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O_2 Activation by Bis(imino)pyridine Iron(II)−Thiolate Complexes

Yosra M. Badiei, Maxime A. Siegler, and David P. Goldberg*

Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21212, United States

Supporting Information

ABSTRACT: The new iron(II)−thiolate complexes [($^{i\mathrm{Pr}}$BIP)Fe$^{\mathrm{II}}$(SPh)(Cl)] (**1**) and [($^{i\mathrm{Pr}}$BIP)Fe$^{\mathrm{II}}$(SPh)(OTf)] (**2**) [BIP = bis(imino)pyridine] were prepared as models for cysteine dioxygenase (CDO), which converts Cys to Cys-SO_2H at a (His)$_3$Fe$^{\mathrm{II}}$ center. Reaction of **1** and **2** with O_2 leads to Fe-oxygenation and S-oxygenation, respectively. For **1** + O_2, the spectroscopic and reactivity data, including ^{18}O isotope studies, are consistent with an assignment of an iron(IV)−oxo complex, [($^{i\mathrm{Pr}}$BIP)Fe$^{\mathrm{IV}}$(O)(Cl)]$^+$ (**3**), as the product of oxygenation. In contrast, **2** + O_2 results in direct S-oxygenation to give a sulfonato product, $PhSO_3^-$. The positioning of the thiolate ligand in **1** versus **2** appears to play a critical role in determining the outcome of O_2 activation. The thiolate ligands in **1** and **2** are essential for O_2 reactivity and exhibit an important influence over the Fe$^{\mathrm{III}}$/Fe$^{\mathrm{II}}$ redox potential.

Determining the factors that govern the activation of dioxygen by both heme and non-heme iron metalloenzymes is of fundamental importance. Mononuclear non-heme iron oxygenases typically contain a 2-His-1-carboxylate ligand set bound to the catalytic iron center. An interesting exception is cysteine dioxygenase (CDO), which utilizes a (His)$_3$Fe$^{\mathrm{II}}$(H_2O) center to activate O_2 and oxidize cysteine to sulfinic acid ($CysSO_2H$), a key metabolic process that is vital for human health.[1] Despite the importance of CDO from a health perspective, little is known about the mechanism of this dioxygenase.[2] The oxidation of Cys to disulfide, sulfenic acid [Cys(O)H], and other oxidized products has been implicated in oxidative stress response.[3] Thus, understanding the fundamental mechanistic pathways of biologically relevant sulfur oxidations is of high current interest.[4]

Although many studies on iron(II) model complexes have yielded key insights into the reactivity of non-heme iron centers, relatively few have involved the use of O_2 as the oxidant, in part because of the inherent difficulties with activating and controlling O_2.[5] In an earlier report, we described the synthesis of a N_3S(thiolate)Fe$^{\mathrm{II}}$ model complex of CDO that contains the three-neutral-N binding motif found in the enzyme and reacts with O_2 selectively to yield an S-oxygenated sulfonato product.[6] The thiolate donor was covalently tethered to a bis(imino)pyridine (BIP) framework, in part to favor S-oxygenation as opposed to disulfide formation. To our knowledge, this reaction was the first example of an Fe$^{\mathrm{II}}$−thiolate complex reacting with O_2 to give S- as opposed to Fe-oxygenation (e.g., Fe$^{\mathrm{III}}$−O−Fe$^{\mathrm{III}}$ species).[7]

Herein we report the synthesis of two new unsymmetrical Fe$^{\mathrm{II}}$−thiolate BIP complexes, [($^{i\mathrm{Pr}}$BIP)Fe$^{\mathrm{II}}$(SPh)(Cl)] (**1**) and [($^{i\mathrm{Pr}}$BIP)Fe$^{\mathrm{II}}$(SPh)(OTf)] (**2**) [$^{i\mathrm{Pr}}$BIP = 2,6-(ArN=CMe)$_2$-C_5H_3N), Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$], in which the thiolate ligands are not covalently tethered to the BIP framework. The reactivity of these complexes toward O_2 has been examined together with non-thiolate-ligated analogues. We show that coordination of the thiolate ligands is crucial for O_2 activation by (BIP)Fe$^{\mathrm{II}}$. We also show that S-oxygenation is possible for a terminal thiolate and furthermore that the positioning of the thiolate donor specifies the outcome of oxygenation at either sulfur or iron.

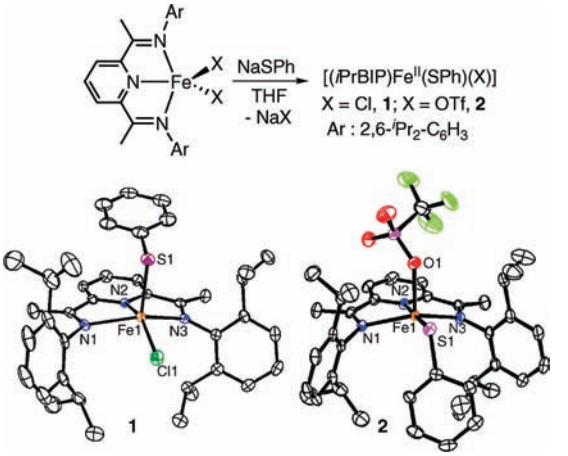

Figure 1. Synthetic scheme and displacement ellipsoid plots (50% probability level) for **1** and **2** at 110 K. H atoms have been omitted for clarity.

Significant efforts have gone into the synthesis and study of (BIP)Fe complexes for their use in N_2 activation and catalysis.[8] However, unsymmetrical derivatives having the formula [(BIP)-Fe$^{\mathrm{II}}$(X)(Y)] (X ≠ Y) are scarce. Careful control of stoichiometry, together with the appropriate conditions (solvent, temperature), allowed for the isolation of the monothiolato complexes **1** and **2** (Figure 1). The molecular structures of **1** and **2** reveal five-coordinate Fe$^{\mathrm{II}}$ ions with the desired single terminal thiolate ligands bound to the iron. The bond distances and angles are consistent with those of high-spin Fe$^{\mathrm{II}}$ BIP complexes.[8a,d,e] A distinguishing feature of the structures of **1** and **2** is the positioning of the thiolate ligand. In complex **1**, the PhS^- group sits in a pseudoaxial position in relation to the N_3Cl plane and is oriented trans to the open coordination site that subtends the obtuse N1−Fe−N3 angle (141.2°). This positioning may be aided by a π-stacking interaction between the pyridine and PhS^- groups. In contrast, the PhS^- ligand in **2** is bound in a pseudoequatorial arrangement with the $^{i\mathrm{Pr}}$BIP ligand and is cis to the open coordination site.

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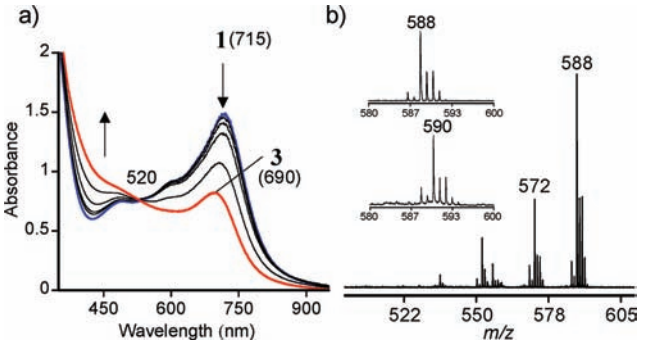

Figure 2. (a) UV−vis spectral changes for the reaction of **1** (715 nm, 0.37 mM) with excess O_2 in CH_2Cl_2, leading to formation of **3** (690 nm). (b) LDIMS of **3** formed in the reaction of **1** + O_2. Peaks at m/z 588 and 572 correspond to $[(^{iPr}BIP)Fe^{IV}(O)(Cl)]^+$ and $[(^{iPr}BIP)Fe^{II}(Cl)]^+$, respectively. Inset: isotopic clusters of **3** prepared from $^{16}O_2$ (top) and $^{18}O_2$ (bottom).

Both **1** and **2** exhibit relatively sharp, paramagnetically shifted peaks in the ^{1}H NMR spectrum (CD_2Cl_2) typical of high-spin (BIP)FeX_2 complexes, and these spectra are consistent with their solid-state structures. The magnetic susceptibility of **1** measured by Evan's method in CD_2Cl_2 gave μ_{eff} = 5.2 μ_B, which is close to the spin-only value for a high-spin Fe^{II} (S = 2) ion.

Reaction of **1** with a slight excess of dry O_2 (5 equiv) led to a color change from dark-blue to green over the course of 1 h. A decrease in the band at λ_{max} = 715 nm for **1** ($\varepsilon \approx 4000$ M^{-1} cm^{-1}) was observed, and a new band for the green species appeared at λ_{max} = 690 nm ($\varepsilon \approx 1500$ M^{-1} cm^{-1}) (Figure 2; for the time dependence, see Figure S5 in the Supporting Information). This spectrum is similar to that reported for a closely related bis(imino)pyridine iron(IV)−oxo complex (λ_{max} 660 nm, $\varepsilon \approx 1200$ M^{-1} cm^{-1}).[9] Analysis by laser desorption ionization mass spectrometry [LDIMS(+)] revealed a dominant isotopic cluster at m/z 588 whose isotope and fragmentation pattern (Figure 2 and Figures S8 and S9) are consistent with an $Fe^{IV}(O)$ complex, $[(^{iPr}BIP)Fe^{IV}(O)(Cl)]^+$ (**3**). The thiolate ligand is oxidized to disulfide during the production of **3**, as determined by ^{1}H NMR spectroscopy (PhS−SPh, 85%). Introduction of $^{18}O_2$ in place of $^{16}O_2$ caused a shift of two mass units for the LDIMS of **3**, giving a peak at m/z 590 (80% ^{18}O incorporation). Finally, green **3** was EPR-silent (X-band, 15 K). These data are consistent with the assignment of **3** as an $Fe^{IV}(O)$ species.

When the reaction of **1** with excess O_2 in CH_2Cl_2 was carried out in the presence of PPh_3 (5 equiv), $OPPh_3$ was produced in good yield (70% by ^{31}P NMR analysis). Alternatively, formation of green **3** followed by removal of O_2 under vacuum and addition of PPh_3 (50−300 equiv) under Ar resulted in the smooth decay of the peak for **3** at 690 nm (Figure S6). This decay followed good pseudo-first-order behavior, and the rate constants (k_{obs}) thus obtained were found to increase linearly with [PPh_3], yielding a second-order rate constant of $k_2 = (3.6 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1} for oxygen atom transfer from **3** to PPh_3 (Figure S7). This relatively slow reactivity may be due to the steric encumbrance imposed by the 2,6-iPr$_2$C$_6$H$_3$ substituents. The ^{18}O-labeled **3** produced $^{18}OPPh_3$ with modest isotopic incorporation ($^{16}O/^{18}O$ = 85:15). However, addition of excess $H_2{}^{18}O$ to the reaction of **3**-^{16}O and PPh_3 resulted in a significant increase in the isotopically labeled product $^{18}OPPh_3$ (50% ^{18}O) (eq 1):

$$\mathbf{1} + {}^{16}O_2 \xrightarrow{\text{PhS-SPh}} [(^{iPr}BIP)Fe(^{16}O)(Cl)]^+ \ (\mathbf{3}) \xrightarrow[H_2{}^{18}O]{PPh_3} {}^{18}OPPh_3 \quad (1)$$

These data indicate that the O atom in **3** undergoes facile exchange with exogenous H_2O, as seen for other terminal iron−oxo species.[10] Although further spectroscopic studies are needed to definitively characterize the structure of **3**, all of the spectroscopic data and reactivity presented here strongly support the formulation of **3** as a terminal iron−oxo complex generated from **1** + O_2, with the PhS^- ligand undergoing concomitant oxidation to disulfide.

The formation of non-heme $Fe^{IV}(O)$ complexes from Fe^{II} and O_2 can be induced by the addition of external coreductants (e.g., cyclohexene or NADH).[5b,c,e] In the case of **1**, the thiolate ligand functions as a built-in coreductant to assist in the activation of O_2. In comparison, the covalently tethered thiolate complex [Fe^{II}((N_3S(thiolate))(OTf)] (**4**) also serves to activate dioxygen, but in that case, participation from sulfur leads to direct oxygenation of the S atom.[6]

To our surprise, the addition of stoichiometric amounts of O_2 to the triflate complex **2** followed a very different oxidation pathway than the one followed by the chloro analogue **1**. An immediate color change from dark-blue to brown was noted upon addition of O_2, and LDIMS revealed a cluster at m/z 694 corresponding to *S-oxygenated* $[Fe^{II}(^{iPr}BIP)(PhSO_3)]^+$. Attempts to crystallize $[Fe^{II}(BIP)(PhSO_3)]^+$ to date have led only to the crystallization of the known $Fe^{II}(^{iPr}BIP)(OTf)_2$ complex; however, the production of benzenesulfonic acid was readily confirmed by ^{1}H NMR spectroscopy, and quantitation by reversed-phase HPLC after hydrolytic workup gave a yield of 30% for $PhSO_3H$ (based on total Fe). The use of labeled $^{18}O_2$ resulted in ~90% incorporation of ^{18}O into the $PhSO_3^-$ ligand. Despite the fact that the thiolate donor in **2** is not part of a chelate ring, S-oxygenation does occur, as seen for the covalently tethered **4**. In contrast, no evidence for $PhSO_3H$ was detected by LDIMS or HPLC for **1** + O_2 in control experiments.

The reactivities of the related non-thiolate-ligated complexes $Fe(^{iPr}BIP)Cl_2$ (**5**) and $Fe(^{iPr}BIP)(OTf)_2$ (**6**) were next examined for comparison with **1** and **2**. These complexes are completely inert toward O_2 in both solution (e.g., CH_2Cl_2, CH_3CN) and the solid state (eq 2):

$$[Fe(BIP)(X)_2] \xrightarrow[CH_2Cl_2]{O_2} \text{no reaction} \quad (2)$$

X = Cl, **5**; X = OTf, **6**

Addition of PPh_3 to oxygenated solutions of **5** and **6** showed no formation of $OPPh_3$. The incorporation of a thiolate donor thus clearly plays a critical role in the activation of O_2 by these non-heme iron(II) complexes.

The redox potentials of **1**, **2**, **5**, and **6** are compared in Table 1. The thiolate-ligated complexes exhibit significantly lower redox potentials than the nonthiolate analogues, correlating nicely with their relative O_2 reactivities. A similar correlation was made for [Fe^{II}(TMC)$(OTf)_2$] (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), which exhibits a solvent-dependent redox potential and reacts with O_2 to give an $Fe^{IV}(O)$ complex only in solvents where $E_{1/2}(Fe^{III/II}) < -0.1$ V (e.g., THF).[5a] Similarly, non-heme iron(II) complexes with more positive $E_{1/2}$ values fail to react with O_2 to give oxoiron(IV) species. An $E_{1/2}(Fe^{III/II}) < -0.1$ V appears to be a prerequisite for O_2 activation in non-heme

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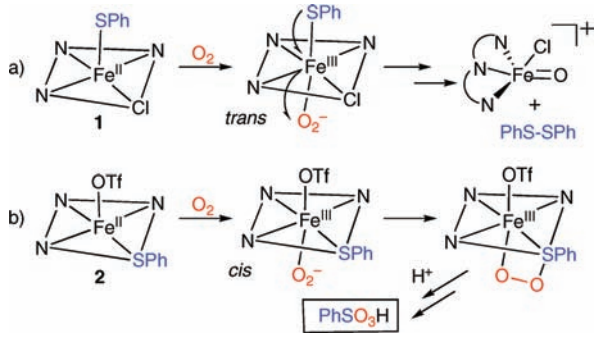
Table 1. Redox Potentials for (^{iPr}BIP)Fe^{II} and Related Non-Heme Fe^{II} Complexes

compound	$E_{1/2}$ (ΔE_{pp})[a]	O_2 reactivity
[(^{iPr}BIP)Fe^{II}(SPh)(Cl)] (**1**)	−0.173[b] (0.114) (r)	yes
[(^{iPr}BIP)Fe^{II}(SPh)(OTf)] (**2**)	−0.372[b] (0.149) (r)	yes
[(^{iPr}BIP)Fe^{II}(Cl)$_2$] (**5**)	0.025[b] (0.153) (r)	no
[(^{iPr}BIP)Fe^{II}(OTf)$_2$] (**6**)	0.613[b,c] (ir)	no
[(TMC)Fe^{II}(OTf)$_2$][d]	−0.14[e] (qr)	yes
[(TMC)Fe^{II}(OTf)$_2$][d]	0.02[f] (r)	no
[(TPA)Fe^{II}]$^{2+}$, [d,g]	0.36[h] (r)	no

[a] Values in V vs Fc^+/Fc. ΔE_{pp} = peak-to-peak separation; *r* = reversible, ir = irreversible, qr = quasi-reversible. [b] In CH_2Cl_2 at a scan rate of 0.1 V/s. [c] Anodic peak potential. [d] Data taken from ref 5a. [e] In 1:1 MeCN/THF. [f] In 1:1 MeCN/CH_2Cl_2. [g] TPA = tris(2-pyridylmethyl)amine. [h] In neat MeCN.

Scheme 1. Proposed Mechanisms of O_2 Activation by 1 and 2



iron(II) complexes, and inclusion of a single thiolate donor is sufficient to lower the redox potential of (^{iPr}BIP)Fe^{II} complexes into this range. It should be noted that the $E_{1/2}$ values for **1** and **2** remain more than 1 V above the one-electron reduction potential for the O_2/O_2^- couple in organic solvents,[5h] ruling out an outer-sphere mechanism for O_2 activation.

In view of the structural and electronic similarities between the two thiolate-ligated complexes **1** and **2**, why do their reactivities with O_2 follow such dramatically different paths? Scrutiny of the structures of **1** and **2** appears to hold the key. The PhS^- ligand in **1** is bound trans to the open site available for O_2 binding, whereas it is bound cis in **2**. A plausible mechanism for O_2 activation in **1** thus begins with coordination of O_2 to the open site trans to the thiolate donor, which is followed by electron transfer from both the iron and sulfur centers to the bound O_2 (Scheme 1a). In this case, intramolecular attack of an Fe−O_2 intermediate on the sulfur donor would be strongly disfavored by the trans orientation of the PhS^- ligand. In contrast, the analogous Fe−O_2 intermediate in **2** would be generated cis to the thiolate ligand, providing a facile pathway for intramolecular S-oxygenation (Scheme 1b). Similarly, the thiolate donor in the covalently tethered **4** is also found cis to the open coordination site.

This hypothesis depends upon the feasibility of attaining a six-coordinate structure with the sterically encumbered BIP ligand in **1** and **2**. For less bulky BIP analogues, where Ar = 2,6-$Me_2C_6H_3$, six-coordinate Fe^{II} complexes are known,[8d] but to our knowledge there are no examples with Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$. Thus we were pleased to isolate [Fe^{II}(^{iPr}BIP)(H$_2$O)$_2$(NCCH$_3$)](OTf)$_2$ (**7**) as a product from the reaction of **2** + O_2; its molecular structure is given in

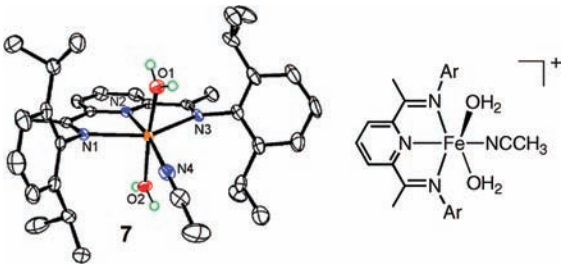


Figure 3. (left) Displacement ellipsoid plot (50% probability level) at 110 K and (right) molecular structure of **7**. H atoms (except those attached to the water molecules) and the OTf^- ions have been omitted for clarity.

Figure 3. Despite the large steric encumbrance provided by the flanking 2,6-^{i}Pr$_2$C$_6$H$_3$ substituents, a six-coordinate geometry is clearly attainable in **7**.

In summary, we have demonstrated that a thiolate donor is essential for the activation of O_2 by non-heme iron (BIP)Fe^{II} complexes and can serve as either a coreductant or a site for O capture. The relative positioning of the PhS^- ligand in relation to the potential O_2 binding site appears to play a critical role in determining whether oxygenation occurs at iron or sulfur.[11] We have also shown that S-oxygenation can occur for terminal, iron-bound thiolates, contrary to established precedent. It has been proposed that the Cys substrate in CDO coordinates to the Fe center through a chelate ring involving sulfur and the amino group.[1] The findings presented here suggest that this unusual binding mode for Cys is not required for S-oxygenation to occur.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and characterization data for **1**−**3**, **7** and X-ray crystallography details and CIFs for **1**, **2**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
dpg@jhu.edu

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