz fibers in Paratone N oil, and data were collected at 193 K in a stream of cold N_2 maintained by a Bruker LT-2A nitrogen cryostat. Data collection and reduction protocols are described in detail elsewhere.[22] The structures were solved by direct methods and refined on F^2 by using the SHELXTL software package.[23] Empirical absorption corrections were applied with the SADABS program,[24] and the structure of **1** was checked for higher symmetry by the PLATON program.[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized locations and given an isotropic thermal parameter 1.2 times the thermal parameter of the carbon atom to which they were attached.

In the structure of **1**, one chlorine atom of a dichloromethane solvent was disordered over two positions, Cl(3A) and Cl(3B), each refined at half-occupancy. The other chlorine atom was also disordered over two positions, Cl(4A) and Cl(4B), refined at occupancies of 0.9 and 0.1, respectively. Another dichloromethane solvent was also disordered, the carbon atom of which was distributed over two positions and refined. The chlorine atoms were distributed accordingly and refined. Important crystallographic information is shown in Table 2.

Table 2. Summary of X-ray Crystallographic Data for **1**·3CH_2Cl_2

empirical formula	$C_{44}H_{47}N_8O_{10}Cl_6F_9S_3Fe_2$	ρ_{calcd}, g cm^{-3}	1.641
fw	1439.48	μ(Mo Kα), mm^{-1}	0.970
space group	$P2_1$	2θ range, deg	3−45
a, Å	10.9593(2)	total no. of data	12 323
b, Å	21.1150(4)	no. of unique data	6903
c, Å	12.75340(10)	no. of obsd data[a]	5683
β, deg	99.2960(10)	no. of params	733
V, Å^{-3}	2912.45(8)	R_1[b]	0.0468
Z	2	wR_2[c]	0.1162
T, °C	−85	max, min peaks, e/Å^{-3}	0.617, −0.728

[a] Observation criterion: $I > 2\sigma(I)$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Low-Temperature UV−Vis Spectroscopy. Spectra were recorded on a HP8453 diode array spectrophotometer by using a custom manufactured low-temperature dewar. A temperature of −40 °C was maintained with a dry ice/acetonitrile bath. In a typical experiment, a solution of **2** in CH_3CN (0.2 mM) at −40 °C was treated with excess (10-fold) 30% aqueous H_2O_2 under a N_2 atmosphere. A red-brown color appeared, and the UV−vis spectrum was recorded.

Resonance Raman Spectroscopy. A Coherent Innova 90C argon laser with an exciting wavelength of 514.5 nm and 85 mW of power was used to acquire Raman data. A 0.6 m single monochromator (1200 grooves/nm grating), with an entrance slit of 100 μm, and a TE-CCD-1100-PB-VISAR detector (Princeton Instruments, Inc.) cooled to −40 °C were used in a standard backscattering configuration. A holographic notch filter (Kaiser Optical Systems) was used to attenuate Rayleigh scattering. Spectra were collected in CH_3CN solution at −30 °C with the same low-temperature dewar used in UV−vis studies. Solute concentrations of 10 mM were employed to ensure an optimal signal-to-noise ratio. A total of 300 scans each with 1 s exposure time were typically collected for each sample. Raman shifts were calibrated with acetonitrile as an internal standard. The 917 cm^{-1} acetonitrile band was used as a calibration standard for isotope substitution experiments. The data were processed on a Gateway 2000 computer using WINSPEC 3.2.1 software (Princeton Instruments, Inc.).

Cryogenic Reduction. Samples of complex **3** were prepared as a 5 mM solution in 2:1 2-methyltetrahydrofuran (2-MeTHF)/acetonitrile at −40 °C. The samples were rapidly cooled to 77 K in 3 mm i.d. quartz tubes immersed in liquid nitrogen and exposed to γ-radiation from a ^{60}Co source as reported previously.[26,27]

EPR and ENDOR Spectroscopy. X-band EPR spectra were recorded on a Bruker ESP300 spectrometer. The continuous wave (CW) 35 GHz ENDOR spectrometer and procedures employed in this study have been described.[28,29]

^{57}Fe Mössbauer Spectroscopy. A powdered solid sample of **1** or **2** (~0.03 mol) was suspended in Apiezon N grease, and the mixture was packed into a nylon sample holder in the drybox. The sample was removed from the drybox and rapidly precooled to 77 K. A frozen solution sample of **3** was prepared by adding excess H_2O_2 (30% aqueous, 80 μL) to 1 mL of an acetonitrile solution of **2** (30 mM) at −30 °C in a nylon sample holder. The mixing of H_2O_2 with the acetonitrile solution was assured by gently bubbling Ar through the mixture for 15 min at −30 °C. The sample was then quickly precooled to 77 K. All data were collected at 4.2 K, and isomer shift (δ) values are reported with respect to iron foil that was used for velocity calibration at room temperature. The spectra were fit to Lorentzian lines by using the WMOSS plot and fit program.[30]

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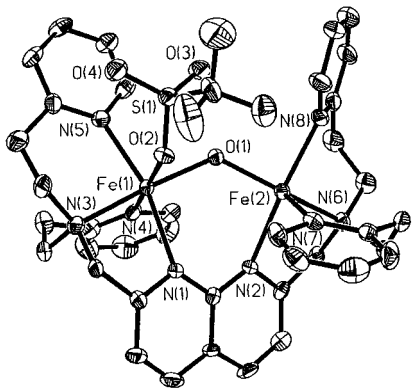

Figure 3. ORTEP diagrams of $[Fe_2(BPEAN)(\mu\text{-}OH)(OTf)](OTf)_2$ (**1**) showing the 40% probability thermal ellipsoids for all non-hydrogen atoms.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

bond length		bond angle	
Fe(1)···Fe(2)	3.534(4)	Fe(1)−O(1)−Fe(2)	127.5(2)
Fe(1)−O(1)	1.997(4)	O(1)−Fe(1)−O(2)	81.40(17)
Fe(1)−O(2)	2.455(5)	N(4)−Fe(1)−O(1)	98.0(2)
Fe(1)−N(1)	2.274(6)	N(3)−Fe(1)−O(2)	85.30(18)
Fe(1)−N(3)	2.173(5)	N(5)−Fe(1)−O(1)	98.1(2)
Fe(1)−N(4)	2.177(6)	N(5)−Fe(1)−O(2)	89.62(19)
Fe(1)−N(5)	2.196(6)	N(6)−Fe(2)−O(1)	146.0(2)
Fe(2)−O(1)	1.945(4)	N(7)−Fe(2)−O(1)	118.4(2)
Fe(2)−N(2)	2.225(5)	N(6)−Fe(2)− N(7)	95.4(2)
Fe(2)−N(6)	2.186(5)	N(2)−Fe(2)−N(8)	164.2(2)
Fe(2)−N(7)	2.115(6)		
Fe(2)−N(8)	2.169(6)		

[a] The numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figure 3.

Gas Chromatographic Analyses. Gas chromatography was performed on a Hewlett-Packard 5890 instrument equipped with a thermal conductivity (TC) detector and a 6 ft Haysep column. He was used as the carrier gas at a flow rate of 25 mL/min. The retention time for N_2/O_2 was determined to be around 2.6 min. A solution of **2** (15 mg, 0.012 mmol) in acetonitrile (2 mL) was cooled to −30 °C in a 5 mL glass vial sealed with a rubber septum under N_2. Excess 15% aqueous H_2O_2 (100 μL) was added to generate **3**. The solution was then purged with He for 30 min at −30 °C. The He purge was stopped, and a 100 μL aliquot of the headspace gases was withdrawn with a Hamilton gastight syringe for GC injection. The solution was warmed to room temperature, and another 100 μL aliquot of the headspace gases was analyzed by GC. An additional 100 μL aliquot of the headspace gases was also analyzed after 2 h. A control experiment was performed under the same conditions following the same procedure in the absence of **2**. Aliquots (100 μL) of the headspace gases were analyzed by GC for samples prepared at −30 °C and room temperature.

Results and Discussion

Preparation and Characterization of Hydroxo-Bridged Diiron(II) Compounds $[Fe_2(BPEAN)(\mu\text{-}OH)(OTf)](OTf)_2$ (1) and $[Fe_2(BEPEAN)(\mu\text{-}OH)](OTf)_3$ (2). Compound **1** was prepared by reacting 2 equiv of $Fe(OTf)_2{\cdot}2CH_3CN_3$, 1 equiv of hydroxide, and 1 equiv of ligand TPEAN in acetonitrile and crystallized from a saturated CH_2Cl_2/Et_2O solution at −30 °C. The structure of **1** is shown in Figure 3, and selected bond lengths and angles are listed in Table 3. The two iron(II) atoms are bridged by a hydroxide group and the 1,8-naphthyridine unit of BPEAN, which mimics a bridging carboxylate group. One iron is best described as six-coordinate with pseudooctahedral geometry imposed by four nitrogen ligands from BPEAN, one oxygen atom from the bridging hydroxide, and a weakly bound triflate counterion at an Fe(1)−O(2) distance of 2.455(5) Å. The other iron is five-coordinate, trigonal bipyramidal with four nitrogen atoms from BPEAN and one oxygen atom from the bridging hydroxide ion. The two iron atoms are 3.534(5) Å apart with $Fe-O_{bridge}$ distances of 1.945(4) and 1.997(4) Å and an Fe(1)−O(1)−Fe(2) angle of 127.5(2)°.

In the crystal structure of **1**, the two iron atoms are in an asymmetric environment like the diiron center in deoxyHr. The five-coordinate, trigonal bipyramidal Fe(2) has systematically shorter bond lengths to the surrounding ligands compared to the six-coordinate, pseudooctahedral Fe(1). The 1,8-naphthyridine unit binds two iron atoms like a bridging carboxylate group. The structural parameters of the hydroxo-bridged diiron(II) core compare well with those of the crystallographically characterized (μ-hydroxo)(μ-carboxylato)diiron(II) complexes.[17,31,32] The five-coordinate iron and the weakly bound triflate delineate potential binding sites for an O_2-derived ligand. The structure shows a dangling oxygen atom, O(3), of the bound triflate to be hydrogen bonded (2.914 Å) to the bridging hydroxide group, O(1). This observation suggests that an O_2-derived terminal ligand could similarly form a hydrogen bond to the bridging oxygen atom.

A sterically more bulky ligand, BEPEAN, was also used to prepare a diiron(II) complex. The analogous hydroxo-bridged diiron(II) compound $[Fe_2(BEPEAN)(\mu\text{-}OH)](OTf)_3$ (**2**) was readily obtained from vapor diffusion of Et_2O into propionitrile or acetonitrile solution by following the same procedure used to prepare **1**. A high-quality structure could not be obtained for the red crystal block, but the outline of the molecule clearly revealed the presence of a hydroxo-bridged diiron(II) unit (Figure S2 in the Supporting Information). Complex **2** has the same UV−vis spectrum as that of **1**, and elemental analysis supports the formula $[Fe_2(BEPEAN)(\mu\text{-}OH)](OTf)_3$.

Preparation of a Hydroperoxodiiron(III) Complex, 3. Compounds **1** and **2** were reactive toward O_2 at ∼ −10 °C in O_2-saturated CH_2Cl_2 or acetonitrile, but decomposition occurred without the formation of a spectroscopically detectable intermediate. When **1** or **2** was treated with excess (10-fold) 30% aqueous H_2O_2 in acetonitrile at −40 °C under dinitrogen, however, a red-brown species formed. With the sterically more bulky ligand BEPEAN, the color fully developed and could be used for spectroscopic analysis. This species **3** is stable in air or under nitrogen up to −30 °C and decays to form a yellow solution when warmed to room temperature.

The low-temperature UV−vis spectrum of **3** showed a broad peak at 505 nm (ϵ = 1500 M^{-1} cm^{-1}) that disappeared upon warming (Figure 4). The position and intensity of this band are close to those observed for the hydroperoxo-bound diiron(III) center in oxyHr, which has an absorption centered at 500 nm (ϵ = 2200 M^{-1} cm^{-1}).[9,10] Another peak at 330 nm (ϵ = 6800 M^{-1} cm^{-1}) was also reported for oxyHr, but the spectrum of **3** in this region was complicated by a strong ligand-derived absorption. No reaction occurred when **2** was treated with excess ^{t}BuOOH in acetonitrile at −40 °C. Treatment of a CH_2Cl_2 solution of **2** with excess H_2O_2 (30% aqueous) at −40 °C did not cause any color change, but addition of one drop of acetonitrile or THF upon stirring yielded the red-brown solution. The acetonitrile or THF solvent may assist in mixing of H_2O_2 with the solution of the starting diiron(II) compound or possibly

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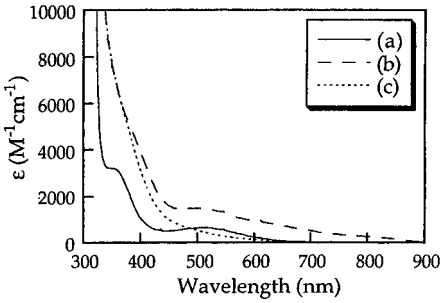

Figure 4. UV−vis spectra accompanying the reaction of $[Fe_2(BEPEAN)(\mu\text{-}OH)](OTf)_3$ (**2**) with excess 30% aqueous H_2O_2 at −40 °C in acetonitrile: (a) **2** in acetonitrile at −40 °C (0.2 mM); (b) **3** generated by the addition of excess 30% aqueous H_2O_2 to the solution of **2** at −40 °C; (c) the solution warmed to room temperature.

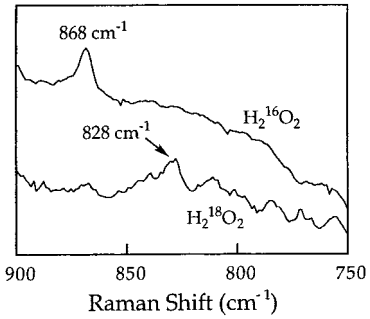

Figure 5. Resonance Raman spectra of **3**. Top spectrum: **3** generated by addition of excess 30% aqueous $H_2{}^{16}O_2$ at −30 °C in acetonitrile. Bottom spectrum: **3** generated by addition of excess 2% aqueous $H_2{}^{18}O_2$ at −30 °C in acetonitrile.

serve as a solvating ligand to one of the iron atoms, which may be required to generate the red-brown species.

Resonance Raman Investigations of 3. The UV−vis spectrum suggested the presence of a peroxide group in **3**. Resonance Raman experiments were therefore conducted at an excitation wavelength of 514.5 nm. As shown in Figure 5, a new band at 868 cm^{-1} appears in the Raman spectrum upon treatment of **2** with H_2O_2. This frequency falls into the right range for the O−O stretch of a peroxo species.[33] The nitrogen-rich environment of **3**, which is less donating than that in oxyHr, may account for the higher O−O stretching frequency compared to those for the oxygenated protein (844 cm^{-1}) and a previous model for oxyHr which had the bridging dicarboxylate ligand Ph_4DBA (843 cm^{-1}, Table 1). The ability of the ligand donor strength to influence the O−O stretching frequency of metal-bound peroxide has been noted previously.[33] When 2% aqueous $H_2{}^{18}O_2$ was used, the O−O stretching band shifted to ∼828 cm^{-1} ($\Delta\nu = -40$ cm^{-1}, Figure 5). The amount of shift is close to that observed for oxyHr ($\Delta\nu = -46$ cm^{-1}) and slightly less than that calculated on the basis of a simple diatomic harmonic oscillator model ($\Delta\nu_{calcd} = -49$ cm^{-1}). These observations indicate the presence of a peroxide group in **3**.

When the resonance Raman spectrum of oxyHr in D_2O was compared to that in H_2O, an upshift of 2−4 cm^{-1} in the O−O stretching frequency was obtained.[13,14] This result was interpreted as proof that the bound peroxide in oxyHr is protonated, since the O−O stretching frequency of a terminally bound hydroperoxide group should be sensitive to isotopic substitution of deuterium for hydrogen. When **3** was generated by using a mixture of 1:1 H_2O_2/D_2O_2 (25% in 1:1 H_2O/D_2O), the resonance Raman spectrum showed a broader band at 870 cm^{-1}, as

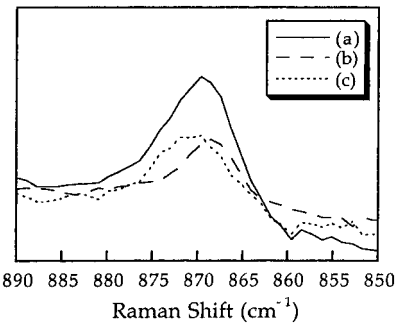

Figure 6. Resonance Raman spectra of **3**: (a) **3** generated by the addition of excess H_2O_2 (30% in H_2O) at −30 °C in acetonitrile; (b) same as (a) except 1:1 H_2O_2/D_2O_2 (25% in 1:1 H_2O/D_2O) was used; (c) difference spectrum of (a) minus (b).

indicated in Figure 6. The width at half-height of this band is approximately 1.5 cm^{-1} greater than the 868 cm^{-1} band recorded for the species generated by addition of H_2O_2 (30% in H_2O). Subtraction of the 868 cm^{-1} band from this 870 cm^{-1} band revealed a new band centered at 871 cm^{-1}. We therefore assign the band at 868 cm^{-1} as the O−O stretching band of terminally bound HOO^-. The 870 cm^{-1} band arises from a 1:1 mixture of HOO^- and DOO^- ligands, and the 871 cm^{-1} band obtained by the subtraction is the O−O stretch of terminally bound DOO^-. A ∼3 cm^{-1} shift in the O−O stretching frequency thus occurs by isotopic substitution of a proton by deuterium in **3**, indicating the presence of a hydroperoxide ligand. This conclusion is confirmed by EPR/ENDOR studies of **3** reduced at 77 K (vide infra), and strongly supports earlier work[5,13,14] proposing the chemistry for Hr shown in Figure 1.

EPR and ENDOR Spectroscopy of Cryoreduced 3. A cryogenic reduction technique was applied to generate a kinetically stabilized mixed-valence diiron(II,III) form of **3**, designated $\mathbf{3_{mv}}$. Previous work established that diiron(III) sites in proteins and model compounds can be reduced by one electron generated by γ-irradiation in frozen solution at 77 K.[26,34] The mixed-valence diiron(II,III) species is trapped in the original geometry of the diiron(III) form owing to the low molecular mobility under the experimental conditions.[27,34] EPR and ENDOR studies on radiolytically produced mixed-valence samples thus provide useful structural information of the original diiron(III) species.

The cryoreduced sample $\mathbf{3_{mv}}$ in a 2-MeTHF/MeCN glass at 77 K showed a narrow EPR signal with $g_{av} = 1.93$ (Supporting Information), as expected for an antiferromagnetically coupled mixed-valence diiron(II,III) species with an $S = 1/2$ ground state. The EPR properties of cryoreduced **3** are consistent with those reported for other oxo-bridged diiron(II,III) units produced under similar conditions, and clearly different from those of hydroxo-bridged analogues.[26,27] For radiolytically generated hydroxo-bridged diiron(II,III) species, the EPR signals have significantly greater g anisotropy and lower g_{av} values. Thus, the proton on the original bridging hydroxide ion in the diiron(II) compound is no longer present in the oxo-bridged diiron(III) core of **3**.

ENDOR Spectroscopy. In Figure 7 are presented ^1H ENDOR spectra of cryoreduced **3** generated with H_2O_2 (30% in H_2O) and D_2O_2 (30% in D_2O) recorded at g values of 1.905 and 1.915. In the ^1H ENDOR spectrum of $\mathbf{3_{mv}}$ a proton signal with a hyperfine coupling value $A \approx 12$ MHz is clearly evident, which disappears in the spectrum of $\mathbf{3_{mv}}$ generated with D_2O_2 (30% in D_2O). This exchangeable proton signal resembles those

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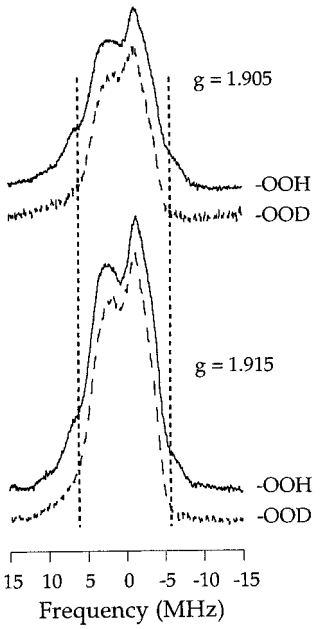

Figure 7. Proton ENDOR spectra at $g = 1.905$ and $g = 1.915$ of $\mathbf{3}_{mv}$ generated with H_2O_2 (30% in H_2O) and D_2O_2 (30% in D_2O). The spectra were collected at 2 K with 35 GHz microwave frequency, centered around the ^1H Larmor frequency and plotted as $\delta\nu = \nu - \nu_H$.

observed for hydroperoxo-bound iron(III) in bleomycin[35] and met-hemoglobin.[36] The same exchangeable proton signal occurs with similar hyperfine coupling values for spectra recorded at two different g values (Figure 7). The ^1H ENDOR results thus reveal a ligand with an exchangeable proton present in the coordination sphere of the paramagnetic iron center. We assign it to a hydroperoxide group bound to iron in agreement with our interpretation of the resonance Raman data.

^{57}Fe Mössbauer Spectroscopic Studies of 1−3. Mössbauer spectra of **1** and **2** in the solid state were recorded at 4.2 K. A fit of the data for **1** gives parameters for the diiron(II) state of $\delta = 1.10(2)$ mm/s and $\Delta E_Q = 2.42(2)$ mm/s (Supporting Information). The spectrum of **2** could be resolved into two quadrupole doublets, with one iron(II) site having $\delta = 1.18(2)$ mm/s and $\Delta E_Q = 2.45(2)$ mm/s and the other having $\delta = 1.04(2)$ mm/s and $\Delta E_Q = 2.54(2)$ mm/s (Figure 8). The Mössbauer spectrum of **3** was recorded at 4.2 K as a frozen CH_3CN solution. The quadrupole doublets were fit to a diiron species with one iron site having $\delta = 0.50(2)$ mm/s and $\Delta E_Q = 1.11(4)$ mm/s and the other having $\delta = 0.51(2)$ mm/s and $\Delta E_Q = 1.78(4)$ mm/s (Figure 8). The approximately equal intensity of two quadrupole doublets suggests the presence of one major diiron-containing species. The values for the isomer shifts (δ) indicate the diiron(III) oxidation state for both iron atoms, which compare well with those for oxyHr (0.51 and 0.52).[12] Very different quadrupole splitting parameters were obtained for the iron(III) sites in oxyHr, one having $\Delta E_Q \approx 1.96$ mm/s and the other having $\Delta E_Q \approx 0.95$ mm/s.[12] The large quadrupole splitting value of 1.5−2.0 mm/s observed for one iron site is typical for oxo-bridged diiron(III) species, where the short $Fe-O_{oxo}$ bond significantly distorts the electric field at the iron nucleus.[37] The unusual small quadrupole splitting of ~1.0 mm/s observed for the other iron site in oxyHr indicates a less distorted

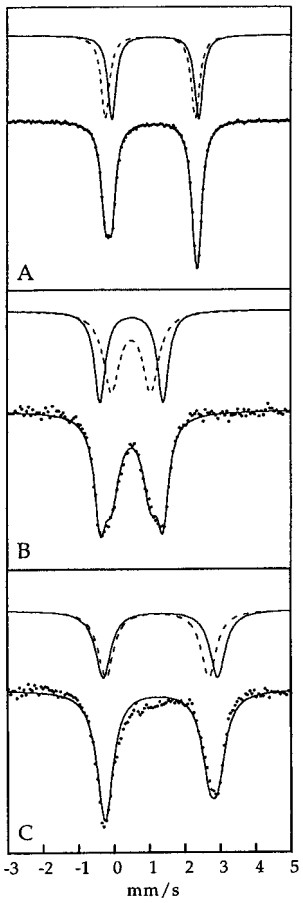

Figure 8. Mössbauer spectra at 4.2 K of (A) **2** recorded as a solid-state sample, (B) **3** recorded as an acetonitrile frozen solution sample, and (C) a frozen solution sample from B warmed to room temperature and recooled to 4.2 K. Lower curve in each spectrum: experimental data (·), calculated fit (−). Upper curve in each spectrum: two subsets for the calculated spectrum.

electronic environment and has been suggested to be the hydroperoxide binding site.[7] A similarly disparate set of quadrupole splitting values is also displayed by the model compound **3** (Table 1), which further indicates the presence of similar core structures in both cases. Although we cannot completely eliminate the possibility, the occurrence of two bound hydroperoxo ligands in **3** is highly unlikely, judging from the asymmetry in diiron(III) sites exhibited by the Mössbauer spectrum.

The frozen solution sample of **3** was allowed to warm to room temperature and cooled again to 4.2 K, after which the Mössbauer spectrum was recorded. The spectrum could be fit by two equally intense quadrupole doublets, with one iron site having $\delta = 1.23(2)$ mm/s and $\Delta E_Q = 2.91(4)$ mm/s and the other having $\delta = 1.32(2)$ mm/s and $\Delta E_Q = 3.24(4)$ mm/s (Figure 8). The isomer shifts indicate the presence of iron(II) species. The diiron(III) center of **3** apparently becomes reduced when it warms to room temperature in acetonitrile in the presence of a significant amount of water under the experimental conditions.

Mechanism for Formation and Decay of 3. All spectroscopic evidence indicates that **3** is a hydroperoxodiiron(III) species, the mechanism of formation for which is postulated in Scheme 1. In this proposal compound **2** is oxidized by the first equivalent of H_2O_2 to give a diiron(III) intermediate and 2 equiv of hydroxide. One hydroxide group deprotonates the second equivalent of H_2O_2, which serves as the hydroperoxo ligand to one iron atom; 2 equiv of water is also generated in this reaction.

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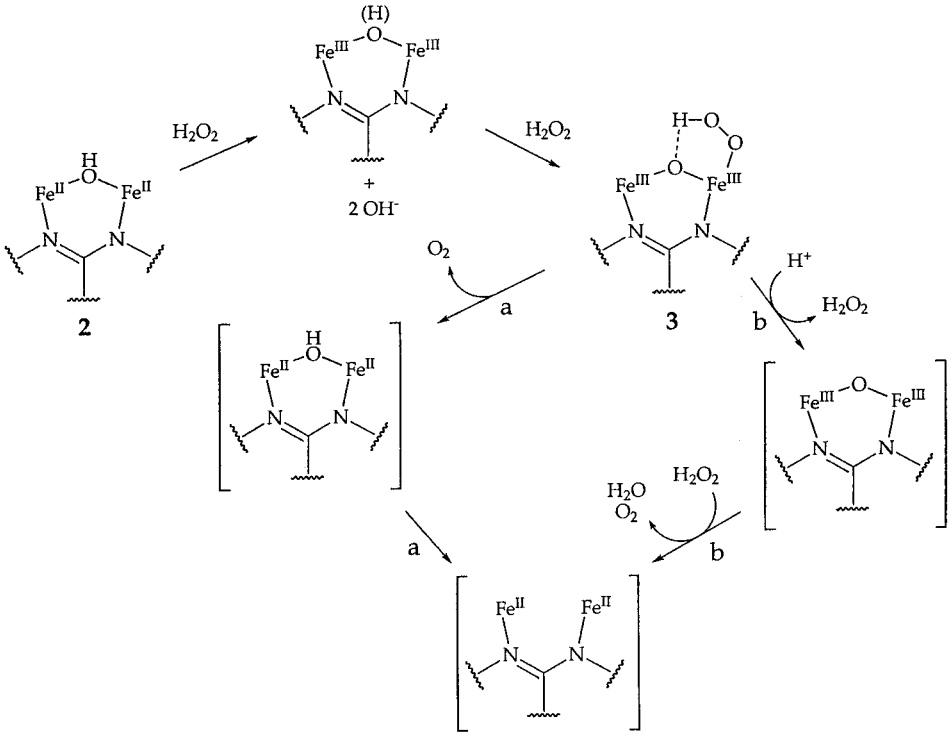
Scheme 1



The hydroperoxide ligand appears to form a hydrogen bond with the bridging oxide, as proposed for oxyHr.

Compound **3** starts to decay at temperatures above −30 °C, as judged by UV−vis spectroscopy. The product of such decay in acetonitrile/water media contains almost exclusively iron(II) species, as revealed by Mössbauer spectroscopy. An attractive candidate for the reducing reagent is the iron-bound hydroperoxide ligand. Thus, the diiron(III) center in **3** could be reduced by the bound hydroperoxide to diiron(II) in the presence of water with the release of O_2, as postulated in Scheme 1, pathway a. Alternatively, the bound hydroperoxide could simply dissociate from **3** upon warming. The resulting (μ-oxo)diiron(III) center could then be reduced by free hydrogen peroxide, the two-electron oxidation potential of which has been measured to be 0.36 V vs NHE in anhydrous acetonitrile.[38] This scenario is depicted in Scheme 1, pathway b. Gas chromatographic (GC) experiments provide evidence supporting the proposed mechanism for decay of **3** in acetonitrile/water at elevated temperatures. The evolution of O_2 into the headspace of the reaction after the solution was warmed to room temperature was observed by GC (Supporting Information). We could not distinguish the two possible mechanisms experimentally, however. If the mechanism proposed in Scheme 1, pathway a, were true, compound **3** would release bound hydroperoxide as dioxygen and return to the diiron(II) state in a manner similar to that of Hr. The reduction of metal by bound hydroperoxide is one of the two half-reactions exhibited by Hr and catalases. The ligand environment in **3** may prefer the diron(II) state, which drives the reduction of the iron centers under the experimental conditions. Compounds **1** and **2** are unreactive toward O_2 at −30 °C.

Reactivity of 3. The deprotonation of terminally bound mononuclear hydroperoxoiron(III) species by 5 equiv of Et_3N or NH_3(aq) affords side-on bound peroxoiron(III) species, as reported previously.[39,40] In contrast to the mononuclear cases, treatment of **3** with 5 equiv of Et_3N or NH_4·OH (30% aqueous) in acetonitrile at −40 °C did not cause a color change, although addition of a large excess (>100 equiv) gave a clear yellow solution. The disappearance of absorption features due to **3** under such basic conditions could be the result of deprotonation of the hydroperoxide group accompanied by decomposition. The greater stability of the hydroperoxide group in **3** to 5 equiv of base than those in the mononuclear hydroperoxoiron(III) compounds might be the consequence of hydrogen bonding with the bridging oxide in **3**. Such hydrogen bonding should raise the pK_a value for the hydroperoxide group compared to the dangling ligands in mononuclear cases. Other factors could also contribute to a higher pK_a value for the bound hydroperoxide in **3**. Neutral, all-nitrogen donor ligands were used for the reported mononuclear hydroperoxoiron(III) species, the terminally bound hydroperoxide group being the only anionic ligand in each case. The pK_a value of the hydroperoxide group would be lower compared to that in **3**, where a dianionic bridging oxide is present in the coordination sphere of the iron(III) atoms. The coordination geometry might also disfavor a side-on peroxide binding mode in **3**. Compound **3** is unreactive toward excess cyclohexene or Ph_3P at low temperature, as monitored by UV−vis spectroscopy.

Summary and Conclusion

We have prepared a pair of hydroxo-bridged diiron(II) complexes using 1,8-naphthyridine-based dinucleating ligands BPEAN and BEPEAN. The compound [Fe_2(BPEAN)(μ-OH)(OTf)](OTf)$_2$ (**1**) has two iron atoms bridged by the 1,8-naphthyridine unit of BPEAN, just like a bridging carboxylate. The two iron atoms have an asymmetric coordination environment with an open site like that in deoxyHr. A dangling oxygen atom of the terminally bound triflate forms a hydrogen bond

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with the bridging hydroxide ion. Treatment of **1** and the related diiron(II) complex $[Fe_2(BEPEAN)(\mu\text{-}OH)(OTf)](OTf)_2$ (**2**) with excess 30% aqueous H_2O_2 at low temperature in acetonitrile produced red-brown species. The UV−vis and resonance Raman spectroscopic studies of **3**, derived from **2**, revealed the presence of a hydroperoxide ligand. Isotopic substitution of a proton by deuterium shifted the O−O stretching band by $\sim$3 cm^{-1}, as was also observed in oxyHr. This result confirms the presence of the hydroperoxide group.

The EPR spectrum of the diiron(II,III) form $\mathbf{3_{mv}}$ generated by cryogenic reduction of **3** suggests the presence of an oxo-bridged diiron motif. The ^{1}H ENDOR spectrum of the diiron(II,III) sample revealed a ligand having an exchangeable proton with $A \approx 12$ MHz. These results provide strong evidence that the peroxo ligand is protonated. The Mössbauer spectroscopic data further confirmed the presence of the (μ-oxo)diiron(III) core in **3**. Similar inequivalent quadrupole splitting values are shared by **3** and oxyHr, indicating the presence of similar core structures. The hydroperoxide ligand in **3** has a relatively high pK_a value compared to mononuclear hydroperoxoiron(III) complexes, as judged from its greater resistance to bases. This result may reflect the presence of a hydrogen bond between the hydroperoxide group and the bridging oxide, stabilizing the proton.

All studies show that **3** serves as a good spectroscopic model for oxyHr. It has structural features similar to those proposed for oxyHr. A terminally bound hydroperoxide ligand forms, and the original hydroxide group is deprotonated to yield an oxo-bridged diiron(III) core. The putative hydrogen bond between the hydroperoxide and the bridging oxide proposed for oxyHr appears to exist in **3**. These studies provide further evidence to support some of the proposed structural features for the diiron center in oxyHr. At room temperature, **3** decays to iron(II) species in acetonitrile/water solution. Release of bound hydroperoxide to form an O_2 molecule may have occurred.

Acknowledgment. This work was supported by grants from the National Institute of General Medical Science and the National Science Foundation. A.M.B. thanks NIH for a predoctoral fellowship. D.L. is the recipient of the Corning Foundation Science Fellowship in chemistry and J.K. is the recipient of an NSERC postgraduate scholarship.

Supporting Information Available: Figures S1 showing the atom labeling diagram of 1, S2 the connectivity of **2**, S3 the UV−vis spectra of **1**, **1** reacting with H_2O_2 (30% aqueous) at −40 °C, and the room-temperature product, S4 the resonance Raman spectra of **3** generated by treatment of 1:1 H_2O_2/D_2O_2 and H_2O_2 and the difference spectrum, S5 the X-band EPR spectrum of the cryoreduced sample $\mathbf{3_{mv}}$, S6 the Mössbauer spectrum of **1**, and S7 the GC spectra of aliquots withdrawn from the headspace before and after a solution of **3** was warmed and for control experiments and tables of X-ray crystallographic data and CIF data for **1** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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