Oxoiron(IV) Complexes

Axial Coordination of Carboxylate Activates the Non-heme Fe^{IV}=O Unit**

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High-valent oxoiron intermediates have been implicated in the dioxygen activation mechanisms of many mononuclear non-heme iron enzymes as the oxidizing species in metabolically important transformations.[1] Recently, the first such species was directly observed in the catalytic cycle of TauD, a member of the superfamily of enzymes with a common 2-His-1-carboxylate facial triad motif that binds the active-site iron center.[2–4] This short-lived intermediate has a high-spin iron(IV) center and the Fe–O bond is 1.62 Å long (determined by extended X-ray absorption fine structure spectroscopy (EXAFS)).[5] Within the same time frame, we reported the first synthetic examples of mononuclear non-heme oxoiron(IV) complexes supported by tetradentate N4 (TMC and TPA) and pentadentate N5 (N4Py and Bn-TPEN) ligands.[6–10] In the case of the TMC complex, $[Fe^{IV}(O)(TMC)(NCMe)](OTf)_2$ was sufficiently stable at −40 °C to be crystallized and characterized by X-ray diffraction.[6] The synthetic complexes, in contrast to the TauD intermediate, have low-spin iron(IV) centers.[6–9] The difference in spin states may arise from the nitrogen-rich nature of the iron coordination environment in the model complexes and the involvement of carboxylate ligands in TauD. This comparison prompted us to investigate whether a carboxylate ligand can be introduced into the iron coordination sphere of a synthetic oxoiron(IV) complex by ligand exchange and thus to assess how such a ligand substitution may affect the spectroscopic properties of the oxoiron(IV) center and its reactivity. We report herein on the reaction of $[Fe^{IV}(O)(TMC)(NCMe)]^{2+}$ (**2**-NCMe) with $NEt_4CF_3CO_2$ and describe the properties of the new intermediate $[Fe^{IV}(O)(TMC)\{OC(O)CF_3\}]^+$ (**2**-O_2CCF_3).

The reaction of $[Fe^{IV}(O)(TMC)(NCMe)]^{2+}$ (**2**-NCMe, $\lambda_{max} = 824$ nm, $\varepsilon = 400\,M^{-1}\,cm^{-1}$) with 10 equivalents of $NEt_4CF_3CO_2$ in MeCN at −20 °C affords a new species designated **2**-O_2CCF_3 within 20 minutes, as indicated by the shift of the absorption maximum to 836 nm with a concomitant loss in intensity ($\varepsilon = 250\,M^{-1}\,cm^{-1}$; Figure 1a). Additional features are also observed to grow at around 940 and 990 nm. This conversion is marked by an isosbestic point, which suggests that **2**-O_2CCF_3 is produced directly from **2**-NCMe (Figure 1a, Scheme 1). Complex **2**-O_2CCF_3 can also be generated by oxygen-atom transfer from PhIO to

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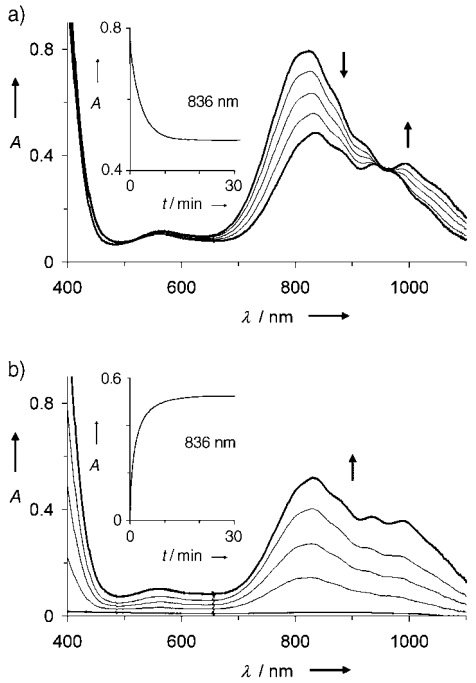
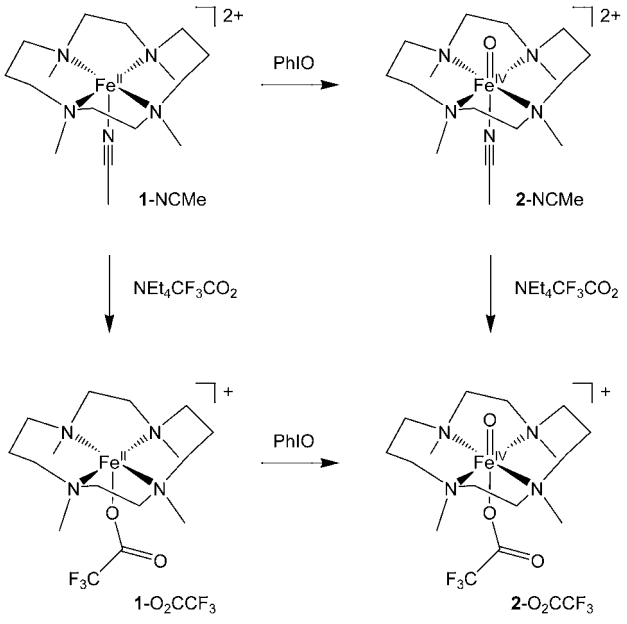


Figure 1. Generation of **2**-O_2CCF_3 by a) addition of $NEt_4CF_3CO_2$ (10 equiv) to **2**-NCMe, and b) addition of PhIO (1 equiv) to **1**-O_2CCF_3 as monitored by UV/Vis/NIR spectroscopy. Reaction conditions: 2 mM iron complex in MeCN at −20 °C. Insets: Corresponding time courses of the reactions monitored at 836 nm.



Scheme 1. Ligand-substitution and oxygen-atom-transfer reactions of Fe(TMC) complexes.

$[Fe^{II}(TMC)\{OC(O)CF_3\}]^+$ (**1**-O_2CCF_3; Figure 1b). Complex **1**-O_2CCF_3 is formed in situ by treatment of $[Fe^{II}(TMC)(NCMe)]^{2+}$ (**1**-NCMe) with 1 equivalent of $NEt_4CF_3CO_2$ as indicated by the shift of the very weak ligand-field band at $\lambda \approx 780$ nm to $\lambda \approx 890$ nm. Thus, **2**-O_2CCF_3 can be formed from **1**-NCMe by two pathways, both involving ligand exchange and oxygen-atom transfer but in different order (Scheme 1).

Direct evidence for the binding of trifluoroacetate to the metal centers in **1**-O_2CCF_3 and **2**-O_2CCF_3 is provided by ^{19}F NMR spectroscopy. In CD_2Cl_2, the starting material $[Fe^{II}(TMC)(OTf)]OTf$ has two equally intense ^{19}F resonance signals at $\delta = 15.6$ ppm and −85.2 ppm (−20 °C); the signal at $\delta = -85.2$ ppm corresponds to free triflate ion in CD_2Cl_2 indicating that the signal at $\delta = 15.6$ ppm arises from triflate that is coordinated to the paramagnetic high-spin iron(II) center, $[Fe^{II}(TMC)(OTf)]OTf$ (Figure 2a). In CD_3CN, only

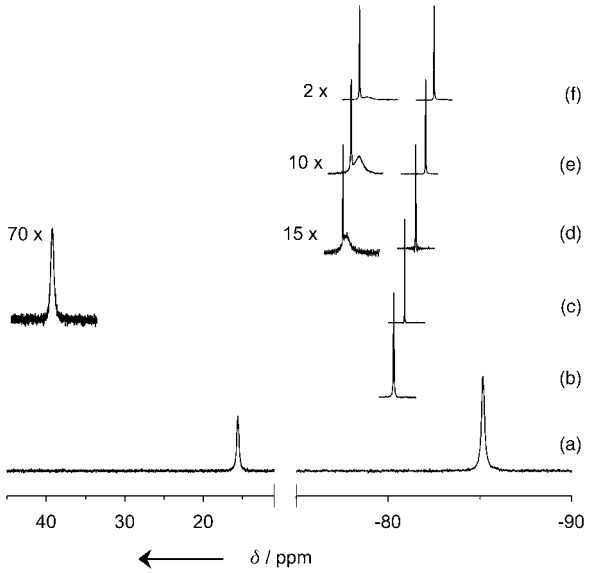


Figure 2. ^{19}F NMR spectra: a) $[Fe^{II}(TMC)(OTf)]OTf$ in CD_2Cl_2 (**1**-OTf) and b) in CD_3CN (**1**-$NCCD_3$), −20 °C; c) equimolar amounts of $[Fe^{II}(TMC)(OTf)]OTf$ and $NEt_4CF_3CO_2$ in CD_3CN (**1**-O_2CCF_3), −20 °C; d) $[Fe^{IV}(O)(TMC)\{OC(O)CF_3\}]OTf$ in CD_3CN (**2**-O_2CCF_3) at −20 °C and e) at −40 °C; and f) after addition of 1 equivalent of $NEt_4CF_3CO_2$ to **2**-O_2CCF_3 in CD_3CN, −40 °C.

one peak at $\delta = -79.9$ ppm is observed, which is attributed to the free triflate counterions (Figure 2b). Addition of 1 equivalent of $NEt_4CF_3CO_2$ to this solution results in the appearance of a resonance at $\delta = 40.3$ ppm, which corresponds to $CF_3CO_2^-$ ligated to high-spin Fe^{II}, with half the intensity of the peak at $\delta = -80.0$ ppm arising from the free triflate counterions (Figure 2c). Addition of a second equivalent of $NEt_4CF_3CO_2$ affords a new peak at $\delta = -76.0$ ppm arising from free $CF_3CO_2^-$ ions (not shown), indicating that the iron center can only bind one trifluoroacetate. Upon addition of PhIO to **1**-O_2CCF_3 at −20 °C, the resonance of bound $CF_3CO_2^-$ disappeared and two new features could be observed close to $\delta = -76$ ppm (Figure 2d). The broader peak is assigned to the $CF_3CO_2^-$ ligated to the paramagnetic Fe^{IV} center ($\delta = -76.3$ ppm, 80%), while the sharper peak corresponds to residual free $CF_3CO_2^-$ ($\delta = -76.1$ ppm, 20%). In support, addition of another equivalent of $NEt_4CF_3CO_2$ results in an increased intensity for the sharper peak (Figure 2f). Thus trifluoroacetate can displace the axial MeCN ligand in **2**-NCMe to form **2**-O_2CCF_3.

Interestingly, the binding of trifluoroacetate affects the stability and reactivity of the oxoiron(IV) unit (Table 1). As previously reported, **2**-NCMe is unexpectedly rather stable and quite unreactive, persisting for at least a month at −40 °C,

Table 1: Properties of **2**-NCMe and **2**-O_2CCF_3.

	2-NCMe	**2**-O_2CCF_3
λ_{max} [nm] (ε [$M^{-1}cm^{-1}$])	824 (400)	836 (250)
$k_{subst.}$ [s^{-1}] (−20 °C)[a]	–	0.0053(2)
for **2**-NCMe→**2**-O_2CCF_3		
k_{decay} [s^{-1}] (25 °C)[b]	$1.8(2)\times10^{-5}$	$2.2(4)\times10^{-4}$
$t_{1/2}$ (25 °C)		
in the absence of substrates[b]	10 h	1 h
+ 1 PPh_3[c]	≈20 s	≈20 s
+ 10 $C_{14}H_{12}$[d]	1 min	<5 s

Reaction conditions: [a] Addition of $NEt_4CF_3CO_2$ (10 equiv) to 2 mM **2**-NCMe in MeCN at −20 °C. [b] Addition of $NEt_4CF_3CO_2$ (1 equiv) to 2 mM **2**-NCMe in MeCN at 25 °C. [c] Addition of PPh_3 (1 equiv) to 2 mM $[Fe^{IV}(O)(TMC)(L)]^{n+}$ (**2**-L) in MeCN at 25 °C. [d] Addition of dihydroanthracene (10 equiv) to 2 mM **2**-L in MeCN at 25 °C.

thereby allowing crystals to be obtained.[6] PPh_3 is the only substrate reported to date to be oxidized at −40 °C by **2**-NCMe[7] and the oxo transfer to one equivalent of substrate occurs over the course of an hour. Raising the temperature to 25 °C shortens its half-life to 10 h and to 20 s in the presence of one equivalent PPh_3. Furthermore, **2**-NCMe reacts with 10 equivalents of dihydroanthracene to form anthracene (half-life of 1 min), so **2**-NCMe appears capable of hydrogen-atom abstraction from weak C–H bonds at room temperature. The yield of anthracene is 45%, the same as that observed for the much more reactive $[Fe^{IV}(O)(N4Py)]^{2+}$,[11] suggesting that both oxoiron(IV) units act as one-electron oxidants in this transformation.

In contrast, **2**-O_2CCF_3 has a half-life at 25 °C an order of magnitude shorter ($t_{1/2}\approx1$ h; Table 1) than **2**-NCMe. Furthermore, **2**-O_2CCF_3 reacts much faster than **2**-NCMe with 10 equivalents of dihydroanthracene ($t_{1/2}\approx5$ s) to produce approximately 0.4 equivalents of anthracene. However, the reaction of **2**-O_2CCF_3 with one equivalent of PPh_3 to afford $OPPh_3$ and regenerate **1**-O_2CCF_3, as monitored by ^{31}P and ^{19}F NMR spectroscopy, occurs on the same time scale as that of **2**-NCMe. So axial coordination of carboxylate to the Fe^{IV}=O unit appears to convert **2**-NCMe into a more reactive oxidant for one-electron oxidations, but not for oxygen atom transfer onto a phosphorus, formally a two-electron process.

The observed lower thermal stability and greater reactivity of **2**-O_2CCF_3 towards dihydroanthracene may at first glance appear counterintuitive, as the replacement of neutral MeCN with a monoanionic $[CF_3CO_2]^-$ ligand might be expected to stabilize the iron(IV) oxidation state by reducing its high effective charge. Indeed Collins has used this principle in his design of tetraanionic macrocyclic tetraamidate ligands that led to the isolation and crystallization of novel iron(IV) complexes.[12] On the other hand, Borovik and co-workers have reported the first example of an iron(III) complex with a terminal oxo ligand, $[Fe^{III}(O)(L)]^{2-}$, where L is a tripodal trianionic tris(ureaylato)amine ligand, which is derived from the reaction of O_2 with the iron(II) precursor. They have invoked the involvement of an oxoiron(IV) species that is too reactive to be detected as the precursor to the oxoiron(III) complex.[13,14] Also, Wieghardt and co-workers have observed the formation of a rather unstable oxoiron(IV) complex containing a cyclam ligand with a carboxymethyl tether from the reaction of its iron(III) precursor with O_3.[15,16] Our results, together with the latter two observations above, suggest that introducing anionic ligands can in fact destabilize the oxoiron(IV) center. In the case of **2**, replacing the nitrile with a carboxylate results in the weakening of the ligand field, as indicated by the red shift observed for the near-IR d–d transitions associated with the $S=1$ oxoiron(IV) unit of **2**-O_2CCF_3 relative to those of **2**-NCMe,[17] and a consequent decrease in the low-spin/high-spin energy gap. The higher reactivity observed for **2**-O_2CCF_3 may thus be associated with enhanced access to a more reactive high-spin $S=2$ reaction surface, although the current limited information available on oxoiron(IV) centers indicates that the strength of the Fe=O bond is comparable for low-spin and high-spin complexes.[4–6,9,17] Nevertheless, there has been considerable discussion on the spin-state-dependent reactivity of oxoiron(IV) species in heme systems to rationalize some of the conflicting observations that have been made for the nature of the active oxidant;[18,19] similar considerations may apply to non-heme oxoiron(IV) oxidations.

In summary, we have introduced a carboxylate ligand *trans* to an oxo group in an iron(IV) complex and, in so doing, have enhanced the reactivity of the $S=1$ oxoiron(IV) unit in **2**.[20] We hypothesize that the higher reactivity may be due to a weakening of the ligand field that provides greater access to a more reactive $S=2$ surface. We note that such $S=2$ iron(IV) centers are utilized by non-heme iron enzymes, such as methane monooxygenase, ribonucleotide reductase, and TauD, to carry out their respective oxidative reactions, and the common feature among these enzymes is the presence of histidine and carboxylate ligands.[1,21,22]

Experimental Section

Physical Methods: UV/Vis spectra were recorded on an HP 8453 A diode array spectrometer with samples maintained at low temperature by using a cryostat from Unisoku Scientific Instruments, Japan. ^{19}F and ^{31}P NMR spectra were recorded on a Varian Inova VXR-300 or Varian Inova VI-300 spectrometer at ambient temperature, unless noted otherwise. Chemical shifts (ppm) are reported referenced to an external standard, $CFCl_3$ ($\delta=0$ ppm) for ^{19}F NMR spectra and H_3PO_4 (85%, 0 ppm) for ^{31}P NMR spectra. GC analyses were performed on a Perkin-Elmer Sigma 3 gas chromatograph (AT-1701 column, 30 m) with flame-ionization detection. The products were identified by comparing their retention times to those of authentic samples.

Generation of [Fe(O)(TMC){OC(O)CF_3}]OTf (**2**-O_2CCF_3(OTf)) via [Fe(O)(TMC)(NCMe)]$(OTf)_2$ (**2**-NCMe$(OTf)_2$). A 2 mM solution of $[Fe^{II}$(TMC)(OTf)]OTf[6] in MeCN (2.5 mL, 0.005 mmol Fe) in a 1-cm UV/Vis cuvette was pre-cooled to −20 °C. (Note: Dissolution of $[Fe^{II}$(TMC)(OTf)]OTf in MeCN readily afforded [Fe(TMC)-(NCMe)]$(OTf)_2$ (**1**-NCMe$(OTf)_2$), as indicated by the ^{19}F resonance of the free triflate ion in its NMR spectrum.) Addition of PhIO[23] (1 equiv, 0.005 mmol) in MeOH (0.05 mL) afforded **2**-NCMe$(OTf)_2$. Subsequent addition of $NEt_4CF_3CO_2$ (10 equiv, 0.050 mmol) in MeCN (0.05 mL) afforded **2**-O_2CCF_3(OTf). ^{19}F NMR for **1**-OTf(OTf)

(CD_2Cl_2, 282.4 MHz, −20 °C): $\delta = 15.6$ (s, $[Fe(TMC)\{OS(O)_2CF_3\}]^+$) and −85.2 ppm (s, $CF_3SO_3^-$); **1**-$NCCD_3(OTf)_2$ (CD_3CN, 282.4 MHz, −20 °C): $\delta = -79.9$ ppm (s, $CF_3SO_3^-$). ^{19}F NMR for **2**-$O_2CCF_3(OTf)$ + NEt_4OTf (CD_3CN, 282.4 MHz, −20 °C): $\delta = -76.1$ (s, $CF_3CO_2^-$), −76.3 (s, $[Fe(O)(TMC)\{OC(O)CF_3\}]^+$), and −80.0 ppm (s, $CF_3SO_3^-$). ^{19}F NMR for $NEt_4CF_3CO_2$ (CD_2Cl_2, 282.4 MHz): $\delta = -75.9$ ppm (s, $CF_3CO_2^-$); $NEt_4CF_3CO_2$ (CD_3CN, 282.4 MHz): $\delta = -75.8$ ppm (s, $CF_3CO_2^-$).

Generation of **2**-$O_2CCF_3(OTf)$ via $[Fe(TMC)\{OC(O)CF_3\}]OTf$ (**1**-$O_2CCF_3(OTf)$). A 2 mM solution of $[Fe^{II}(TMC)(OTf)]OTf$ in MeCN (2.5 mL, 0.005 mmol Fe) in a 1-cm UV/Vis cuvette was converted into **1**-$O_2CCF_3(OTf)$ by addition of $NEt_4CF_3CO_2$ (1 equiv, 0.005 mmol) in MeCN (0.05 mL). This solution was then cooled to −20 °C. **2**-$O_2CCF_3(OTf)$ was generated by addition of PhIO (1 equiv, 0.005 mmol) in MeOH (0.05 mL). ^{19}F NMR for **1**-$O_2CCF_3(OTf)$ + NEt_4OTf (CD_3CN, 282.4 MHz, −20 °C): $\delta = 40.3$ (s, $[Fe(TMC)\{OC(O)CF_3\}]^+$) and −80.0 ppm (s, $CF_3SO_3^-$).

Reaction of **2**-L with PPh_3. A 2 mM solution of **2**-$NCMe(OTf)_2$ or **2**-$O_2CCF_3(OTf)$ in MeCN (2 mL), generated from **1**-$NCMe(OTf)_2$ or **1**-$O_2CCF_3(OTf)$ and PhIO (1 equiv) at 25 °C, was treated with PPh_3 (1 equiv, 0.004 mmol) in a solvent mixture of MeCN and CH_2Cl_2 (1:1; 0.04 mL). Products were analyzed by ^{31}P NMR (CD_3CN, 121.4 MHz): $\delta = 27.9$ ppm (s, $OPPh_3$), and ^{19}F NMR (CD_3CN, 282.4 MHz): $\delta = 21.4$ (s, $[Fe(TMC)\{OC(O)CF_3\}]^+$) and −80.0 ppm (s, $CF_3SO_3^-$).

Reaction of **2**-L with dihydroanthracene: A 2 mM solution of **2**-$NCMe(OTf)_2$ or **2**-$O_2CCF_3(OTf)$ in MeCN (2 mL), generated by addition of PhIO (1 equiv) to **1**-$NCMe(OTf)_2$ or **1**-$O_2CCF_3(OTf)$ at 25 °C, was treated with dihydroanthracene (10 equiv, 0.040 mmol; recrystallized from EtOH)[24] in a solvent mixture of MeCN and CH_2Cl_2 (1:1; 0.08 mL). Products were analyzed by GC: Reaction with **2**-$NCMe(OTf)_2$ yielded 0.0018 mmol anthracene (45% based on equivalents of Fe complex) and reaction with **2**-$O_2CCF_3(OTf)$ gave 0.0016 mmol anthracene (40%).

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[10] Abbreviations used: Bn-TPEN = *N*-benzyl-*N*,*N*′,*N*′-tris(2-pyridylmethyl)-1,2-diaminoethane, N4Py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine, OTf = trifluoromethylsulfonate (or triflate) anion, TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (or tetra(*N*-methyl)cyclam), TPA = *N*,*N*,*N*-tris(2-pyridylmethyl)amine.
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