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A Diferric Peroxo Complex with an Unprecedented Spin Configuration: An $S = 2$ System Arising from an $S = 5/2$, 1/2 Pair**

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Dioxygen binding and activation are important biological steps in the mechanisms of a number of metalloproteins. For metalloenzymes containing non-heme diiron active sites,[1] such as methane monooxygenase, a diferric peroxo species is a key intermediate in the enzymatic mechanism.[2] To date, the binding modes of the peroxide at these active centers remain to be fully established and more chemical models are required. So far, three coordination modes of this anion have been determined in iron coordination chemistry, namely μ-1,2-peroxo,[3] η^1-hydroperoxo,[4] and η^2-peroxo modes.[5] We recently showed that the (μ-oxo)-diferric complex $[Fe_2O(pb)_4(H_2O)_2](ClO_4)_4$ (**1**-$(ClO_4)_4$) with the (−)4,5-pinene derivative pb as ligand reacted with H_2O_2 to afford a mixture of two peroxo adducts, as indicated by resonance Raman spectroscopy.[6] Here, we demonstrate with new spectroscopic studies that one is a μ-1,2-peroxo adduct (**2**) and the other is a μ-oxo-diferric complex in which the peroxide binds in a monodentate fashion to one iron center (**3**; Scheme 1). This new structural motif engenders an unprecedented ground spin state ($S = 2$) derived from the coupling of an $S = 5/2$ and an $S = 1/2$ ion in the diferric unit.

The addition of 50 equivalents of H_2O_2 to 1 mM complex **1** in acetonitrile at $-40\,^{\circ}C$ caused the appearance of an intense, broad charge-transfer band at 680 nm ($\varepsilon = 2000\,M^{-1}cm^{-1}$,

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author. S1: ESI-MS spectrum and characteristic fragments of $\mathbf{1} + H_2O_2$ solution; S2: Mössbauer spectrum of the mixture recorded at 20 mT.

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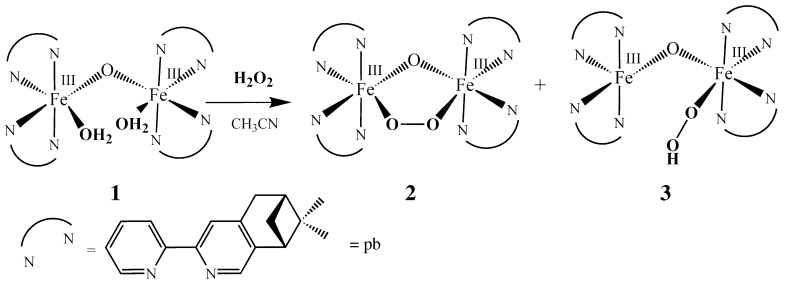

Scheme 1. Products of the reaction between **1** and H_2O_2.

based on a dinuclear unit) in the UV/Vis spectrum. The presence of two pairs of vibrations in the resonance Raman spectrum of the deep green solution indicated the presence of two different peroxo species.[3–5] Excitation profile studies showed that the 867 and 491 cm^{-1} features in the Raman spectrum are associated with one chromophore, named complex **2**, that is red shifted relative to a second chromophore, complex **3**, associated with the 806 and 618 cm^{-1} features.[6] Furthermore, the shift of -44 and -48 cm^{-1} for the features at 806 and 867 cm^{-1}, respectively, observed with $H_2{}^{18}O_2$ is consistent with O–O vibrations for distinct iron peroxo species. The 867 and 491 cm^{-1} pair of vibrations of complex **2** closely matches those associated with (μ-1,2-peroxo)diiron(III) complexes,[3] while the 806 and 618 cm^{-1} features of complex **3** correspond to the Raman features of mononuclear low-spin Fe^{III}-OOH species.[4] The appearance of the latter prompted us to confirm the presence of a low-spin Fe^{III}-OOH species by X-band EPR spectroscopy.[4] However, the solution displayed only minor amounts of EPR active high-spin and low-spin ferric species (less than 5% total).

A Mössbauer study was then initiated to shed more light on this apparently contradictory situation. A 4.2 K Mössbauer spectrum was obtained for a sample derived from the reaction of ^{57}Fe-labeled complex **1** with H_2O_2, and revealed the presence of several different iron species.[7] The 20 mT spectrum could be fitted with four quadrupole doublets (see Supporting Information). That all four components were quadrupole doublets indicated that most of the Fe ions in the sample were not slowly relaxing half-integer spin ions, which would give rise to a six-line pattern at 4.2 K in such small applied fields (20 mT). The latter situation has been observed in activated bleomycin[8] and a mononuclear low-spin ferric η^1-hydroperoxo species $Fe(pb)_2$-OOH, recently characterized.[9] The absence of a prominent six-line pattern, even at 0.17 T (Figure 1a), is thus consistent with the absence of intense EPR signals from half-integer spin species.[10] One doublet, denoted as (A) in Figure 1a has parameters that correspond to the initial diferric complex **1** ($\delta_1 = 0.48$ mm s^{-1}, $\Delta E_{Q1} = 1.53$ mm s^{-1}, 38%). Two other doublets, (B) and (C) ($\delta_2 = 0.49$ mm s^{-1}, $\Delta E_{Q2} = 0.62$ mm s^{-1}, 36% and $\delta_3 = 0.43$ mm s^{-1}, $\Delta E_{Q3} = 0.49$ mm s^{-1}, 13%), correspond to two new species with parameters typical for high-spin Fe^{III} centers. The fourth doublet (D) can be fitted with parameters typical of a low-spin Fe^{III} center ($\delta_4 = 0.23$ mm s^{-1}, $\Delta E_{Q4} = 1.64$ mm s^{-1}, 13%). The only way to rationalize the presence of a low-spin Fe^{III} component in the Mössbauer spectrum without a corresponding X-band EPR signal is to couple it with another half-integer spin ion to form an integer spin species. The presence of a high-spin Fe^{III} component in the exact percentage as the low-spin iron center (both 13%) suggests that these two components could be exchange-coupled to afford an effective $S = 2$ or $S = 3$ species.

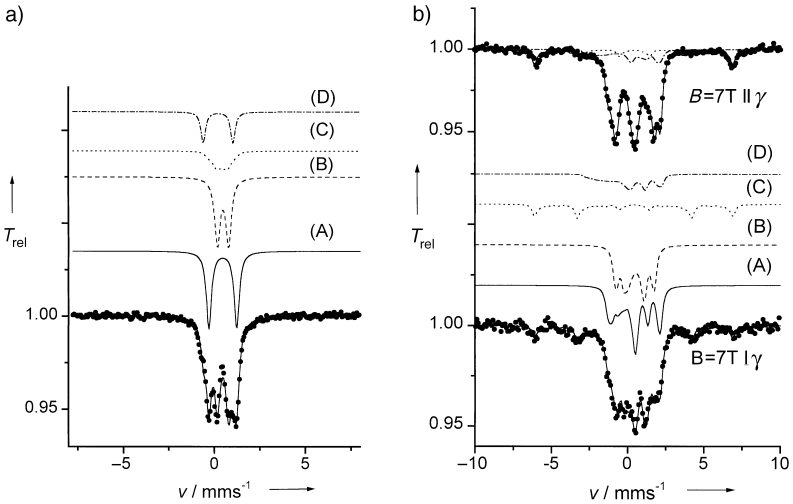

Figure 1. Mössbauer spectra of ^{57}Fe-labeled complex **1** with 50 equivalents H_2O_2 in acetonitrile. a) 0.17 T; b) 7 T (γ-rays perpendicular to the applied magnetic field); (——) Fe_A; (- - - -) Fe_B; (·····)Fe_C; (·—·—) Fe_D (for parameters, see Table 1).

In fact, signals for such an integer spin system were observed with the use of high-frequency EPR spectroscopy (HF-EPR). A temperature-dependent study could not be carried out because all the signals disappeared above 5 K. In all cases the spectra were incomplete, a result of the large zero-field splitting of the system and of the fact that all the observed transitions are forbidden ($\Delta m_s > 1$). However, thanks to a multifrequency analysis (190–345 GHz), the data shown in Figure 2 could be simulated using a full-matrix

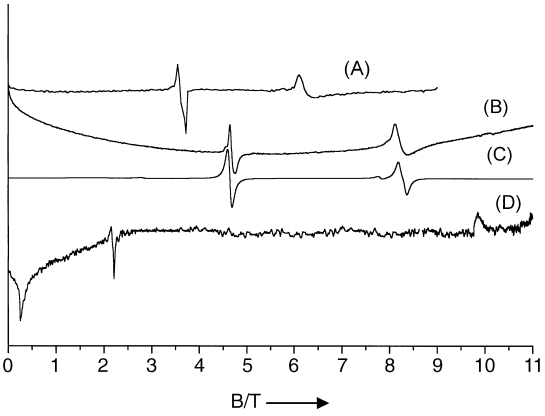

Figure 2. Experimental (A, B, and D) and simulated (C) HF-EPR spectra of 5 mM **1** + 50 equivalents of H_2O_2 in acetonitrile measured at 230 GHz (A), 285 (B and C), and 345 GHz (D) at 5 K; the parameters used for the simulation are reported in the main text.

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diagonalization procedure for Equation (1), where $\boldsymbol{B}$ = magnetic field, $\boldsymbol{g}$ = elecronic g tensor, D = zero-field splitting, E/D = rhombicity parameter.[11] Fitting parameters acceptable for all frequencies were found only by taking into account an $S=2$ ground state in the limit of strong exchange.[12] This $S=2$ system is axial ($E/D=0$) with $D=(-4.15\pm0.05)$ cm^{-1}, $g_{\parallel}=1.97\pm0.005$, and $g_{\perp}=2.00\pm0.005$.

$$\mathcal{H} = \beta \boldsymbol{B}\boldsymbol{g}\boldsymbol{S} + D[\boldsymbol{S}_z^2 - 1/3S(S+1) + E/D(\boldsymbol{S}_x^2 - \boldsymbol{S}_y^2)] \quad (1)$$

The $S=2$ assignment has been confirmed by high-field Mössbauer spectroscopy (Figure 1 b). This analysis confirmed that doublets (A) and (B) have $S=0$ ground states, which correspond to complexes **1** and **2**, respectively.[6, 8] Different behavior was found for the remaining two components (C) and (D) which represent 26% of the total iron, and were assigned to the proposed coupled $S=5/2$, 1/2 pair of complex **3**. Using the fine structure parameters derived from the HF-EPR fitting (see above), we have applied the spin projection technique to determine the magnetic hyperfine coupling tensor $\boldsymbol{A}$ of complex **3** which determines its magnetic splitting in the Mössbauer spectrum.[12] Assuming that the electronic ground state of the spin-coupled $S=1/2$ site is similar to that of the low-spin hydroperoxo species (pb)$_2$Fe^{III}-OOH characterized previously,[9] we have used $\boldsymbol{A}_{local}/\mu_N g_N = (-40, -8, +5)$ T for the $S=1/2$ site in our analysis of the spin Hamiltonian.[8] To reproduce the magnetic Mössbauer spectra shown in Figure 1 we get for the $S=5/2$ site $\boldsymbol{A}_{local}/\mu_N g_N = -20.1$ T, a value which is usually observed for five-coordinate ferric high-spin centers.[13] Therefore, we consider it as very likely that the ferric high-spin site of complex **3** is five coordinate. The $\boldsymbol{A}$ tensors of the coupled $S=2$ spin system given in Table 1 are calculated by means of $\boldsymbol{A}=C\boldsymbol{A}_{local}$, where $\boldsymbol{A}_{local}$ is the $\boldsymbol{A}$ tensor of the individual paramagnetic site. The value of C is obtained from ref. [12] (7/6 for $S=5/2$ and $-1/6$ for $S=1/2$ sites). Taken together, HF-EPR and Mössbauer data definitively define complex **3** as an $S=2$ system derived from the antiferromagnetic coupling of an Fe^{III} ($S=1/2$) ion and an Fe^{III} ($S=5/2$) ion, perhaps mediated by the μ-oxo bridge. Spin projection afforded the spin-Hamiltonian parameters for the high-spin iron(III) center, in particular the D value: $D_{(S=5/2)}=-3.11$ cm^{-1},[12] the highest value observed thus far for high-spin non-heme ferric systems.[14]

The formulations for **2** and **3** (Scheme 1) have been further confirmed by electrospray mass spectrometry.[15] We detected two new intense ESI-MS peaks at m/z 580.4 (80%) and 630.2 (50%), which can be attributed to the $[Fe_2(pb)_4O(OO)]^{2+}$ and $\{[Fe_2(pb)_4O(OOH)](ClO_4)\}^{2+}$ ions, associated to **2** and **3**, respectively. The observed isotopic distribution patterns of these two peaks matched the calculated isotopic distributions (se the Supporting Information).

In conclusion, we have demonstrated that the reaction of **1** with hydrogen peroxide generated two (μ-oxo)diferric peroxo adducts, differentiated by the coordination mode and the protonation state of the peroxide ligand (Scheme 1). Although a μ-oxo-μ-peroxo complex similar to **2** has been observed,[16] to our knowledge complex **3** is the first example of a diferric coupled system in which the two local spin configurations are different. This particular electronic structure certainly results from the binding of the hydroperoxide anion to a pyridine-rich Fe^{III} ion which makes it low-spin, as seen previously,[5] while the other Fe^{III} ion remains high-spin. Complex **3** thus differs from the oxy state of hemerythrin (Hr)[17] and its recent models,[18] which display a $S=0$ ground state Fe(OOH)-O-Fe site with two coupled $S=5/2$ ferric ions. Finally, complex **3** could also be considered as a new possible peroxo intermediate in the catalytic cycle of non-heme iron enzymes.

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Table 1. Mössbauer parameters obtained from the spin-Hamiltonian analysis of the spectra shown in Figure 1.[a]

Rel. area [%]	S	D [cm^{-1}]	E/D	$\boldsymbol{g}$	δ [mm s^{-1}]	ΔE_Q [mm s^{-1}]	Γ [mm s^{-1}]	η[b]	β[c] [°]	$\boldsymbol{A}/\mu_N g_N$ [T]
(A) 38	0			–	0.48	−1.53	0.33	0.4	–	–
(B) 36	0			–	0.49	−0.62	0.35	0.7	–	–
(C) 13	2	−4.15	0	2.00,	0.43	0.49	0.28		60	−23.5
				2.00,						−23.5
				1.97						−23.5
(D) 13	2	−4.15	0	2.00,	0.23	−1.64	0.28	0	90	−6.7
				2.00,						1.3
				1.97						−0.8

[a] The $\boldsymbol{g}$-tensor, the zero-field splitting D, and the rhombicity parameter E/D of components (C) and (D) originating from complex **3** have been taken from the high-field EPR analysis. [b] The asymmetry parameter of the electric field gradient tensor $\boldsymbol{V}_{ii}$ is given as $\eta=\frac{V_{xx}-V_{yy}}{V_{zz}}$ with $|\boldsymbol{V}_{zz}| \geqslant |\boldsymbol{V}_{yy}| \geqslant |\boldsymbol{V}_{xx}|$. [c] Euler angle between the axes system of the $\boldsymbol{A}$ tensor and of the electric field gradient tensor.

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Thermal Intramolecular Electron Transfer in a Ferrocene–Naphthoquinone Linked Dyad Promoted by Metal Ions**

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Electron transfer (ET) in a fixed donor–acceptor distance plays an essential role in photosynthesis, respiration, and redox-mediated enzyme catalysis in biological redox reactions as well as many simple chemical redox reactions.[1, 2] Thus, ET reactions between donor and acceptor molecules bound to proteins have been studied extensively to understand the factors to control the ET process.[3] A number of donor–acceptor linked systems with inert rigid spacers have also been developed to study the ET reactions between the donor and acceptor molecules at a fixed distance.[4–8] In each case, however, photoexcitation of the donor or acceptor moiety or radiolysis is required to start the ET reaction. To date there has been no report on ET in donor–acceptor linked systems started thermally. This situation is taken as a matter of course since it would be impossible to connect donor and acceptor molecules if an ET occurred thermally. However, a number of examples report intermolecular ET reactions with a significant acceleration in the presence of a third component acting as a catalyst or promoter.[9, 10] Most importantly, thermal intermolecular ET reactions, which would otherwise be unlikely to occur, proceed efficiently in the presence of metal ions which can promote the ET reactions.[9, 10] In theses cases, addition of a metal ion to the donor–acceptor systems can start ET reactions. ET reactions can also be attenuated through noncovalent interactions, such as hydrogen bonding, which plays an important role in biological ET systems.[11]

We report herein the first example of an intramolecular ET reaction in a donor–acceptor linked system started thermally by addition of a metal ion. A newly designed ferrocene–naphthoquinone dyad (Fc–NQ) is employed to examine the metal-ion promoted thermal intramolecular ET reaction (Scheme 1).

Details on the synthesis and characterization of Fc–NQ are given as Supporting Information (S1–S3). The cyclic voltammograms of Fc-NQ in acetonitrile (MeCN) exhibited two reversible one-electron redox couples of two redox-active

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author. Synthetic procedures of Fc–NQ (S1–S3), the absorption spectrum of Fc–NQ in the Sc^{3+}-promoted ET (S4), ESR spectrum of $Fc–NQ^{\bullet-}$ (S5), DFT calculation of $Ph–NQ^{\bullet-}$ (S6), cyclic voltammograms of Fc–NQ in the presence of metal ions (S7) (7 pages, print/PDF).

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