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A Synthetic High-Spin Oxoiron(IV) Complex: Generation, Spectroscopic Characterization, and Reactivity**

Jason England, Marlène Martinho, Erik R. Farquhar, Jonathan R. Frisch, Emile L. Bominaar,* Eckard Münck,* and Lawrence Que, Jr.*

High-valent oxoferryl intermediates have been proposed as the active oxidants in the catalytic cycles of a wide range of mononuclear non-heme oxygen-activating enzymes.^[1] These high-valent species have now been spectroscopically characterized for four enzymes, and were found in all instances to contain high-spin ($S=2$) iron(IV) centers.^[2] Contemporaneously, the first examples of the existing family of synthetic nonheme oxoiron(IV) complexes were characterized,^[3–5] which are exclusively octahedral and in all but one case exhibit the $S=1$, rather than $S=2$, spin state. Given that DFT suggests higher reactivity for an $S=2$ oxoiron(IV) unit,^[6,7] it is perhaps not surprising that there is a scarcity of such complexes. Indeed, the only example to date is $[\text{Fe}^{\text{IV}}(\text{O})(\text{H}_2\text{O})_5]^{2+}$ (**1**), which is generated by treating $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$ with ozone in acidic aqueous solution.^[8a] Complex **1** has a $t_{1/2}$ value of only 7 s at 25 °C,^[8b] and the aqueous medium limits our options for significantly lengthening its lifetime by working at low temperature ($T < 0^\circ\text{C}$). We have consequently sought an alternative approach to obtain an $S=2$ oxoiron(IV) complex.

Consideration of the crystal-field splitting diagram for an octahedral oxoiron(IV) complex reveals that the spin state is determined by the energy gap between the d_{xy} and the $d_{x^2-y^2}$ orbitals.^[7] In the $S=1$ complexes reported thus far, this energy gap is larger than the spin-pairing energy. Therefore, weakening the strength of the equatorial ligand field is one strategy to obtain $S=2$ complexes, a principle demonstrated by the tetraaqua ligand set of **1**.^[8] An alternative approach is

to adopt a trigonal bipyramidal (TBP) geometry, where the d_{xy} and $d_{x^2-y^2}$ orbitals would become degenerate. Thus, a tetradentate tripodal ligand with sufficient steric constraints to enforce local C_{3v} symmetry at the iron(II) center could afford, upon introduction of an axial oxo ligand, a trigonal bipyramidal oxoiron(IV) complex with an $S=2$ ground state. Such a geometry is found for the oxoiron(III) complex of the tris(ureaylato) ligand employed by Borovik and co-workers.^[9] This complex was obtained from the reaction of its iron(II) precursor with O_2 , and proposed to derive from the reduction of an initially formed oxoiron(IV) species, but to date direct evidence for the latter has not been obtained. TMG₃tren (Figure 1A) is another example of such a ligand.^[10] This ligand has recently found use in the successful stabilization of a superoxocopper(II) complex and its subsequent structural characterization.^[11] Furthermore, the high level of steric encumbrance provided by TMG₃tren should inhibit intermo-

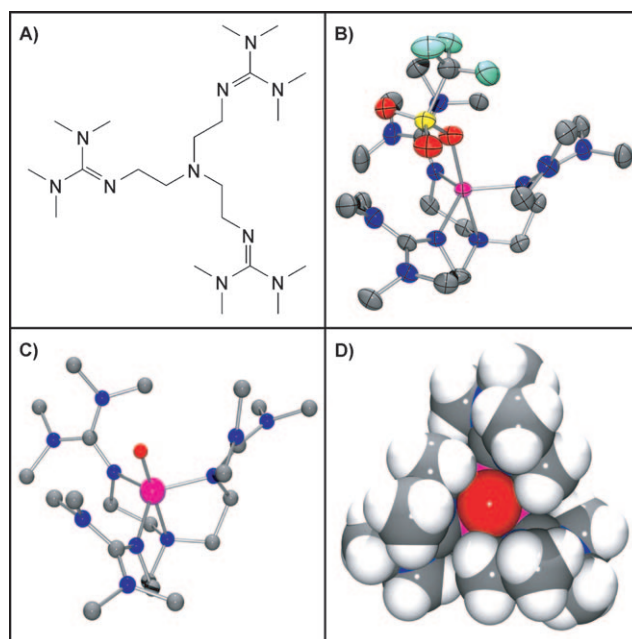


Figure 1. A) Schematic structure of the TMG₃tren ligand. B) Solid-state structure of $[\text{Fe}^{\text{II}}(\text{TMG}_3\text{tren})(\text{OTf})]^+$ (**2**; OTf = trifluoromethanesulfonate), with ellipsoids shown at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å]: Fe–O, 2.156(2); Fe–N_{axial}, 2.118(3); Fe–N_{guanidine(ave)}, 2.094. C) Ball-and-stick and D) space-filling models of the geometry-optimized structure of **3** calculated by DFT. Selected bond distances [Å]: Fe=O, 1.648; Fe–N_{axial}, 2.121; Fe–N_{guanidine(ave)}, 2.034. Atom color scheme: C, gray; N, blue; O, red; S, yellow; F, light blue; Fe, magenta.

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lecular decay processes, thereby stabilizing the highly reactive $\text{Fe}^{\text{IV}}=\text{O}$ unit.

The combination of equimolar amounts of TMG_3tren and $[\text{Fe}^{\text{II}}(\text{OTf})_2(\text{CH}_3\text{CN})_2]$ in THF afforded $[\text{Fe}^{\text{II}}(\text{TMG}_3\text{tren})(\text{OTf})](\text{OTf})$ (**2**), whose crystal structure (Figure 1B)^[12] exhibited the desired TBP geometry ($\tau = 0.96$ ^[13]). Reaction of **2** in CH_3CN with one equivalent of 2-(*tert*-butylsulfonyl)-iodosylbenzene ($t\text{BuSO}_2\text{C}_6\text{H}_4\text{IO}$)^[14] led to the formation of an orange complex **3** ($t_{1/2} = 4.3$ h at -30°C ; $t_{1/2} \approx 30$ s at 25°C) with absorption maxima λ_{max} (ϵ_{max}) centered at 400 (9800), 825 (260), and 866 (250) nm (Figure 2). The electrospray mass

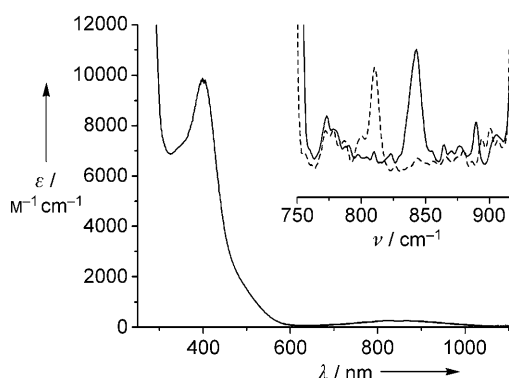


Figure 2. Electronic spectrum of **3** in CH_3CN solution. Inset: resonance Raman spectra ($\lambda_{\text{ex}} = 514.5$ nm, power = 10 mW) of $[\text{Fe}^{16}\text{O}]\text{-3}$ (solid line) and $[\text{Fe}^{18}\text{O}]\text{-3}$ (dashed line) recorded in frozen CH_3CN solution.

spectrum of **3** exhibited signals at $m/z = 661.3$ and 256.2 , with isotope distribution patterns consistent with their respective formulation as $\{[\text{Fe}^{\text{IV}}(\text{O})(\text{TMG}_3\text{tren})](\text{OTf})\}^+$ and $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMG}_3\text{tren})]^{2+}$ (see Figures S1 and S2 in the Supporting Information). The presence of an $\text{Fe}=\text{O}$ unit in **3** was confirmed by resonance Raman spectroscopy, which revealed a vibration at 843 cm^{-1} that shifted to 810 cm^{-1} upon ^{18}O -labeling of **3** (Figure 2, inset). This vibrational frequency and isotope shift ($\Delta\nu_{\text{theor}} \approx 37\text{ cm}^{-1}$) are both consistent with its assignment as $\nu(\text{Fe}=\text{O})$. Furthermore, the ^{19}F NMR spectrum of **3** displayed a single resonance at $\delta = -79.9$ ppm, which corresponds to free triflate. This observation, coupled with the fact that **3** exhibits the same UV/Vis spectrum in both coordinating (CH_3CN) and noncoordinating (CH_2Cl_2) solvents, indicates that no exogenous ligands bind to the iron center and that, by extension, the five-coordinate geometry found in **2** is retained in **3**, thus leading us to formulate the latter as $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMG}_3\text{tren})]^{2+}$.

Mössbauer spectroscopy demonstrates that **3** has an $S = 2$ iron(IV) center. The zero-field spectrum (Figure 3A) exhibits a doublet with a quadrupole splitting $\Delta E_Q = -0.29\text{ mm s}^{-1}$ and isomer shift $\delta = 0.09\text{ mm s}^{-1}$. The observation of a doublet in the spectrum at 4.2 K indicates that **3** has integer electronic spin. The δ value is strongly indicative of an iron(IV) complex, and although the value of δ is distinctly lower than those for **1** (0.38 mm s^{-1})^[8a] and TauD intermediate **J** (TauD-J; 0.30 mm s^{-1})^[15c] it is similar to that of the Fe^{IV} site of $[\text{Fe}^{\text{IV}}(\text{O})(6\text{-Me}_3\text{tpa})(\mu\text{-O})\text{Fe}^{\text{III}}(6\text{-Me}_3\text{tpa})(\text{H}_2\text{O})]$ (0.10 mm s^{-1} ; 6-Me₃-tpa = tris(6-methylpyridyl-2-methyl)amine),^[17] reflect-

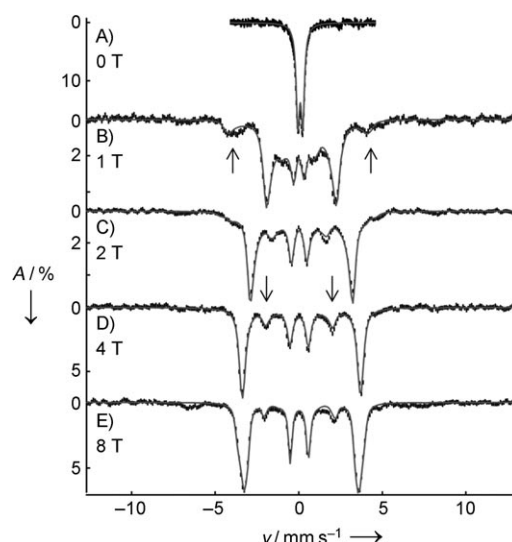


Figure 3. Mössbauer spectra of **3** in CH_3CN recorded at 4.2 K in parallel applied magnetic fields B as indicated. Downward arrows indicate nuclear $\Delta m = 0$ transitions of the $M_S = 0$ ground-state spectrum. Upward arrows mark outer absorption features of the spectrum associated with the $M_S = -1$ excited state. Solid lines are spectral simulations using the parameters listed in Table 1 with the $S = 2$ spin Hamiltonian $H = D(S_z^2 - 2) + E(S_x^2 - S_y^2) + 2\beta\mathbf{S}\cdot\mathbf{B} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I} - g_n\beta_n\mathbf{B}\cdot\mathbf{I} + H_Q$. In spectra (B), (C), and (D) a high-spin Fe^{III} impurity, representing 12% of the iron, has been subtracted from the raw data. In trace (E), this impurity has not been subtracted and exhibits weak absorption bands at ca. -6.5 and $+7\text{ mm s}^{-1}$.

ing the nitrogen-rich ligand environment of **3**. Approximately 88% of the Fe in the sample belongs to **3**. A minor high-spin Fe^{III} contaminant accounts for the remaining absorption (see Figure S3 in the Supporting Information). The spectra of **3** exhibit paramagnetic hyperfine structure in applied magnetic fields. Fitting these spectra with an $S = 2$ spin Hamiltonian yields a parameter set that compares well with other high-spin oxoiron(IV) systems (Table 1). In contrast, analysis of the data by assuming an $S = 1$ center yields an unacceptable \mathbf{A} tensor, with $A_{\text{iso}} = (A_x + A_y + A_z)/3 \approx -29.0\text{ T}$, which is nearly twice as large as A_{iso} values reported for $S = 1$ complexes.^[4,5,16,18] Moreover, the spin-dipolar part of the \mathbf{A} tensor, $(\mathbf{A} - A_{\text{iso}})$, would be about four times smaller than observed for $S = 1\text{ Fe}^{\text{IV}}=\text{O}$ complexes.

The Fe K-edge X-ray absorption spectrum of **3** reveals an edge energy of 7123.2 eV (versus 7121.1 eV for **2**) and a pre-edge peak assigned to $1s \rightarrow 3d$ transitions with an area of 27 units (Figure 4, top), both features being within the range of values found for the synthetic $\text{Fe}^{\text{IV}}=\text{O}$ complexes previously studied.^[16,19] In contrast to the pre-edge features of existing $S = 1$ complexes, which can be modeled with a single Gaussian, the pre-edge region of **3** contains two discernible features at 7113.8 and 7115.6 eV that have areas of 24 and 3 units, respectively (see Figure S4 and Table S1 in the Supporting Information). This phenomenon was predicted in a recent DFT study,^[20a] and was rationalized in terms of a splitting of the α and β d_{z^2} orbitals by spin polarization, which is expected to be significantly larger in the $S = 2$ case.^[20] EXAFS analysis of **3** (Figure 4, bottom) yields a best-fit plot (see Table S2 in the Supporting Information) with an O/N

Table 1: Spectroscopic parameters of selected oxoiron(IV) complexes.

Complex	<i>S</i>	λ_{max} [nm]	$\nu_{\text{Fe=O}}$ [cm ⁻¹]	<i>D</i> [cm ⁻¹]	<i>E/D</i>	$A_{x,y,z}/g_{\text{eff}}\beta_n$ [T]	ΔE_Q [mm s ⁻¹]	η	δ [mm s ⁻¹]	<i>E</i> ₀ [eV]	Pre-edge area
3 (exp)	2	400	843	5.0(3)	0.02(1)	-15.5(4), -14.8(4), -28.0(8)	-0.29(3)	0	0.09(1)	7123.2	27
3 (DFT) ^[a]	2	—	—	—	—	-15, -15, -27.6	-0.49	0.02	0.11	—	—
TauD-J ^[b]	2	318	821	10.5	0.01	-18.4, -17.6, -31.0	-0.9	0	0.30	7123.8 ^[d]	not reported
1 ^[c]	2	320	—	9.7	0	-20.3, -20.3, nd	-0.33	0	0.38	7126	60-70
4 ^[c]	1	820	834	29	0	-22.6, -18.3, -2.9	1.24	0.5	0.17	7124.5	32.8

[a] The **A** tensor was calculated by taking the experimentally determined $A_{\text{iso}} = -19.4$ T and adding the spin-dipolar term obtained from DFT. [b] Data from Refs [2a, 15]. [c] **1** = [Fe^{IV}(O)(OH₂)₅]²⁺ from Ref. [8]; **4** = [Fe^{IV}(O)(TMC)(NCCH₃)]²⁺ (TMC = 1,4,8,11-tetramethylcyclam) from Refs. [4, 16]. [d] Assuming an Fe foil reference *E* of 7112.0 eV.

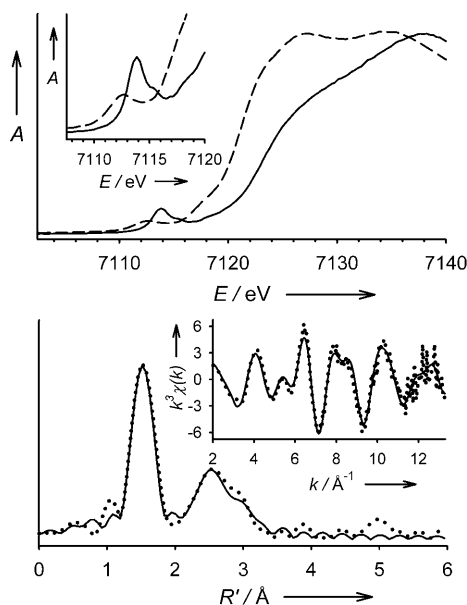


Figure 4. Top: X-ray absorption edge spectra of **2** (----) and **3** (—). The inset shows an expansion of the pre-edge region. Bottom: Fe K-edge unfiltered EXAFS data ($k^3\chi(k)$, inset) and the corresponding Fourier transform of **3**. Experimental data are shown with dotted lines and fits with solid lines. See the Supporting Information for further details of the EXAFS analysis.

scatterer at 1.65 Å (assigned to the Fe=O unit) and a further shell of 4 O/N scatterers at 1.99 Å (corresponding to the N donors of the supporting ligand). This Fe=O distance is essentially the same as that found crystallographically for other oxoiron(IV) complexes.^[4,18,21]

DFT calculations performed on **3** further support our *S* = 2 spin-state assignment. Geometry optimization yields a structure with *C*₃ symmetry (Figure 1C) and an Fe=O bond length of 1.648 Å, which is in close agreement with that obtained from the EXAFS analysis. In contrast, the Fe–N_{ave} bond length of 2.055 Å obtained from DFT is significantly longer than that found by EXAFS. Complex **3** has a ⁵A ground state with the four d electrons in two half-filled E levels (see Table S3 in the Supporting Information), with the lowest *S* = 1 and *S* = 0 configurations calculated to be about 10000 cm⁻¹ and 12000 cm⁻¹, respectively, above the *S* = 2 ground state. Notably, the calculated Mössbauer parameters (ΔE_Q , δ , and the spin-dipolar contribution to the **A** tensor) are

in excellent agreement with the experimental data (Table 1). The small value for ΔE_Q results from cancellation of opposing valence and ligand contributions, the latter arising from the donation of electron density from the oxo ligand into the vacant E{d_{xz}, d_{yz}} and empty A{d_{z²}} orbitals of the iron center. Lastly, the calculated spin populations at the iron center and the oxo group are +3.08 and +0.64, respectively, similar to the results obtained for **1** and TauD-J.^[8a,15c]

The oxidative reactivity of **3** has been investigated with several substrates, and the second-order rate constants derived from these studies in CH₃CN solution at -30°C are listed in Table 2, together with those of the well-studied *S* = 1

Table 2: Second-order rate constants (*k*₂) for oxidation reactions of Fe^{IV}=O complexes.

Complex	<i>k</i> ₂ [M ⁻¹ s ⁻¹] in CH ₃ CN at -30°C		
	PPh ₃	DHA	CHD
3	1.1	0.090	1.2
4	0.22	0.016	0.018
5	1.5	2.0	1.3

complexes [Fe^{IV}(O)(TMC)(CH₃CN)]²⁺ (**4**)^[4,16,22] and [Fe^{IV}(O)(N4Py)]²⁺ (**5**; N4Py = bis(2-pyridylmethyl)bis(2-pyridyl)methylamine).^[21,23] Complex **3** acts as a stoichiometric oxo-transfer agent to PPh₃, but behaves as a 1 e⁻ oxidant in reactions with dihydroanthracene (DHA) and 1,4-cyclohexadiene (CHD), with two equivalents of **3** yielding one equivalent of anthracene and benzene, respectively. In general, **3** is a more active oxidant than **4**, but comparable to **5**. Surprisingly, **3** oxidizes DHA 13 times more slowly than CHD, despite there being no significant difference in the oxidation rates of these two substrates by either **4** or **5**. Since DHA and CHD have similar C–H bond dissociation energies,^[24] the large rate difference observed for **3** suggests that the TMG₃tren ligand impedes access of the bulkier DHA to the Fe=O unit (Figure 1D and Figure S5 in the Supporting Information). Such a sterically derived mitigation of reactivity has been observed for other systems with tetramethylguanidyl ligands.^[25] Lastly, the use of [D₄]DHA as the substrate for **3** afforded a kinetic isotope effect (KIE) of 18, which is above the semiclassical limit of 7. Thus, as for the *S* = 2 oxoferryl enzymatic intermediates^[1] and the *S* = 1 complexes **4** and **5**,^[22,23] there appears to be a significant contribution

from hydrogen atom tunneling in the cleavage of the C–H bond by **3**.

Herein we have described the high-yield synthesis of an $S=2$ oxoiron(IV) complex that has been characterized fully by spectroscopy. Complex **3** resembles TauD-J in several respects (Table 1). Both **3** and TauD-J exhibit a near-UV charge-transfer band that is likely to be associated with an oxo-to-iron(IV) charge-transfer transition, as excitation into these bands results in the observation of resonance-enhanced Fe=O vibrations.^[15a] The charge-transfer band of **3** is red-shifted relative to that of TauD-J. This observation is in line with the greater Lewis acidity expected for an oxoiron(IV) unit supported by the neutral TMG₃tren ligand, instead of the dianionic bis(carboxylato)-containing coordination sphere of TauD-J.^[2a,15c] Differences in the coordination environment are also reflected in the Mössbauer parameters. Interestingly, **3** exhibits an oxidative efficacy that is merely comparable to that of the $S=1$ complex **5** (Table 2), rather than exceeding it. This finding appears to belie the prevailing DFT-derived consensus that the $S=2$ manifold is inherently more reactive than the corresponding $S=1$ state.^[6,7] This attenuation in the reactivity of **3** most likely derives from the protection of the high-spin oxoiron(IV) moiety afforded by the sterically bulky TMG₃tren ligand, a design strategy we have successfully employed here to attain the elusive $S=2$ spin state. Further ligand tuning may allow access to more-reactive $S=2$ oxoiron(IV) model complexes that might provide invaluable insight into the inherent reactivity and spectroscopic properties of these key biologically relevant entities.

Experimental Section

2: A solution of TMG₃tren (0.55 g, 1.25 mmol) in THF (10 mL) was added to a Schlenk flask charged with [Fe(OTf)₂(CH₃CN)₂] (0.54 g, 1.25 mmol), and the resultant mixture stirred overnight. The cream precipitate obtained was isolated by filtration, washed with THF (3 × 5 mL) and diethyl ether (2 × 15 mL), and dried under vacuum to give an off-white powder (0.97 g, 93 %) that analyzed as a monoacetonitrile adduct. Elemental analysis calcd for C₂₅H₅₁F₆FeN₁₁O₆S₂: C 35.93, H 6.15, N 18.44; found: C 35.89, H 6.21, N 18.24. The acetonitrile-free compound was obtained as a pale yellow crystalline solid (0.84 g, 85 % overall) by vapor diffusion of diethyl ether into a concentrated dichloromethane solution of the iron(II) complex. ¹H NMR (300 MHz, CD₃CN, all signals appear as broad singlets): δ = 213.2 (3H, CH₂), 86.7 (3H, CH₂), 61.7 (3H, CH₂), 34.3 (9H, NMe), 20.9 (9H, NMe), 9.9 (9H, NMe), 1.3 (3H, CH₂), –13.6 ppm (9H, NMe). MS (+ESI): m/z 645.1 [(M–OTf)⁺], 248.1 [(M–(OTf)₂)²⁺]. Elemental analysis calcd for C₂₃H₄₈F₆FeN₁₀O₆S₂: C 34.76, H 6.09, N 17.63; found: C 34.67, H 6.19, N 17.51.

3(OTf)₂: Solutions of the orange complex **3** were obtained by treatment of a solution of **2** in CH₃CN or CH₂Cl₂ with a solution of one equivalent of *t*BuSO₂C₆H₄IO^[14] in CH₂Cl₂. Solutions of oxidant up to a concentration of 60 mM were routinely used.

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