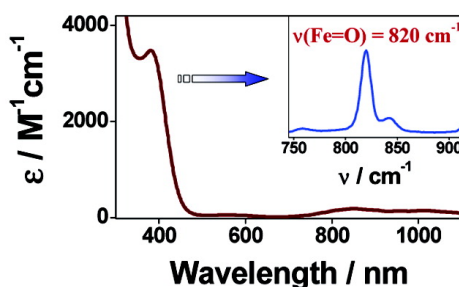
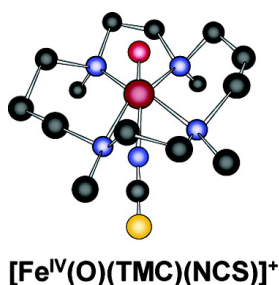


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Axial Ligand Substituted Nonheme Fe^{IV}=O Complexes: Observation of Near-UV LMCT Bands and Fe=O Raman Vibrations

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High-valent oxoiron(IV) intermediates have been implicated as the active oxidizing species in metabolically important oxidative transformations performed by mononuclear nonheme iron enzymes.¹ Very recently, such oxoiron(IV) species were directly observed in enzymatic and biomimetic reactions.^{2,3} For example, an intermediate with a high-spin oxoiron(IV) unit was identified in the catalytic cycle of *Escherichia coli* taurine:αKG dioxygenase (TauD).² In biomimetic studies, mononuclear nonheme oxoiron(IV) complexes bearing tetradentate N4 and pentadentate N5 ligands were synthesized and characterized with various spectroscopic techniques, and the reactivities of these complexes were investigated in a number of oxidation reactions.³

In heme iron enzymes, proximal ligands, such as cysteine (cytochrome P450), histidine (peroxidase), and tyrosine (catalase), are believed to play crucial roles in generating and tuning reactivities of oxoiron(IV) porphyrin π-cation radicals, the so-called Compound I (Cpd I) state.⁴ Indeed, it has been well demonstrated in iron porphyrin models that the reactivity and spectroscopic properties of Cpd I are markedly influenced by the axial ligands trans to the iron–oxo moiety.^{5,6} We are, therefore, exploring the axial ligand effect on the chemical properties of nonheme oxoiron(IV) complexes. In this communication, we report that axial ligand substitution of a mononuclear nonheme oxoiron(IV) complex, [Fe^{IV}(O)(TMC)(NCCH₃)₂]²⁺ (**1**) (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane),^{3a} leads to the formation of new Fe^{IV}=O species with relatively intense electronic absorption features in the near-UV region. The presence of these near-UV features permits the first observation of Fe=O vibrations using resonance Raman spectroscopy. We also report that the oxidizing power of the oxoiron(IV) species is significantly affected by the identity of the axial ligand.

The reaction of [Fe^{II}(TMC)(X)(CF₃SO₃)] (**2**–NCS and **2**–N₃ for X[−] = NCS[−] and N₃[−], respectively)⁷ with 1.2 equiv of PhIO in CH₃CN at 25 °C affords **1**–NCS and **1**–N₃, respectively, that exhibit the electronic spectra shown in Figure 1. To establish the elemental composition of **1**–NCS and **1**–N₃, electrospray ionization mass spectrometry (ESI MS) experiments were performed. The ESI mass spectra of **1**–NCS and **1**–N₃ exhibit prominent ion peaks at *m/z* = 386.1 and 370.1, respectively (Supporting Information, Figure S3), which both upshift accordingly upon introduction of ¹⁸O when PhI¹⁸O is used instead of PhI¹⁶O to generate the intermediates. These data are consistent with the formulation of **1**–NCS and **1**–N₃ as [Fe^{IV}(O)(TMC)(NCS)]⁺ and [Fe^{IV}(O)(TMC)(N₃)]⁺, respectively, where the oxo ligands are derived from PhIO.

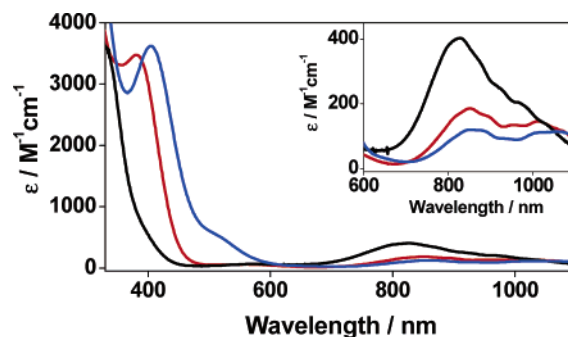


Figure 1. UV–vis spectra of [Fe^{IV}(O)(TMC)(NCS)]⁺ (red), [Fe^{IV}(O)(TMC)(N₃)]⁺ (blue), and [Fe^{IV}(O)(TMC)(NCCH₃)₂]²⁺ (black). Inset shows the expanded near-IR absorptions.

Table 1. Properties of Fe^{IV}(O)(TMC)(X) Complexes

X =	NCCH ₃	N ₃ [−]	NCS [−]
λ_{\max} (nm)	282 (10000) ^b	407 (3600) ^b	387 (3500) ^b
	820 (400) ^a	850 (130) ^b	850 (200) ^b
$\nu(\text{Fe}=\text{O})$ (cm ^{−1})	834 ^a	812	820
δ (mm/s)	0.17 ^a	0.17	0.18
E_Q (mm/s)	1.23 ^a	0.70	0.55
$k_{\text{ox}}(\text{PPh}_3)$ (M ^{−1} s ^{−1})	6.4	0.61	0.22

^a From ref 3a. ^b The corresponding ϵ (M^{−1} cm^{−1}) values are given in parentheses.

To probe the oxidation and spin states of the iron centers in **1**–NCS and **1**–N₃, zero-field Mössbauer spectra were obtained (Table 1). **1**–NCS and **1**–N₃ have isomer shifts (δ) of 0.18 and 0.17 mm/s, respectively, which are virtually identical to that of parent complex **1** (Table 1). As the δ value is sensitive to the oxidation and spin state of iron centers and given the results of our ESI MS studies, we conclude that **1**–NCS and **1**–N₃ contain *S* = 1 Fe^{IV}=O units. It is interesting, however, that both **1**–NCS and **1**–N₃ exhibit smaller quadrupole splitting parameters (ΔE_Q) than **1** (Table 1), indicating perturbation of the ground-state electronic structure of the Fe^{IV}=O unit by the axial ligation of NCS[−] and N₃[−].

Further evidence for electronic perturbation imposed by the presence of these anionic ligands is provided by comparing the electronic absorption spectra of **1**–NCS and **1**–N₃ with that of **1** (Figure 1; Table 1). Relative to **1**, the near-IR absorption features of **1**–NCS and **1**–N₃ are red-shifted and significantly less intense (Figure 1; Table 1), similar to what was observed when the NCCH₃ ligand of **1** was replaced with trifluoroacetate.⁸ As the near-IR features of *S* = 1 Fe^{IV}=O complexes are known to arise from Fe^{IV} d → d transitions,⁹ the red-shifting of the near-IR features upon

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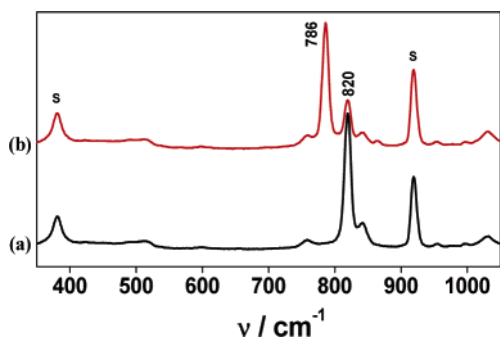


Figure 2. Resonance Raman spectra of (a) $[\text{Fe}^{16\text{O}}(\text{TMC})(\text{NCS})]^+$ (black) and (b) $[\text{Fe}^{18\text{O}}(\text{TMC})(\text{NCS})]^+$ (red) in CH_3CN obtained at $-20\text{ }^\circ\text{C}$ with 406.7 nm excitation. The peaks marked with s are from solvent.

NCS^- and N_3^- binding suggests that these anions impose a weaker ligand field than NCCH_3 .

Perhaps most striking of the properties of $\mathbf{1-NCS}$ and $\mathbf{1-N}_3$ are the intense new bands at 387 and 407 nm, respectively (Figure 1; Table 1), which are not observed in the parent oxoiron(IV) complex $\mathbf{1}$.^{3a} Resonance Raman (RR) experiments were performed to gain insight into the nature of these unique electronic transitions. The RR spectrum of $\mathbf{1-NCS}$ exhibits a vibration at 820 cm^{-1} that shifts to 786 cm^{-1} upon introduction of ^{18}O (Figure 2). This observed isotopic shift of -34 cm^{-1} with ^{18}O -substitution is in good agreement with the calculated value ($\Delta\nu_{\text{calcd}} = -33\text{ cm}^{-1}$) for an Fe–O diatomic vibration. Thus, we assign this RR feature as the $\nu(\text{Fe}=\text{O})$ mode of $\mathbf{1-NCS}$. The RR spectrum of $\mathbf{1-N}_3$ displays a vibration at 812 cm^{-1} that shifts to 779 cm^{-1} upon introduction of ^{18}O (Supporting Information, Figure S4), which we assign as the corresponding $\nu(\text{Fe}=\text{O})$ mode of $\mathbf{1-N}_3$. Importantly, these represent the first Raman observations of $\nu(\text{Fe}=\text{O})$ vibrations for nonheme $S = 1\text{ Fe}^{\text{IV}}=\text{O}$ complexes. In contrast, the $\nu(\text{Fe}=\text{O})$ frequency of $\mathbf{1}$ was observed at 834 cm^{-1} using Fourier transform infrared spectroscopy (Table 1).^{3a} RR spectroscopy was used, however, to determine the $\nu(\text{Fe}=\text{O})$ energy for the high-spin oxoiron(IV) intermediate of TauD that exhibits an absorption band at 318 nm.^{2b} Notably, the downshifts of the $\nu(\text{Fe}=\text{O})$ modes of $\mathbf{1-NCS}$ and $\mathbf{1-N}_3$ relative to that of $\mathbf{1}$, which reflect the substitution of the π -acidic CH_3CN with the more π -basic N_3^- and NCS^- ligands, yield $\nu(\text{Fe}=\text{O})$ frequencies closer to that observed for the TauD intermediate (821 cm^{-1}).^{2b}

Intriguingly, no NCS^- - or N_3^- -related vibrations were observed in the RR spectra of $\mathbf{1-NCS}$ and $\mathbf{1-N}_3$, suggesting that the near-UV features of these two complexes do not arise from transitions involving these axial ligands but are instead $\text{O}^{2-} \rightarrow \text{Fe}^{\text{IV}}$ charge transfer (CT) in nature. While the corresponding $\text{O}^{2-} \rightarrow \text{Fe}^{\text{IV}}$ CT transition of parent complex $\mathbf{1}$ has not yet been identified, the lowest energy electronic absorption band for $\mathbf{1}$ that carries significant intensity ($\epsilon \approx 10\,000\text{ M}^{-1}\text{ cm}^{-1}$) is observed at 282 nm, placing a lower energy limit on the $\text{O}^{2-} \rightarrow \text{Fe}^{\text{IV}}$ CT transition energy of this species. Thus, taken together, these data suggest that replacement of NCCH_3 in $\mathbf{1}$ by NCS^- or N_3^- dramatically lowers the energy of the $\text{O}^{2-} \rightarrow \text{Fe}^{\text{IV}}$ CT transition, shifting it to a value just 5000–6000 cm^{-1} below that of the corresponding transition of the high-spin oxoiron(IV) intermediate of TauD.^{2a}

The axial ligand effect on the reactivity of our nonheme oxoiron(IV) complexes was also investigated by carrying out the oxidation of PPh_3 with $\mathbf{1}$, $\mathbf{1-NCS}$, and $\mathbf{1-N}_3$. Upon addition of PPh_3 to solutions containing the nonheme oxoiron(IV) species, these intermediates reverted back to the starting iron(II) complexes, yielding Ph_3PO quantitatively. Second-order rate constants extracted from these experiments at $0\text{ }^\circ\text{C}$ (Table 1; Supporting Information, Figure S5) showed a difference of as much as a factor of 30, with

reactivity decreasing in the order of $\mathbf{1}$, $\mathbf{1-N}_3$, and $\mathbf{1-NCS}$. These results demonstrate that the reactivity of these nonheme oxoiron(IV) complexes can be significantly affected by the identity of the axial ligand, as observed for oxoiron(IV) porphyrin π -cation radical complexes.^{5,6}

In conclusion, treatment of $\mathbf{2-NCS}$ and $\mathbf{2-N}_3$ with PhIO yields the $S = 1\text{ Fe}^{\text{IV}}=\text{O}$ species $\mathbf{1-NCS}$ and $\mathbf{1-N}_3$, respectively, which have ΔE_Q parameters and electronic absorption spectra quite different from those of parent complex $\mathbf{1}$. The unique near-UV absorption features of $\mathbf{1-NCS}$ and $\mathbf{1-N}_3$ have allowed us to make the first observation of $\nu(\text{Fe}=\text{O})$ vibrations of $S = 1$ mononuclear nonheme oxoiron(IV) complexes by RR spectroscopy. Additionally, we have demonstrated that the reactivity of nonheme oxoiron(IV) intermediates is markedly influenced by the axial ligands. Given the paucity of either $S = 1$ or $S = 2$ nonheme oxoiron(IV) complexes, it is not well established which chemical properties are governed by the Fe^{IV} spin state. It is thus noteworthy that $\mathbf{1-NCS}$ and $\mathbf{1-N}_3$, which have $S = 1\text{ Fe}^{\text{IV}}$ centers, exhibit $\text{O}^{2-} \rightarrow \text{Fe}^{\text{IV}}$ CT transition energies and $\nu(\text{Fe}=\text{O})$ frequencies quite similar to those of the $S = 2$ oxoiron(IV) intermediate of TauD. Therefore, these spectroscopic signatures, which are largely governed by the $\text{Fe}^{\text{IV}}=\text{O}$ bonding interactions, may be more sensitive to the ligand environment than the Fe^{IV} spin state, in agreement with a theoretically based proposal that $\text{Fe}^{\text{IV}}=\text{O}$ bonding is largely unaffected by changes in spin state.⁹

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Supporting Information Available: Text containing experimental details and Figures S1–S5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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