Published in final edited form as:

Eur J Inorg Chem. 2013 August ; 2013(22-23): 3858–3866. doi:10.1002/ejic.201300162.

An Iron(II)(1,3-bis(2'-pyridylimino)isoindoline) Complex as a Catalyst for Substrate Oxidation with H₂O₂. Evidence for a Transient Peroxodiiron(III) Species

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Abstract

The complex [Fe(indH)(solvent)₃](ClO₄)₂ (**1**) has been isolated from the reaction of equimolar amounts of 1,3-bis(2'-pyridylimino)isoindoline (indH) and Fe(ClO₄)₂ in acetonitrile and characterized by X-ray crystallography and several spectroscopic techniques. It is a suitable catalyst for the oxidation of thioanisoles and benzyl alcohols with H₂O₂ as the oxidant. Hammett correlations and kinetic isotope effect experiments support the involvement of an electrophilic metal-based oxidant. A metastable green species (**2**) is observed when **1** is reacted with H₂O₂ at –40 °C, which has been characterized to have a Fe^{III}(μ-O)(μ-O₂)Fe^{III} core on the basis of UV-Vis, electron paramagnetic resonance, resonance Raman, and X-ray absorption spectroscopic data.

Author Keywords

Nonheme iron complex; Isoindoline; Iron-peroxo intermediate; Tridentate ligand; Catalytic oxidation

Introduction

Dioxygen activation by nonheme diiron enzymes occurs in a number of metabolically important transformations,^[1] including the hydroxylation of methane by soluble methane monooxygenase (sMMO),^[2–4] the conversion of ribonucleotides to deoxyribonucleotides by ribonucleotide reductase (RNR),^[5–7] the formation of unsaturated fatty acids by fatty acid desaturases,^[8] the biosynthesis of antibiotics (CmlA, CmlI),^[9] and the hydroxylation of eukaryotic initiation factor 5a by human deoxyhypusine hydroxylase (hDOHH) in the regulation of eukaryotic cell proliferation.^[10] In general, O₂ activation is thought to be initiated by the binding of O₂ to the diiron(II) center to form a peroxodiiron(III) intermediate that in turn converts to the oxidizing species. Peroxodiiron(III) intermediates with visible features between 600–750 nm have been identified for sMMO,^[11–13] RNR R2,^[14–18] stearyl-acyl carrier protein (Δ⁹D),^[19,20] frog M ferritin,^[21,22] and hDOHH.^[10] Several of these species have been characterized by resonance Raman (rRaman) spectroscopy and

Supporting Information Available: Additional crystallographic information, the EPR spectrum of **2**, and kinetics data for the Hammett studies. This material is available on the WWW under <http://dx.doi.org/ejicxxx>.

shown to exhibit vibrational features associated with a (μ -1,2-peroxo)diiron(III) unit.^[17,23,24]

For sMMO and RNR R2, the peroxodiiron(III) intermediate has been shown to undergo O–O bond scission to generate a high-valent oxidant capable of X–H bond cleavage. Kinetic studies of this conversion in sMMO show that a proton is required for O–O bond cleavage to occur,^[25,26] leading to the formation of the high-valent intermediate, designated as **Q**, that carries out methane hydroxylation. Intermediate **Q** is generally accepted to possess a diiron(IV) center with two bridging oxo-ligands to form a $[\text{Fe}^{\text{IV}}_2(\text{O})_2]$ “diamond core” that cleaves the methane C–H bond.^[27] On the other hand, O–O bond cleavage of the peroxodiiron(III) intermediate of RNR R2 is initiated by proton-coupled electron transfer, resulting in the formation of an $\text{Fe}^{\text{III}}\text{O}-\text{Fe}^{\text{IV}}$ intermediate called **X**,^[28,29] this is the oxidant responsible for forming a nearby tyrosyl radical that in turn generates a cysteinyl radical by long distance proton-coupled electron transfer to initiate the deoxygenation of ribonucleotides.^[7]

Understanding the factors that lead to O–O bond cleavage at nonheme diiron centers has been a major goal of researchers in this field. Studies of synthetic complexes that mimic O_2 binding and activation can complement and augment the information available from enzyme studies. Particularly useful are complexes for which intermediates along the O_2 -activation pathway can be trapped. To date, polydentate ligands with combinations of N-heterocycles and amine donors have afforded peroxodiiron(III) complexes that can be spectroscopically characterized.^[30–46] In this study, we report our results using the rigid, meridional 1,3-bis(2'-pyridylimino)isoindoline (indH, Scheme 1), which has been shown to function as a neutral^[47–52] or a monoanionic ligand.^[53–56] The isoindolines normally occupy three meridional sites at a metal ion and form either 1:1 or 2:1 (ligand:metal) complexes. We have previously reported the preparation and crystal structures of a μ -oxo-bridged diiron(III) complex, $[(\text{Fe}(\text{ind})\text{Cl})_2\text{O}]$ and a homoleptic iron(II) complex $[\text{Fe}(\text{ind})_2]$.^[57,58] Herein, we present the synthesis and structure of a new iron(II) complex, $[\text{Fe}(\text{indH})(\text{CH}_3\text{CN})_3](\text{ClO}_4)_2$ (**1**) and the spectroscopic characterization of a transient green species (**2**) derived from the reaction of **1** with H_2O_2 . We also report an initial investigation into the catalytic reactivity of **1** in combination with H_2O_2 focusing on the oxidation of thioanisoles and benzyl alcohols.

Results and Discussion

Synthesis and structure of the iron(II) complex of indH (**1**)

Complex **1** was synthesized by mixing equimolar amounts of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with free ligand (indH) in anhydrous acetonitrile, which resulted in an immediate color change of the solution to brown. X-ray quality crystals of **1** were obtained by vapor diffusion of Et_2O into a concentrated MeCN solution of **1**. Complex **1** is air stable and affords a satisfactory elemental analysis for C, H, N and Cl.

Initial crystallographic refinement of **1** at room temperature revealed a 1:1 iron-ligand complex with one acetonitrile and two water ligands in a distorted octahedral geometry. However the refinement resulted in abnormal ellipsoids on the MeCN ligand and an R_1 value > 8% (see Figure S1 and discussion in SI). Recrystallization of **1** from MeCN/ Et_2O afforded crystals for which data collection at 173 K gave a solution with an R_1 value 4.1%. This structure (Figures 1 and S2) revealed a 1:1 iron-ligand complex with three MeCN ligands. The crystallographic refinement data of **1** are collected in Table S1, and selected bond lengths are listed in the caption of Figure 1 and in Table S2.

The geometry around the iron(II) center can be described as a distorted octahedron with the equatorial plane defined by three nitrogen atoms of the tridentate ligand and the nitrogen

atom of one acetonitrile with an average Fe–N distance of 2.16 Å. The axial positions are occupied by two acetonitrile molecules with Fe–N distances of ~2.2 Å. The Fe–N bond lengths are similar to those obtained for Fe(ind)₂^[58] and consistent with the longer Fe–N distances associated with high-spin Fe(II) centers.^[59] The isoindoline molecule is bound to the iron as a neutral ligand. The proton, H4B, bound to N1 in the free ligand, resides on N4 in the complex; H4B was found on an electron difference map and confirmed by its participation in hydrogen bonding interactions with a perchlorate counterion (Figure S3). An asymmetric bond length pattern was observed for the nearly planar N2–C8–N1–C1–N4 fragment of the bound indH ligand in **1**, showing the typical bond lengths (see Figure 1 caption for data) found for a metal-coordinated neutral isoindoline ligand.^[52]

Spectroscopic measurements corroborate the crystallographic conclusions. Complex **1** exhibits an electronic absorption spectrum with bands at 283 and 332 nm that can be assigned to intraligand π - π^* transitions and weaker bands at 571 and 770 nm that may arise from MLCT transitions from the iron(II) to the indH ligand. Similarly weak bands have been observed in iron(II) complexes of bidentate α -keto acid ligands.^[60–62] Its IR spectrum displays absorptions at 1626 and 1613 cm⁻¹, indicating that the complex contains the neutral isoindoline ligand (indH), as complexes with indH have multiple strong absorptions in the range 1600–1660 cm⁻¹, while those with the monoanionic ligand exhibit only weak bands above 1600 cm⁻¹.^[47,54]

Reaction of **1** with hydrogen peroxide

The addition of 4 eq. H₂O₂ to an acetonitrile solution of **1** generated an intermediate green species (**2**) at –40 °C (Figure 2). Titration of **1** with H₂O₂ showed that the chromophore associated with **1** disappeared upon introduction of the first 0.5 eq. of H₂O₂, but the chromophore associated with **2** was not observed until after additional H₂O₂ was introduced and achieved maximal formation with 4–5 eq. H₂O₂ (Fig. S4). Complex **2** exhibited a significant lifetime at –40 °C, permitting further spectroscopic characterization (see below), but it decomposed within 50 s at 25 °C.

Complex **2** has been characterized by several spectroscopic techniques to be a peroxo-bridged diferric complex. It exhibits a visible absorption spectrum with a λ_{max} at 690 nm (ϵ = 1500 M⁻¹ cm⁻¹ per Fe and assuming 100% conversion). Such a feature likely arises from a peroxo-to-iron(III) charge transfer transition, as found in related peroxo-bridged diferric complexes.^[17,30–46] Complex **2** is essentially EPR-silent in MeCN at 2.5 K, with only two weak signals at g = 4.3 and g = 2.2 (Figure S5) that represent only a very small fraction (<5 %) of the total 1 mM sample. The g = 4.3 signal is typical of a high-spin Fe(III) impurity, while that at g = 2.2 has yet to be assigned. The EPR-silent nature of **2** suggests that it is either diamagnetic or, more likely, an antiferromagnetically coupled diiron(III) complex.

Resonance Raman spectra of **2** obtained by excitation at 647.1 nm reveal the presence of four vibrations at 874, 560, 520, and 458 cm⁻¹ (Figure 3), reminiscent of features previously reported for diferric-peroxo complexes with an additional oxo bridge (Table 1). Isotope labeling studies show that the preparation of **2** with H₂¹⁸O₂ (2% solution in H₂¹⁶O) leads to shifts of the peaks at 874 and 458 cm⁻¹ to 836 and 445 cm⁻¹, whereas the generation of **2** in the presence of 100 equiv. H₂¹⁸O results in shifts of the peaks at 560 and 520 cm⁻¹ to 548 and 504 cm⁻¹ (Fig. 3). Thus, the H₂¹⁸O₂-sensitive features may be assigned to the $\nu(\text{O}=\text{O})$ and $\nu_{\text{sym}}(\text{Fe}-\text{O}_2-\text{Fe})$ vibrations of the Fe–O₂–Fe unit, respectively, with frequencies comparable to the complexes listed in Table 1. We note however that the ¹⁸O shift for the $\nu(\text{O}=\text{O})$ of –38 cm⁻¹ is somewhat smaller than the downshift of 50 cm⁻¹ calculated for a simple O–O harmonic oscillator, but it is similar to that observed for complex **C** in Table 1,^[39] suggesting the coupling of these features to other vibrational modes of the respective

complexes. On the other hand, the presence of H_2^{18}O -sensitive features shows the presence of an additional Fe–O–Fe unit in **2**. The 520-cm^{-1} peak is downshifted by 16 cm^{-1} upon H_2^{18}O labeling and is assigned to $\nu_{\text{sym}}(\text{Fe–O–Fe})$, based on the similarity of these values to those reported for related $[\text{Fe}^{\text{III}}_2(\mu\text{-O})(\mu\text{-1,2-O}_2)]$ complexes **A** and **B**.^[46,63] However, the assignment for the 560 cm^{-1} band is uncertain, as its frequency and H_2^{18}O -derived isotope shift do not match with those of any other feature in Table 1. Taken together, the Raman data support the formulation of **2** as a peroxo-bridged diferric complex with an additional single-atom bridge derived from water.

Figure 4 shows the excitation profiles for several Raman vibrations of **2**. All four ^{18}O -sensitive features discussed above are clearly in resonance with the peroxo-to-iron(III) charge transfer band at 690 nm. Note in particular the strong enhancement for the $\nu(\text{O–O})$ mode at 874 cm^{-1} . The fact that vibrations associated with the Fe–O–O–Fe unit as well as those of the Fe–OFe units follow the same excitation profile demonstrates that these vibrations arise from one molecule, rather than a mixture of complexes with either an Fe–O–O–Fe or an Fe–O–Fe unit. Furthermore, oxo-bridged diiron(III) complexes without an associated peroxo ligand typically have LMCT bands in the near UV region,^[64] so the Fe–O–Fe vibrations would be expected to exhibit resonance enhancement at much shorter wavelengths, which is not observed for **2**. Interestingly, the non- ^{18}O -sensitive features at 637 and 658 cm^{-1} follow a different profile with higher resonance enhancement as excitation shifts to shorter wavelengths, consistent with an indH ligand vibrational mode that is in resonance with a higher energy transition.

Comparison of the vibrational data for **2** with related diferric-peroxo complexes in Table 1 raises the question regarding the nature of the water-derived bridging ligand, *i. e.* whether **2** is an oxo-bridged complex like **A**, **B**, and **C** or a hydroxo-bridged one like **B'** and **C'**. We note that the $\nu(\text{O–O})$ of **2** is $20\text{--}25\text{ cm}^{-1}$ higher in frequency than those of **A**, **B**, and **C** but $26\text{--}54\text{ cm}^{-1}$ lower in frequency than **B'**, **C'** and **D**. The correlation established by Fiedler et al.^[43] between the observed $\nu(\text{O–O})$ frequencies and the $\text{Fe}\cdots\text{Fe}$ distances suggests that **2** should have an $\text{Fe}\cdots\text{Fe}$ distance of $\sim 3.25\text{ \AA}$, which is about $0.1\text{ \AA}$ longer than found for complexes with $\text{Fe}^{\text{III}}_2(\mu\text{-O})(\mu\text{-1,2-O}_2)$ cores but $0.2\text{ \AA}$ shorter than found for complexes with $\text{Fe}^{\text{III}}_2(\mu\text{-OR})(\mu\text{-1,2-O}_2)$ cores ($\text{R} = \text{H}$ or alkyl). In addition, the frequency of the $\nu_{\text{sym}}(\text{Fe–O–Fe})$ mode has also been correlated with the Fe–O–Fe angle in $(\mu\text{-oxo})$ diiron(III) complexes,^[65] and this correlation indicates an Fe–OFe angle of 120° like those associated with $(\mu\text{-oxo})(\mu\text{-1,2-peroxo})$ diiron(III) complexes **A** and **B** in Table 1. Thus, consideration of all Raman data leads us to favor a $(\mu\text{-oxo})(\mu\text{-1,2-peroxo})$ diiron(III) core for **2**.

X-ray absorption spectroscopy studies were carried out to obtain further characterization of **2**. The X-ray absorption near-edge region of **2** exhibits a pre-edge feature at 7114.3 eV with an area of $13.3(5)$ and a K-edge energy of 7124.2 eV , values similar to those previously reported for complexes with $[\text{Fe}^{\text{III}}_2(\mu\text{-O})(\mu\text{-1,2-O}_2)]$ cores.^[43] Of note is the strong similarity of these parameters to those recently characterized for **A**, a complex of the tridentate BnBQA ligand, which has very similar pre-edge and edge energies of 7114.4 and 7124.2 eV , respectively, and has been shown to have a $[\text{Fe}^{\text{III}}_2(\mu\text{-O})(\mu\text{-1,2-O}_2)]$ core.^[46] Protonation of the BnBQA complex to form a $[\text{Fe}^{\text{III}}_2(\mu\text{-OH})(\mu\text{-1,2-O}_2)]$ core results in a downshift of the pre-edge and edge energies to 7112.4 and 7123.3 eV , respectively.

Table 2 details an analysis of **2** by extended X-ray absorption fine structure (EXAFS). The r' -space spectrum of **2** (Figure 5) shows a number of distinct features that can be fit to scatterers at 1.79 , 1.96 , 2.13 , 2.99 , 3.13 , and $3.36\text{ \AA}$ (Fit #13). For the first coordination sphere, the scatterer at $1.79\text{ \AA}$ represents the oxo bridge, the two at $1.96\text{ \AA}$ correspond to the proximal O atom of the peroxo bridge and the central N donor of indH, and those at $2.13\text{ \AA}$ arise from the remaining N donors on the indH ligand and the likely solvent ligand. For the

outer shell, features at 2.99 and 3.36 Å correspond respectively to second-shell and third-shell carbon atoms of the indH ligand, while that at 3.13 Å is an Fe scatterer. Together, the EXAFS analysis supports a $\text{Fe}^{\text{III}}_2(\mu\text{-O})(\mu\text{-1,2-O}_2)$ core for **2** (Scheme 2). Consistent with the titration of **1** with H_2O_2 described earlier (Fig. S4), we propose that **2** is formed by a two-step reaction involving the initial oxidation of 2 eq. of iron(II) complex **1** by H_2O_2 to form a ($\mu\text{-oxo}$)diferric species and the subsequent reaction of the latter with a second H_2O_2 to form **2** (Scheme 2).

Substrate Oxidation Studies

We have carried out an investigation of the properties of **1** as a catalyst for the oxidation of thioanisole and benzyl alcohol with H_2O_2 to obtain an initial assessment of the oxidizing power of this catalyst/oxidant combination. Complex **1** is capable of catalyzing both oxygen-atom transfer and hydrogen-atom abstraction. For example, thioanisole readily underwent oxidation to the corresponding sulfoxide and sulfone at 25 °C. With 1 μmol **1**, 0.25 mmol H_2O_2 , and 0.1 mmol substrate in 10 mL of acetonitrile, 56 turnovers were observed in the course of an hour, after which time there was no further product formation. Monitoring the substrate concentration by GC during the time course of the reaction showed an exponential decay of thioanisole with a pseudo-first-order rate constant k_{obs} of $5.6 \times 10^{-4} \text{ s}^{-1}$. A $k_{\text{rel}}(\text{PhSOCH}_3/\text{PhSCH}_3)$ value of 0.70 was also determined by comparing an individual reaction using methylphenylsulfoxide as substrate with the ArSMe oxidation under identical conditions. Oxidations of *para*-substituted thioanisoles were also carried out, and k_{obs} values were determined from $\ln[p\text{-X-C}_6\text{H}_4\text{SCH}_3]$ vs. t plots for reactions executed individually for each *p*-X- $\text{C}_6\text{H}_4\text{SCH}_3$ derivative. The ratios of the various k_{obs} values relative to that of PhSCH_3 gave $k_{\text{rel}}(k_{\text{X}}/k_{\text{H}})$ values that afforded a Hammett correlation shown in Figure 6 with a ρ value of -0.40 , suggesting that the oxidant generated from **1**/ H_2O_2 is electrophilic.

Another approach to analyze our thioanisole oxidation data was presented in ref. [68]. In this method, the $\log k_{\text{obs}}$ values were plotted against the E^0_{ox} potentials of *para*-substituted thioanisole derivatives and *N,N*-dimethylanilines (DMAs, where only electron transfer is possible) for three different catalysts. Slopes of -8.5 and -10.5 were associated with an electron transfer/oxygen rebound pathway, based on the comparison with DMAs, but slopes of much smaller magnitude (-2.2 and -2.3) were attributed to direct oxygen-atom transfer to the sulfide as this pathway should be less sensitive to variations in E^0_{ox} of the substrates. When our data were analyzed in this manner, the resulting plot shown in Figure 7 reveals a slope of -0.8 , consistent with a direct oxygen-atom transfer mechanism for **1**/ H_2O_2 .

Oxidation of benzyl alcohol at 25 °C by **1**/ H_2O_2 resulted in the formation of benzaldehyde in 24% yield. A pseudo-first order rate constant of $5.1 \times 10^{-5} \text{ s}^{-1}$ could be extracted by monitoring substrate loss and product formation. Reactions with *para*-substituted benzyl alcohols showed changes in oxidation rate as a function of the nature of the *para* substituent. A Hammett plot of k_{rel} values ($k_{\text{X}}/k_{\text{H}}$) gave a ρ value of -0.85 , indicative of an electrophilic oxidant (Fig. 6). Experiments comparing the rates of oxidation of benzyl alcohol and benzyl alcohol- d_7 revealed a kinetic isotope effect of 9, excluding the possibility of hydroxyl radical as the oxidant and implicating instead a metal-based oxidant.

Taken together, the oxidation results presented above indicate the formation of an electrophilic metal-based oxidant that is capable of both oxygen-atom and hydrogen-atom transfer. Its oxidizing properties are compared in Table 3 with those of related iron complexes. This metal-based oxidant appears to be mildly electrophilic, when considering that its Hammett ρ value for thioanisole oxidation of -0.40 is comparable to that of the closely related $[\text{Fe}^{\text{III}}_2\text{O}(\text{L})_4(\text{OH}_2)_2]^{4+}/\text{H}_2\text{O}_2$ system ($\rho = -0.55$)^[69] but 2.5- to 4-fold smaller

than those obtained for oxygen-atom transfer reactions by $[\text{Fe}^{\text{III}}(\text{salen})]^+/\text{H}_2\text{O}_2$ ($\rho = -1.5$),^[70] $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMP}^+)]$ ($\rho = -1.2$),^[68] and $[\text{Fe}^{\text{IV}}(\text{O})(\text{PyMAC})]^{2+}$.^[71] On the other hand, its Hammett ρ value of -0.85 for benzyl alcohol oxidation is twofold larger than those obtained with oxoiron(IV)(porphyrin radical cation) complexes (-0.4) and tenfold larger than those obtained with *bona fide* nonheme oxoiron(IV) complexes (-0.07). Furthermore the $k_{\text{H}}/k_{\text{D}}$ value for benzyl alcohol oxidation by **1**/ H_2O_2 is smaller than those for corresponding oxidations by oxoiron(IV) complexes. Thus, the comparisons in Table 3 suggest that the oxidant generated by **1**/ H_2O_2 has oxidizing properties distinct from those of *bona fide* oxoiron(IV) species.

An obvious candidate for the metal-based oxidant is **2**, the peroxo species we observed at -40°C and characterized in this paper. However $(\mu\text{-oxo})(\mu\text{-1,2-peroxo})\text{diiron(III)}$ complexes characterized thus far such as **A**,^[63] **B**,^[46] and **C**^[39] in Table 1 appear to be unreactive. To investigate whether species **2** plays the role of metal-based oxidant, a solution of **2** was prepared by treatment of a 1-mM solution of **1** in CH_3CN with a 100-fold excess of H_2O_2 at 5°C . Upon formation, **2** undergoes a monotonic decay over the next hour at a rate of $1.5 \times 10^{-7} \text{ M s}^{-1}$, which is unaffected by the addition of 0.2 or 0.4 M PhSCH_3 . Nevertheless, the corresponding sulfoxide product is observed to form, but at a rate that is two orders of magnitude faster than the decay rate of **2**. It would thus appear that **2** is not directly involved in substrate oxidation but is still somehow linked to the observed oxidative reactivity. Related diiron(III)-peroxo complexes that have previously been found to carry out substrate oxidations include the protonated derivative of the $(\mu\text{-oxo})(\mu\text{-1,2-peroxo})\text{diiron(III)}$ intermediate from the $[\text{Fe}_2\text{OL}_4(\text{H}_2\text{O})_2]^{4+}/\text{H}_2\text{O}_2$ system^[69,74] noted earlier in Table 3 and the $(\mu\text{-alkoxo})(\mu\text{-1,2-peroxo})\text{diiron(III)}$ intermediate obtained at -40°C from the reaction of O_2 with the diiron(II) complex of the dinucleating ligand HPTP (*N,N,N',N'*-tetrakis(2-pyridylmethyl)-2-hydroxy-1,3-diaminopropane).^[75] Efforts are in progress to draw reactivity and mechanistic parallels between **2** and these reactive intermediates in order to gain insight into what factors activate the $\text{Fe}^{\text{III}}_2(\mu\text{-OX})(\mu\text{-O}_2)$ core for oxidative reactivity. Answering this question would enhance our understanding of how dioxygen activation can take place at biological nonheme diiron active sites.^[1–4,10]

Materials and Methods

Materials

All manipulations were performed under a pure argon atmosphere using standard Schlenk-type inert-gas techniques unless otherwise stated. Solvents used for the reactions were purified by standard methods and stored under argon. Iron(II) perchlorate was purchased from commercial sources. The ligand 1,3-bis(2'-pyridylimino)isoindoline (indH) was prepared according to published procedures.^[57,58]

$\text{Fe}^{\text{II}}(\text{indH})(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2$ (1**)**—A solution of indH (0.269 g, 0.9 mmol) in acetonitrile (20 mL) was stirred at room temperature for 2 h with $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.362 g, 1 mmol). After addition of diethyl ether, dark brown crystals precipitated upon standing for a day. The product was collected by filtration, washed with ether and dried in vacuum (0.35 g, 70 %). M.p. $258\text{--}260^\circ\text{C}$. IR (KBr) cm^{-1} : 3332 w, 1654 m, 1626 s, 1613 w, 1594 w, 1554 m, 1524 s, 1485 s, 1467 m, 1432 m, 1375 w, 1306 w, 1262 w, 1207 m, 1145 m, 1115 m, 1082 s, 864 w, 780 m, 712 m, 625 m. UV-Vis (CH_3CN) λ_{max} (log ϵ): 239 (4.73); 283 (4.50); 332 (4.52); 382 (4.47) 571 (2.39), 770 (1.86). Anal. Calc. for $\text{C}_{22}\text{H}_{23}\text{N}_7\text{FeCl}_2\text{O}_{10}$: C, 39.31; H, 3.45; N, 14.59; Cl, 10.55 %. Found: C, 39.67; H, 3.30; N, 14.61; Cl, 10.03 %.

Caution! Perchlorate salts are potentially explosive and should be handled with care and in small quantities.

Physical measurements

Infrared spectra were recorded on an Avatar 330 FT-IR Thermo Nicolet instrument. UV-visible (UV-vis) spectra were recorded on an Agilent 8453 diode-array spectrophotometer using quartz cells. Microanalyses were done by the Microanalytical Service of the University of Pannonia and Atlantic Microlab. The crystal evaluation and intensity data collection for **1** were performed on a Bruker–Nonius Kappa or Smart 1000 CCD single-crystal diffractometer using Mo K α radiation ($\lambda = 0.71070$ Å) at 293(2) or 173(2) K. Additional crystallographic data (Tables S1 and S2) and details of the structure solution and refinement are given in the SI. The CIF files are available in the CCDC database (CCDC 855411 and 888012).

X-band EPR spectra (9.64 GHz, 200 μ W, 2.5 K) were obtained on a Bruker Elexsys E-500 spectrometer equipped with an Oxford ESR-910 cryostat and Oxford temperature controller in perpendicular mode. Data collection was carried out using Xepr (Bruker).

Resonance Raman spectra were collected using Spectra-Physics Model 2060 Kr⁺ and 2030-15 Ar⁺ lasers and an ACTON AM-506 monochromator equipped with a Princeton LN/CCD data collection system. Low temperature spectra in CH₃CN or CD₃CN were obtained at 77 K using a 135° backscattering geometry. Samples were frozen onto a gold-plated copper cold finger in thermal contact with a Dewar flask containing liquid nitrogen. Raman frequencies were calibrated to indene prior to data collection. Rayleigh scattering was attenuated using a holographic notch filter (Kaiser Optical Systems) for each excitation wavelength. The monochromator slit width was set for a band-pass of 4 cm⁻¹ for all spectra. The spectra of **2** were collected using a laser excitation power of 100 mW. The plotted spectra are an average of 32 scans with collection times of 30 s. All spectra were intensity corrected to the 710 or 773 cm⁻¹ solvent peak of CD₃CN and CH₃CN, respectively.

X-ray Absorption Spectroscopy

Data Collection—X-ray absorption data were collected on beam line 7-3 of the Stanford Synchrotron Radiation Lightsource (SSRL) at the SLAC National Accelerator Laboratory. Fe K-edge XAS data were collected for frozen samples prepared in SSRL solution cells with [Fe]_T = 5.9 mM. The SPEAR storage ring was operated at 3.0 GeV and ~350 mA, and energy resolution of the focused incoming X-rays was achieved using a Si(220) double crystal monochromator, which was detuned to 50% of maximal flux to attenuate second harmonic X-rays. The sample temperature (7–10 K) was controlled utilizing an Oxford Instruments CF1208 continuous flow liquid helium cryostat. Harmonic rejection was achieved by a 9 keV cutoff filter. Data was obtained as fluorescence excitation spectra with a 25-element solid-state germanium detector array (Canberra). In fluorescence mode, photon scattering “noise” was reduced using a 3-micron Mn filter and a Soller slit. An iron foil spectrum was recorded concomitantly for internal energy calibration and the first inflection point of the K-edge was assigned to 7112.0 eV. The edge energies were routinely monitored during data collection for red-shifts indicative of sample photoreduction, but none were observed in the present study.

Data Analysis—Data reduction, averaging, and normalization were performed using the program EXAFSPAK.^[76] The data for **2** are the average of 16 data sets, respectively. Following calibration and averaging of the data, background absorption was removed by fitting a Gaussian function to the pre-edge region and then subtracting this function from the entire spectrum. A three-segment spline with fourth order components was then fit to the EXAFS region of the spectrum in order to extract $\chi(k)$.

Theoretical phase and amplitude parameters for a given absorber-scatterer pair were calculated using FEFF 8.40 and were utilized by the “opt” program of the EXAFSPAK package during curve-fitting. FEFF parameters for **2** were calculated using similar coordinates of other peroxodiferric complexes. In all analyses, the coordination number of a given shell was a fixed parameter, and was varied iteratively while bond lengths (r) and mean square deviation (σ^2) were allowed to freely float. The amplitude reduction factor S_0 was fixed at 0.9, while the edge shift parameter E_0 was allowed to float as a single value for all shells (thus in any given fit, the number of floating parameters was typically equal to $(2 \times \text{num shells}) + 1$). The goodness-of-fit F was defined simply as $\sum (\chi_{\text{exptl}} - \chi_{\text{calc}})^2$. For fits to unfiltered data, a second goodness-of-fit parameter, F -factor, was defined as $[\sum k^6 (\chi_{\text{exptl}} - \chi_{\text{calc}})^2 / \sum k^6 \chi_{\text{exptl}}^2]^{1/2}$. In order to account for the effect that additional shells have on improving fit quality, a third goodness-of-fit metric F' was employed. $F' = F^2 / (N_{\text{IDP}} - N_{\text{VAR}})$, where N_{VAR} is the number of floated variables in the fit, while N_{IDP} is the number of independent data points and is defined as $N_{\text{IDP}} = 2\Delta k \Delta r / \pi$. In the latter equation, Δk is the k -range over which the data is fit, while Δr is the back-transformation range employed in fitting Fourier-filtered data. F' is thus of principal utility in fitting Fourier-filtered data, but can also be employed for unfiltered data by assuming a large value of Δr .

Pre-edge analysis was performed on data normalized in the Ifeffit program Athena^[77] and pre-edge features were fit using the program Fityk^[78] with Gaussian functions and a pseudoVoigt baseline function composed of a 50:50 Gaussian:Lorentzian combination.

Oxidation reactions

All reactions were carried out at room temperature under an argon atmosphere. For product analysis, the samples were filtered through alumina to remove the complex. The products were identified by GC-MS spectrometry and confirmed by comparison with authentic samples. The products were quantified by GC relative to cyclopentanone as an internal standard as a function of time over the course of the reactions. Pseudo-first order rate constants (k_{obs} , s^{-1}) for the reactions were extracted from plots of $\ln[\text{substrate}]_t$ (calculated as $[\text{substrate}]_t = [\text{substrate}]_0 - [\text{product}]_t$) vs. time.

For the oxidation of thioanisoles, the reactions were carried out by mixing a solution of the thioanisole (0.1 mmol in 4 mL acetonitrile) with solutions of the complex (1 μmol in 1 mL acetonitrile) and H_2O_2 (0.25 mmol in 5 mL acetonitrile). The disappearance of substrate and the formation of product were monitored as a function of time. From these data, k_{obs} values for the parent thioanisole and *para*-substituted derivatives, $p\text{-XC}_6\text{H}_4\text{SCH}_3$ (where X = OMe, Me, Cl, and NO_2), were determined (Table S3). The k_{rel} values for the Hammett plot were calculated as k_X/k_H for the different substrates.

For the oxidation of benzyl alcohols, the reactions were carried out under an argon atmosphere by mixing a solution of H_2O_2 (0.25 mmol in 5 mL acetonitrile) with solutions of **1** (1 μmol) in 1 mL acetonitrile and the benzyl alcohol (0.1 mmol) in 4 mL acetonitrile. Product formation was quantified by GC and monitored as a function of time; k_{obs} values were then obtained for the parent benzyl alcohol and various *para*-substituted derivatives 4-X- $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ (where X = OMe, Me, Cl, and NO_2) (Table S3). The k_{rel} values for the Hammett plot were calculated as k_X/k_H for the different substrates.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the János Bolyai research scholarship to J. S. P., grant TÁMOP-4.2.2.A-11/1/KONV-2012-0071 to J. K., and the U. S. National Institutes of Health (grant GM-38767 to L. Q. and postdoctoral fellowship ES017390 to M. A. C.). X-ray absorption spectroscopy was carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University. The SSRL Structural Molecular Biology Program is supported by the DOE Office of Biological and Environmental Research, and by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program (P41RR001209)

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Figure 1.

Molecular structure of **1** with crystallographic numbering. Hydrogen atoms (except for H4B), two perchlorate counter ions and the water solvate are omitted for clarity. Thermal ellipsoids are plotted at the 50% probability level. Selected bond distances (Å) for **1**: Fe–N1, 2.0722(18); Fe–N3, 2.1798(19); Fe–N5, 2.219(2); Fe–N6, 2.184(2); Fe–N7, 2.189(2); Fe–N8, 2.202(2); N(1)–C(1), 1.336(3); N(1)–C(8), 1.423(3); N(2)–C(8), 1.279(3); N(4)–C(1), 1.332(3).

Figure 2. UV-Vis spectra of **1** (1 mM, $l = 1$ cm) (solid line) in CH₃CN at -40 °C and **2** (dashed line), which was formed after addition of 4 eq. H₂O₂ to the 1 mM solution of **1** in CH₃CN.

Figure 3.

Resonance Raman spectra of **2** generated by the addition of 4 eq. $\text{H}_2^{16}\text{O}_2$ (top), generation of **2** with 4 eq. $\text{H}_2^{16}\text{O}_2$ in the presence of 100 eq. H_2^{18}O (middle), and 4 eq. $\text{H}_2^{18}\text{O}_2$ (bottom) to **1** with 647.1 nm excitation of frozen CH_3CN solutions. * denotes laser plasma lines, and L is a Raman band arising from the bound indH.

Figure 4.
Excitation profiles for selected Raman vibrations of **2**.

Figure 5. Best fits (solid red line) to the experimental (black dashed line) unfiltered EXAFS data (inset) and Fourier transform of **2** corresponding to Fit #13 in Table 2. k range = 2–13 $\text{\AA}^{-1}$. Back transformation range ~0.6–3.3 Å.

Figure 6. Hammett plots for the oxidation of *para*-substituted thioanisoles (■) and benzyl alcohols (□) with σ values taken from ref. [67]. See Table S3 for further details..

Figure 7. Plot of $\log k_{obs}$ values for thioanisole oxidation versus the oxidation potentials of thioanisole substrates, supporting a direct oxygen-atom transfer mechanism for **1**/H₂O₂.

Scheme 1.
Structure of the indH ligand.

Scheme 2.

Proposed steps in the formation of **2**. In the proposed structure for **2**, N represents the N donors of the meridional indH ligand.

Table 1

Resonance Raman features of **2** and related (μ -oxo or hydroxo)(μ -1,2-peroxo)diferric complexes

Complex ^a	λ_{max} (ϵ_M) [r(Fe...Fe)]	$\nu(\text{O}-\text{O})$ [$\Delta H_2^{18}\text{O}$, $\Delta H_2^{18}\text{O}_2$]	$\nu_{\text{sym}}(\text{Fe}-\text{O}_2-\text{Fe})$ [$\Delta^{18}\text{O}$, $\Delta^{18}\text{O}_2$]	$\nu_{\text{asym}}(\text{Fe}-\text{O}_2-\text{Fe})$ [$\Delta^{18}\text{O}$, $\Delta^{18}\text{O}_2$]	$\nu_{\text{sym}}(\text{Fe}-\text{O}-\text{Fe})$ [$\Delta^{18}\text{O}$, $\Delta^{18}\text{O}_2$]	$\nu_{\text{asym}}(\text{Fe}-\text{O}-\text{Fe})$ [$\Delta^{18}\text{O}$, $\Delta^{18}\text{O}_2$]
2	690 (1500)	874 [0, -38]	458 [0, -13]		520 [-16, 0]	560 [-12, 0] ^b
A (μ -O)	505 (1250) 650 (1300) [3.16 Å]	854 [0, -47]	460 [0, -13]	511 [0, -19]	523 [-16, 0]	714 [-42, -]
A' (μ -OH)	730 (2400) [3.46 Å]	928 [-2, -53]	468 [0, -6]	550 [-4, -17]	424 [-7, -11]	--
B (μ -O)	494 (1100) 648 (1200) [3.14 Å]	847 [0, -44]	463 [-, -21]	533 [-, -25]	511 [-12, -]	696 [-30, -6]
C (μ -O)	577 (1500) [3.171 Å]	847 [-, -33]	465 [-, -19]	--	--	695 [-, -2]
C' (μ -OH)	644 (3000) [3.396 Å]	908 [-, -47]	460 [-, -13]	548 [-, -18] ^d	498 [-, -5]	--
D (μ -OR)	588 (1500) [3.462 Å]	900 [-, -50]	471 [-, -16]			

^a **A** = $[\text{Fe}^{\text{III}}_2(\mu\text{-O})(\mu\text{-O}_2)(\text{BnBQA})_2(\text{NCCH}_3)_2]^{2+}$ (BnBQA = *N*-benzyl-bis(2-quinolylmethyl)amine); **A'** = $[\text{Fe}^{\text{III}}_2(\mu\text{-OH})(\mu\text{-O}_2)(\text{BnBQA})_2(\text{NCCH}_3)_2]^{3+}$; data from ref. [46]. **B** = $[\text{Fe}^{\text{III}}_2(\mu\text{-O})(\mu\text{-O}_2)(6\text{-Me}_3\text{TPA})_2]^{2+}$ (6-Me₃TPA = tris(6-methyl-2-pyridylmethyl)amine); data from refs. [43 and 63]. **C** = $[\text{Fe}^{\text{III}}_2(\mu\text{-O})(\mu\text{-O}_2)(6\text{-Me}_2\text{BPP})_2]^{2+}$ (6-Me₂BPP = bis(6-methyl-2-pyridylmethyl)-3-aminopropionate); **C'** = $[\text{Fe}^{\text{III}}_2(\mu\text{-OH})(\mu\text{-O}_2)(6\text{-Me}_2\text{-BPP})_2]^{3+}$; data from ref. [39]. **D** = $[\text{Fe}^{\text{III}}_2(\mu\text{-O}_2)(\text{N-Et-HPTB})(\text{OPPh}_3)_2]^{3+}$ (N-Et-HPTB = tetrakis(2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane); data from refs. [33 and 43].

^b Although it must arise from a water-derived ligand, the assignment of this vibration is uncertain.

Table 2

Fit parameters for the EXAFS analysis of **2**.^a

Fe-N/O				Fe•••Fe			Fe-C			F	F-factor (× 10 ³)	
Fit	N	r (Å)	σ ²	N	r (Å)	σ ²	N	r (Å)	σ ²			E ₀
1	6	2.11	11							5.12	358	663
2	5	2.11	8.5							5.59	329	636
3	4	2.12	6.3							6.3	315	622
4	3	2.12	4.2							6.89	326	633
5	6	2.09	8.4							2.22	302	609
	1	1.83	5.8									
6	5	2.10	6.6							2.64	297	605
	1	1.85	7.5									
7	4	2.11	5.2							3.49	302	609
	1	1.91	11.1									
8	5	2.1	6.7	1	3.07	8				3.33	250	554
	1	1.86	8									
9	4	2.12	5.3	1	3.08	7.8				4.25	253	557
	1	1.92	12.3									
10	3	2.12	4.5	1	3.08	7.5				5.43	259	564
	1	2.03	15.3									
11	5	2.1	6.9	1	3.11	5.1	5	2.98	9	2.56	270	576
	1	1.84	7.5									
12	4	2.11	5.6	1	3.12	2.2	4	2.98	3.7	3.07	253	558
	1	1.89	11.4									
<i>13^b</i>	<i>4</i>	<i>2.13</i>	<i>2</i>	<i>1</i>	<i>3.13</i>	<i>2.1</i>	<i>4</i>	<i>2.99</i>	<i>2.5</i>	<i>-0.4</i>	<i>206</i>	<i>503</i>
	<i>1</i>	<i>1.79</i>	<i>0.7</i>				<i>4</i>	<i>3.36</i>	<i>2.6</i>			
	<i>2</i>	<i>1.96</i>	<i>0.3</i>									

^a k range = 2–13 Å⁻¹ and back-transform range ~0.6–3.3 Å. σ^2 = mean-squared deviation in units of 10⁻³ Å². Scale factor S_0^2 = 0.9. GOF = Goodness of fit calculated as

$$F = \sqrt{\sum k^6 (\chi_{\text{exp}} - \chi_{\text{calc}})^2} \cdot F' = \sqrt{\sum k^6 (\chi_{\text{exp}} - \chi_{\text{calc}})^2} / \sum k^6 \chi_{\text{exp}}^2$$

^b The coordination number of 7 for the first coordination sphere in Fit #13 is acceptable, as it is well within the 25–30% uncertainty associated with coordination numbers obtained from EXAFS fits. [66]

Table 3Comparison of ρ and KIE values of **1** with related complexes.

Substrate	Oxidant ^a	ρ	k_H/k_D	Ref.
<i>p</i> -X-C ₆ H ₄ SCH ₃	1 /H ₂ O ₂	-0.40		This work
	[Fe ₂ OL ₄ (H ₂ O) ₂] ⁴⁺ /H ₂ O ₂	-0.55		[69]
	Fe ^{III} (salen)] ⁺ /H ₂ O ₂	-1.5		[70]
	[Fe ^{IV} (O)(TMP ⁺⁺)] ⁺	-1.2 ^b		[68]
(<i>p</i> -X-C ₆ H ₄) ₃ P	[Fe ^{IV} (O)(PyMAC)] ²⁺	-1.05		[71]
<i>p</i> -X-C ₆ H ₄ CH ₂ OH	1 /H ₂ O ₂	-0.85	9	This work
	[Fe ^{IV} (O)(N4Py/TPA)] ²⁺	-0.07	21	[72]
	[Fe ^{IV} (O)(TMP ⁺⁺ /Cl ₈ TPP ⁺⁺)] ⁺	-0.4	50	[72]
<i>p</i> -X-anthracene	[Fe ^{IV} (O)(N4Py)] ²⁺	-3.9		[73]

^aL = (-)-4,5-pinenepipyridine; salen = ethylene-1,2-bis(salicylideneamine); TMP = *meso*-tetramesitylporphyrin; Cl₈TPP = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin; TPA = tris(pyridyl-2-methyl)amine; N4Py = bis(pyridyl-2-methyl)bis(2-pyridyl)methylamine; PyMAC = 2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[1.3.1]heptadeca-1(17),13,15-triene.

^bData reported in ref. [68] were used to calculate ρ .