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Characterization of Mononuclear Non-heme Iron(III)-Superoxo Complex with a Five-Azole Ligand Set[**]

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***Abstract:** Reaction of O_2 with a high-spin mononuclear iron(II) complex supported by a five-azole donor set yields the corresponding mononuclear non-heme iron(III)–superoxo species, which was characterized by UV/Vis spectroscopy and resonance Raman spectroscopy. ^1H NMR analysis reveals diamagnetic nature of the superoxo complex arising from antiferromagnetic coupling between the spins on the low-spin iron(III) and superoxide. This superoxo species reacts with H-atom donating reagents to give a low-spin iron(III)–hydroperoxo species showing characteristic UV/Vis, resonance Raman, and EPR spectra.*

In biological systems, interaction between O_2 and iron centers in heme and non-heme proteins/enzymes occurs in aerobic respiration and metabolic processes. Oxidative addition of O_2 to the ferrous centers of the proteins/enzymes yields the corresponding ferric complexes of reduced O_2 species (O_2^- and O_2^{2-}).[1] The O_2 activation mechanism of heme iron oxygenases has been explored extensively both on the enzymes and related model compounds.[2] In line with the chemical analogy, a mononuclear iron center of non-heme oxygenases is inferred to activate O_2 by a similar mechanism.[3] To date, a few mononuclear non-heme iron(III)–superoxo species have been characterized in some enzymes and synthetic model systems.[4,5] However, information of the chemical properties of such non-heme iron(III)–superoxo species is still scarce. To clarify the correlation between the coordination environments and properties of mononuclear non-heme iron centers such as spin state and reactivity, interests in investigation of synthetic model compounds are much growing.[5–10] As reported herein, we have successfully characterized a mononuclear iron(III)–superoxo complex with azole-based ligands.

We have designed a single-site unsaturated iron(II) complex with five azole donors by assembling tridentate hydrotris(3,5-dimethylpyrazolyl)borate (Tp^{Me2})[11] and bidentate imidazolyl-based borate $[B(Im^{N\text{-}Me})_2MePh]^-$ ($\mathbf{L^{Ph}}$)[12] ligands. A family of Tp^R (where R denotes substituent groups on the pyrazolyl rings) is one of extensively explored ligands for the synthetic models of non-heme O_2-activating iron centers because facially capping N3-donating Tp^R ligands can reproduce the coordination structures of the active sites of some enzymes involving $(imidazole)_2X$ triad motif where X is an imidazole residue of His or a carboxylate of Glu or Asp.[3] To date, several O_2-activating mononuclear iron(II)–Tp^R complexes bearing an additional bidentate ligand Y, $[Fe^{II}(Y)(Tp^R)]$ (Y = carboxylate, α-keto carboxylate, β-diketonate, cysteinate, etc.) have been reported. But putative mononuclear iron(III)–superoxo species have never been detected in these Tp^R systems because of the formation of dinuclear iron(III)–μ-peroxo compounds occurring through the change of coordination mode of Y from terminal chelating ligand to bridging one, or intramolecular oxygenation of the coordinating Y proceeds immediately as found in the enzymatic reactions.[13] In this study, the imidazolyl-based ligand $\mathbf{L^{Ph}}$ has been employed because of its strong bidentate chelating nature as well as robustness toward oxidative degradation. A desired mixed ligand complex, $[Fe^{II}(\mathbf{L^{Ph}})(Tp^{Me2})]$ (**2**), was prepared by ligand exchange reaction between $Li\mathbf{L^{Ph}}$ and an iron(II) acetate complex, $[Fe^{II}(OAc)(Tp^{Me2})]$ (**1**) (Scheme 1). The molecular structure of **2** was revealed by X-ray crystallography (Figure 1). The iron center is surrounded by five azole donors with square-pyramidal geometry. Equatorial Fe–N bonds are composed of two

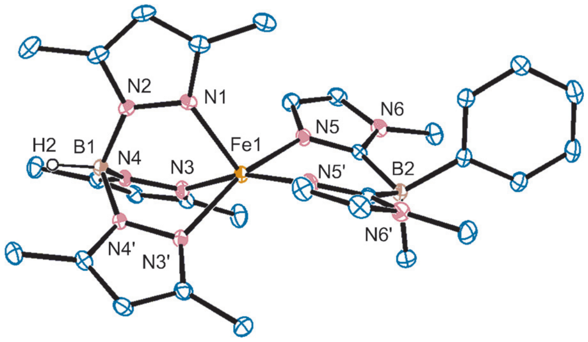

Figure 1. ORTEP of $[Fe(\mathbf{L^{Ph}})(Tp^{Me2})]$ **2**. Hydrogen atoms are omitted for clarity; ellipsoids are set at 30% probability.[23]

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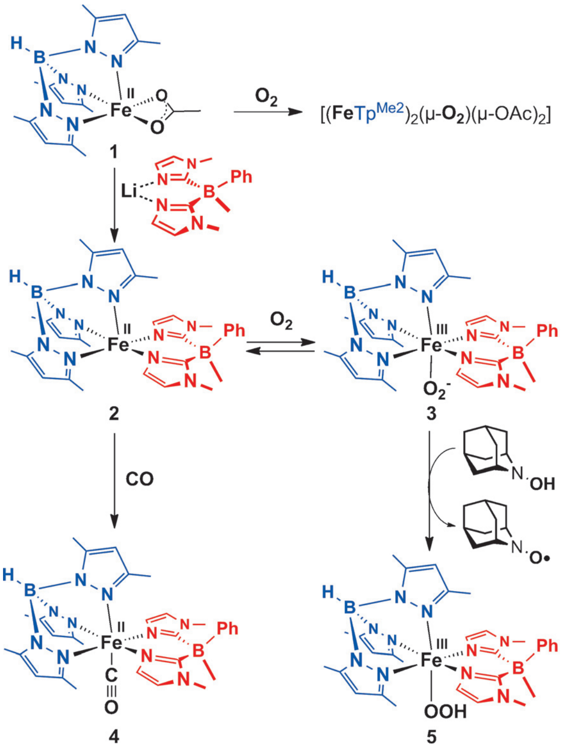

Scheme 1. Reactions of iron complexes in this study.

longer bonds derived from $\mathrm{Tp}^{\mathrm{Me2}}$ and two shorter bonds from $\mathbf{L}^{\mathbf{Ph}}$. This *trans* influence indicates that the imidazolyl groups on $\mathbf{L}^{\mathbf{Ph}}$ are stronger donors compared to the pyrazolyl ligands of $\mathrm{Tp}^{\mathrm{Me2}}$.

As we expected, the five-coordinate iron(II) complex **2** reacted with O_2 to give the corresponding O_2 adduct **3**. Bubbling of O_2 gas to a THF solution of **2** at −60 °C led to change of the solution color from pale yellow to pale brown with increasing the absorption bands around 350 nm (Figure 2; red spectrum). Although the acetate complex **1** also reacted with O_2, a resulting blue–green-colored species exhibited $\lambda_{\max} = 700$ nm, which would be attributed from a dinuclear iron(III)–μ-peroxo species analogous to the previously reported $\mathrm{Tp}^{i\mathrm{Pr2}}$ derivatives.[13a,b] The observed spectral pattern of the pale brown species **3** is similar to those of the synthetic complexes such as the recently characterized mononuclear non-heme iron(III)–superoxo species with a pentadentate ligand (330 nm)[5a] and a terminal superoxide complex of iron(III) (325 nm)[8] found in a oxygenation of the dinuclear iron(II) complex rather than that of the most recently reported mononuclear side-on iron (III)–superoxo species (490 nm).[5b] Upon bubbling of Ar gas at low temperature (−60 °C) or raising the temperature to −20 °C, the pale brown color of **3** disappeared to recover the precursor **2**. Repetitious O_2 and Ar bubbling showed reversible change of the UV/Vis spectra corresponding to the addition and dissociation of O_2 to the iron center of **2**. The oxygenation process was also observed by low-temperature ^{1}H NMR spectroscopy in [D$_8$]THF solution (Supporting Information, Figures S13, S14). Under an argon atmosphere, paramagnetically shifted signals of **2** were observed. On the basis of Evans method analysis, an iron(II) center of **2** in THF solution has $S = 2$ spin configuration as expected from its pseudo-square pyramidal geometry determined by X-ray crystallography. Upon introduction of O_2 into this NMR sample, major signals were observed only in the 0–10 ppm region.[14] The formed O_2 adduct **3** might be a diamagnetic species in which a low-spin iron(III) center ($S = 1/2$) was antiferromagnetically coupled with superoxide anion radical ($S = 1/2$). Such electronic configuration is found in the O_2 adduct of heme–iron compounds[2,15] and Fe-Bleomycin.[3,16] Furthermore, the high-spin ferrous center of **2** reacted with CO to give the corresponding low-spin iron(II)–carbonyl complex **4**, which exhibited characteristic features such as the ν(C–O) band at 1967 cm^{-1} in the IR and diamagnetic signals in the ^{1}H NMR spectra (Figures S4, S15).[17] Such behavior of **2** is also consistent with that of the iron(II) centers in the heme compounds and Fe-Bleomycin.

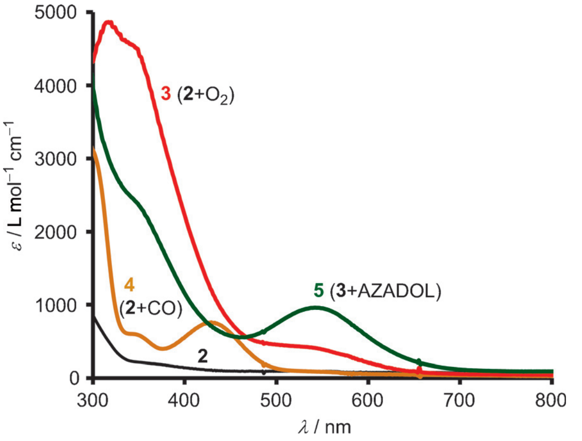

Figure 2. UV/Vis spectra of **2**, **3**, **4**, and **5** (0.5 mM) in THF at −60 °C. Complexes **3** and **5** were prepared from **2** by in situ addition of O_2 gas (1 atom) and subsequent addition of AZADOL (50 equiv), respectively. Complex **4** was prepared from **2** by in situ addition of CO gas (1 atom).

A resonance Raman spectrum of **3** generated in situ (derived by reaction of a THF solution of **2** with $^{16}O_2$) recorded at −60 °C with 413 nm excitation exhibited an isotope sensitive Fermi doublet band at 1168 cm^{-1} (Table 1; Figure S6). This band was shifted to 1090 cm^{-1} on the $^{18}O_2$ derivative. These values are similar to those reported for O–O stretching frequencies of the metal–superoxide complexes including mononuclear non-heme iron(III) species.[1] Furthermore, Fe–O stretching bands were observed at 592 cm^{-1} on the $^{16}O_2$ derivative and 568 cm^{-1} on the $^{18}O_2$ derivative,

Table 1: O–O and M–O stretching frequencies [cm^{-1}].

Compound	ν(O–O) (Δ^{18}O)	ν(M–O) (Δ^{18}O)
3	1168[a] (78)	592 (24)
[Fe(BDPP)(O_2)][b]	1125 (63)	not reported
[Fe(TAML)(η^2-O_2)][b]	1260 (77)	not reported
$\mathbf{3}^{\mathbf{Co,Ph}}$	1150 (60)	543 (21)
5	778 (40)	598 (25)
Heme Fe$^{\mathrm{III}}$-OOH[c]	799–810 (39-47)	566–617 (25-27)
LS Fe$^{\mathrm{III}}$-OOH[d]	784–811 (31-51)	609–632 (16-26)
HS [Fe$^{\mathrm{III}}$(TMC)(OOH)][e]	868 (48)	658 (25)

[a] Center of Fermi doublet. [b] Ref. [5]. [c] Ref. [18]. [d] Ref. [3b]. [e] Ref. [20a].

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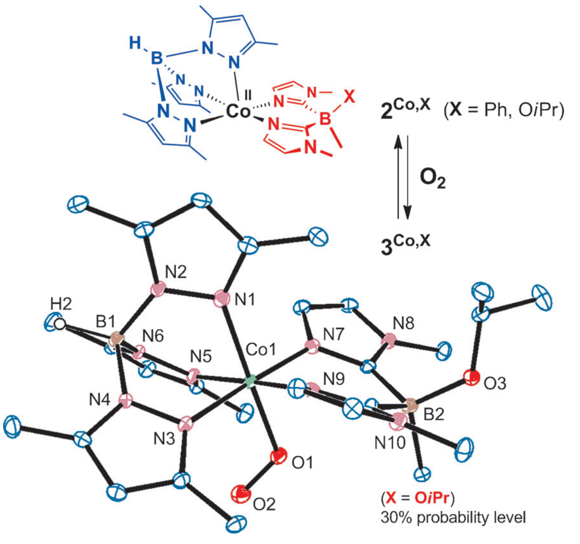
respectively.[18,19] These features suggest that **3** is a mononuclear iron(III)–superoxo species.

We did not meet with success in the isolation and structure determination of **3** so far. Therefore, we explored the synthesis and structural characterization of cobalt analogues. Mononuclear cobalt(II) complexes, $[\mathrm{Co^{II}}(\mathbf{L^X})(\mathrm{Tp^{Me2}})]$ ($\mathbf{2^{Co,X}}$; X = Ph and O*i*Pr), also reacted with O_2 reversibly (Figures S1, S17, S18). The resulting O_2 adducts $\mathbf{3^{Co,X}}$ exhibited O–O stretching bands at 1150 cm^{-1} for the $^{16}O_2$ derivative and 1090 cm^{-1} for the $^{18}O_2$ derivative of $\mathbf{3^{Co,Ph}}$ observed by resonance Raman with 413 nm excitation, and 1147 cm^{-1} for the $^{16}O_2$ derivative and 1088 cm^{-1} for the $^{18}O_2$ derivative of $\mathbf{3^{Co,O\mathit{i}Pr}}$ measured by IR, respectively (Figures S5, S7).[19] EPR spectra of $\mathbf{3^{Co,X}}$ bearing a signal at about $g = 2$ with eight-line hyperfine coupling were characteristic of mononuclear low-spin cobalt(III)–superoxo species of which the spin state is $S = 1/2$ (Figure S11). Finally, the molecular structure of $\mathbf{3^{Co,O\mathit{i}Pr}}$, $[\mathrm{Co^{III}}(\eta^1\text{-}O_2)(\mathbf{L^{O\mathit{i}Pr}})(\mathrm{Tp^{Me2}})]$, could be determined by X-ray crystallography. An O–O bond length (1.301(5) Å) is typical for superoxide. The superoxo ligand is coordinated to the sixth site of the cobalt center with end-on fashion (Scheme 2). On the basis of structural analogy of the iron(II) precursor **2** and the cobalt analogues $\mathbf{2^{Co,X}}$ as well as the similarity of ν(O–O) values, the iron(III)–superoxo species **3** can be assigned to a mononuclear end-on O_2^- complex, formulated as $[\mathrm{Fe^{III}}(\eta^1\text{-}O_2)(\mathbf{L^{Ph}})(\mathrm{Tp^{Me2}})]$. Furthermore, the relatively high ν(Fe–O) frequency of **2** is similar to those observed on η^1-O_2 adducts of heme iron species.[2a] Moreover, frequency of ν(Fe–O) is committed to the coordination mode of peroxides in non-heme iron complexes. η^1-hydroperoxo species shows a higher ν(Fe–O) frequency (> 550 cm^{-1}) in comparison to η^2-peroxo species (< 500 cm^{-1}).[3b,18,20]

Investigation on H-abstraction ability revealed that **3** reacted with substrates having a weak X–H bond (where X = O or N; BDE of X–H < 72.6 kcal mol^{-1}) such as 2-hydroxy-2-azaadamantane (AZADOL) and phenylhydrazine. The reaction of **3** with these substrates afforded a new species assigned to an iron(III)–hydroperoxo adduct, $[\mathrm{Fe^{III}}(\mathrm{OOH})(\mathbf{L^{Ph}})(\mathrm{Tp^{Me2}})]$ (**5**), which exhibited a characteristic absorption band at 542 nm, and resonance Raman features at 778 and 598 cm^{-1} with 514 nm excitation corresponding to the vibration of the O–O and Fe–O bonds, respectively (Figures S2, S8, S9). The bands of this $^{16}O_2$ derivative were shifted to 738 and 573 cm^{-1} on the $^{18}O_2$ derivative of **5**. The observed values are close to those of ν(O–O) and ν(Fe–O) reported for the heme and non-heme low-spin ferric hydroperoxo species.[3b,18,20] Thermal decomposition of complex **5** was confirmed by UV/Vis spectroscopy upon raising the temperature to −20 °C. Conversion of **3** to **5** was also observed by EPR spectroscopy (Figures S10, S11). A frozen THF solution of **3** was EPR-silent at 77 K. Addition of AZADOL at −60 °C led to the appearance of signals at the $g = 2$ region attributed to a rhombic low-spin iron(III) species with a N–O$^\bullet$ radical of the resulting 2-oxyl-2-azaadamantane. Noteworthy, relatively large kinetic isotope effect was observed during the formation of **5** by using deuterated AZADOL ($k_H/k_D \approx 18$ at 213 K) under low concentration of this substrate, and that suggests the O–H bond cleavage is involved in the rate-determining step (Supporting Information, Figure S2). However, the formation rates of **5** were saturated with increasing the concentration of AZADOL. Such kinetic behavior supports the existence of an equilibrium process for the formation of adduct of **3** with AZADOL. Unfortunately, **3** was unable to abstract hydrogen atoms from C–H bonds of alkanes, alkenes, and BNAH (1-benzyl-1,4-dihydronicotinamide), the last of which the C–H BDE is only 67.9 kcal mol^{-1}.



Scheme 2. Formation of superoxide complexes of cobalt analogues.[23]

Furthermore, **3** was inert toward oxidation of exogenous electrophilic substrates including aldehydes and acyl halides at low temperature.[21] Sluggishness of **3** in nucleophilic reaction might be attributed to the low electron density on the superoxide moiety owing to strong antiferromagnetical coupling with low-spin iron(III) center. In contrast to **3**, high-spin iron(III)–superoxo complexes are more reactive. $[\mathrm{Fe(BDPP)(O_2)}]$ abstracts H atom from 9,10-dihydroanthracene.[5a] Although $[\mathrm{Fe(TAML)}(\eta^2\text{-}O_2)]$ ($S = 3/2$ on Fe) cannot activates hydrocarbon substrates with weak C–H bonds (for example, 1,4-cyclohexadiene), this side-on superoxo complex reacts with phenols and aldehydes showing its H-abstracting and nucleophilic reactivity, respectively.[5b] Although 1 e$^-$ reduction of **3** by permethylferrocene did not occur without any additive, **3** reacted with permethylferrocene in the presence of strong acid such as trifluoroacetic acid (Supporting Information, Figure S3). Accordingly, PCET or PT/ET would proceed on the superoxo ligand of **3**.[22]

In summary, the mononuclear superoxo complex of non-heme low-spin iron(III) was characterized successfully. This low-spin ferric superoxo compound is converted into the corresponding low-spin ferric–hydroperoxo species. The iron(II) center of **2** is supported by the non-heme ligands $\mathrm{Tp^{Me2}}$ and $\mathbf{L^{Ph}}$; however, its reactivity (the high-spin iron(II) center reacts with O_2 and CO to give the corresponding adducts of low-spin iron(III) and iron(II), respectively) is close to that of the heme iron systems as well as the non-heme ferrous center of Fe-Bleomycin. In Fe-Bleomycin, an equatorial pyrimidine ligand is critical to control the chemical properties of the iron center.[3,16] In our system, strong electron donation from the equatorial locating $\mathbf{L^{Ph}}$ seems to

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be responsible for the above described nature of the iron center. The square-pyramidal iron(II) supported by five azoles is found in the O_2-binding center of hemoglobin/myoglobin. Interestingly, reproducing such coordination environment results in mimicking the reversible O_2-binding/releasing rather than substrate oxidizing functions in a non-heme system. Further investigations including theoretical analysis are undergoing.

Keywords: bioinorganic chemistry · cobalt · dioxygen ligands · iron · O–O activation

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[23] CCDC 1053457 (**2**), 1053458 ($\mathbf{2}^{\mathbf{Co,Ph}}$), 1053459 ($\mathbf{2}^{\mathbf{Co,O\mathit{i}Pr}}$), and 1053460 ($\mathbf{3}^{\mathbf{Co,O\mathit{i}Pr}}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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