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Evaluating the Identity and Diiron Core Transformations of a (μ -Oxo)diiron(III) Complex Supported by Electron-Rich Tris(pyridyl-2-methyl)amine Ligands

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Abstract

The composition of a (μ -oxo)diiron(III) complex coordinated by tris((3,5-dimethyl-4-methoxy)pyridyl-2-methyl)amine (R_3 TPA) ligands was investigated. Characterization using a variety of spectroscopic methods and X-ray crystallography indicated that the reaction of iron(III) perchlorate, sodium hydroxide, and R_3 TPA affords $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(R_3\text{TPA})_2](\text{ClO}_4)_3$ (**2**), rather than the previously reported species, $[\text{Fe}_2(\mu\text{-O})(\text{OH})(\text{H}_2\text{O})(R_3\text{TPA})_2](\text{ClO}_4)_3$ (**1**). Facile conversion of the (μ -oxo)(μ -hydroxo)diiron(III) core of **2** to the (μ -oxo)(hydroxo)(aqua)diiron(III) core of **1** occurs in the presence of water and at low temperature. When **2** is exposed to wet acetonitrile at room temperature, the CH_3CN adduct is hydrolyzed to CH_3COO^- , which forms the compound $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})(R_3\text{TPA})_2](\text{ClO}_4)_3$ (**10**). The identity of **10** was confirmed by comparison of its spectroscopic properties with those of an independently prepared sample. To evaluate whether or not **1** and **2** are capable of generating the diiron(IV) species $[\text{Fe}_2(\mu\text{-O})(\text{OH})(\text{O})(R_3\text{TPA})_2]^{3+}$ (**4**), which has previously been generated as a synthetic model for high-valent diiron protein oxygenated intermediates, studies were performed to investigate their reactivity with hydrogen peroxide. Because **2** reacts rapidly with hydrogen peroxide in CH_3CN but not in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, conditions that favor conversion to **1**, complex **1** is not a likely precursor to **4**. Compound **4** also forms in the reaction of **2** with H_2O_2 in solvents lacking a nitrile, suggesting that hydrolysis of CH_3CN is not involved in the H_2O_2 activation reaction. These findings shed light on the formation of several diiron complexes of electron-rich R_3 TPA ligands and elaborate on conditions required to generate synthetic models of diiron(IV) protein intermediates with this ligand framework.

INTRODUCTION

Because of the importance of carboxylate-bridged diiron enzymes as powerful and selective oxidizing agents in bacterial systems such as soluble methane monooxygenase (sMMO),^{1,2} understanding the chemical and physical characteristics of synthetic diiron(IV) units, which model the reactive species of the sMMO hydroxylase (sMMOH), is of considerable interest.^{3–5} Among the various constructs employed to access such species, one convenient platform is based on a tripodal tris(pyridyl-2-methyl)amine (TPA) ligand. Stable dinuclear

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SUPPORTING INFORMATION

 X-ray crystallographic data and table, structural comparison table, and UV-vis absorption data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

species can be readily prepared by linking two monomeric [Fe(TPA)] complexes through oxo-, hydroxo-, or carboxylato bridges.^{6–8} A notable achievement in diiron TPA modeling chemistry is the crystallographic characterization of a mixed-valent di(μ -oxo)diiron(III,IV) unit, [Fe₂(μ -O)₂(5-Et₃-TPA)₂](ClO₄)₃, where 5-Et₃-TPA = tris((5-ethylpyridyl)-2-methyl)amine) (Chart 1).^{9,10} This complex contains the quadrilateral {Fe₂(μ -O)₂} core believed to be present in the diiron(IV) intermediate **Q** of sMMOH,¹¹ a remarkable enzyme that is capable of transforming methane to methanol.¹²

The electronic and steric properties of the diiron TPA complexes can be tuned by appending various substituents around the pyridine rings. Recently, studies using an electron-rich tris((3,5-dimethyl-4-methoxy)pyridyl-2-methyl)amine (R₃TPA) derivative have enabled high-valent diiron units to be prepared.^{13–15} Treatment of the diiron(III) precursor [Fe₂(μ -O)(OH)(H₂O)(R₃TPA)₂](ClO₄)₃ (**1**, Chart 1) with H₂O₂ results in the formation of a di(μ -oxo)diiron(III,IV) [Fe₂(μ -O)₂(R₃TPA)₂]³⁺ (**7**) species.¹³ When **7** was subjected to controlled bulk electrolysis at an applied potential of +900 mV (vs. ferrocene/ferrocenium) in acetonitrile at –40 °C, a diiron(IV) [Fe₂(μ -O)₂(R₃TPA)₂]⁴⁺ (**5**) complex was quantitatively generated (Scheme 1). Compound **5** could also be accessed by chemical oxidation.¹⁴ It was proposed that reaction of **1** with hydrogen peroxide and protons rapidly leads to formation of **5** through the transient generation of (μ -hydroperoxo)diiron(III,III) (**3**) and (μ -oxo)(hydroxo)(oxo)diiron(IV) (**4**) intermediates (Scheme 1). Compound **5**, however, exhibits poor H-atom abstraction ability. When the valence-delocalized diiron(III,IV) **7** was treated with tetrabutylammonium hydroxide, or the diiron(IV) unit **4** was reduced by ferrocene, the valence-localized species **6** was obtained.¹⁵ Compound **6** has a high-spin (*S* = 2) Fe^{IV}=O unit that displays a rate enhancement in H-atom abstraction reactions of several orders of magnitude compared to previously characterized high-valent diiron complexes with *S* = 1 Fe^{IV}=O units. In addition, conversion of the diamond core of **7** to a ring-opened structure by reaction with water or alcohol substrates also generates diiron species that are more reactive toward C–H bonds.¹⁶

During the course of extending these studies, we discovered that the reported procedure for preparing the starting material [Fe₂(μ -O)(OH)(H₂O)(R₃TPA)₂](ClO₄)₃ (**1**) produced the (μ -oxo)(μ -hydroxo)diiron(III) species (**2**) and an unidentified iron(III) side product. In this report, we describe the identity of **2** and provide an improved procedure for its preparation. The tendency of {Fe₂(μ -O)₂} units to undergo diiron core interconversion reactions in the presence of coordinating solvents was examined, which revealed that **2** can promote the hydrolysis of acetonitrile to form acetate. In light of these new findings, the reactivity of **2** with hydrogen peroxide was also more fully investigated. From these studies we propose a revised reaction scheme for the generation of high-valent diiron units from diiron(III) R₃TPA precursors.

EXPERIMENTAL

Materials and Methods

Reagents obtained from commercial suppliers were used as received. Tris((3,5-dimethyl-4-methoxypyridyl)-2-methyl)amine (R₃TPA) deuterated at the benzylic positions was prepared as previously described.¹³ All manipulations were performed in air using standard laboratory techniques. Solvents were used as received from commercial suppliers without further purification.

General Physical Methods

NMR spectra were recorded at 500 MHz using Varian Mercury spectrometers; chemical shifts for ¹H and ¹³C spectra were referenced to residual solvent peaks. ¹H NMR spectral data of paramagnetic compounds were obtained by widening the sweep window (+100 to

–30 ppm) and collecting for longer acquisition times (~1024 scans). IR spectra were recorded on a ThermoNicolet Avatar 360 spectrophotometer with the OMNIC software. Absorption spectra were recorded on a Cary 50 spectrophotometer using 6Q Spectrosil quartz cuvettes (Starna) with 1 cm path lengths. For low temperature UV-vis measurements, a custom-made quartz cuvette (path length = 1.74 cm) containing a jacketed dewar was employed. An acetonitrile/dry ice bath maintained the samples at –30 °C. Alternatively, absorption spectra and kinetic time traces at –40 °C were recorded on a Hewlett-Packard 8453A diode array spectrometer equipped with a cryostat from Unisoku Scientific Instruments, Osaka, Japan. Mössbauer spectra were recorded on an MSI spectrometer (WEB Research Company) with a ⁵⁷Co source in a Rh matrix at ambient temperature. Solid samples were prepared by suspension of the complex (~40 mg) in Apiezon M grease and placed in a nylon sample holder. Samples were measured over the course of ~5 d at 80 K. Isomer shift (δ) values are reported with respect to metallic iron used for velocity calibration at room temperature. Spectra were fit to Lorentzian lines using the WMOSS plot and fit program. Resonance Raman spectra were recorded on an Acton AM-506 spectrophotometer, using a Kaiser Optical holographic supernotch filter with a Princeton Instruments LN/CCD-1100-PB/UVAR detector cooled with liquid nitrogen. Laser excitation was provided by a Spectra Physics BeamLok 2060-RM argon ion laser. The spectra were obtained at 77 K by using a 135°-backscattering geometry, and the Raman frequencies were referenced to indene.

X-ray Data Collection and Refinement

Single crystals were mounted in Paratone oil using 30 μ m aperture MiTeGen MicroMounts (Ithaca, NY) and frozen under a 100 K KRYO-FLEX nitrogen cold stream. Data were collected on a Bruker SMART APEX CCD X-ray diffractometer with Mo K α radiation (λ = 0.71073 Å) controlled by the APEX 2 (v. 2010.1-2) software package. Data reduction was performed using SAINT and empirical absorption corrections were applied with SADABS.¹⁷ The structures were solved by direct methods with refinement by full-matrix least squares based on F² using the SHELXTL-97 software package¹⁸ and checked for higher symmetry by the PLATON software.¹⁹ All non-hydrogen atoms were located and refined anisotropically. Hydrogen atoms were fixed to idealized positions unless otherwise noted and given thermal parameters equal either to 1.5 (methyl hydrogen atoms) or 1.2 (non-methyl hydrogen atoms) times the thermal parameters of the atoms to which they are attached.

Complex **2** sits on an inversion center; thus, only half of the molecule is present in the asymmetric unit, along with 1.5 perchlorate anions and two acetonitrile molecules. Both perchlorate groups exhibit positional disorder and were modeled accordingly. One of the ClO₄[–] anions located on a special position was refined with 50% occupancy by suppressing generation of special position constraints. Due to charge considerations, the {Fe₂(μ -O)₂} core of **2** is best described as a (μ -oxo)(μ -hydroxo)diiron(III) unit, the overall complex having the empirical formula [Fe₂(μ -O)(μ -OH)(R₃TPA)₂](ClO₄)₃. Thus, the observed Fe–O distances must result from disorder imposed by the symmetry of the unit cell averaged over Fe–O(oxo) and Fe–O(hydroxo) bond lengths. Although the core structures of **10a** and **10b** are identical, both containing the [Fe₂(μ -O)(μ -CH₃CO₂)(R₃TPA)₂]³⁺ cation, they differ in the number of solvent molecules in their crystal lattices as well as their unit cell dimensions. The asymmetric unit of **10a** contains a single [Fe₂(μ -O)(μ -CH₃CO₂)(R₃TPA)₂]³⁺ cation, together with three perchlorate anions and three acetonitrile moieties. Two of the ClO₄[–] groups were modeled with positional disorder using appropriate similarity restraints and equal anisotropic displacement parameters. In contrast to that in **10a**, the asymmetric unit of **10b** has two independent molecules of [Fe₂(μ -O)(μ -CH₃CO₂)(R₃TPA)₂](ClO₄)₃, one diethyl ether and five acetonitrile molecules. The diethyl ether unit is severely disordered, as

evident by the large anisotropic displacement parameters of its component atoms. Attempts to model this disorder did not give a stable refinement; thus, no attempt was made to do so in the final structure.

Kinetic Measurements

The rate of hydrolysis of acetonitrile by **2** was determined by UV-vis spectroscopic measurements. The data were recorded by scanning at 5 min intervals for 900 min. The absorption changes at 550 nm were fit to an A→B→C reaction sequence (eq. 1), with rate constants k_1 and k_2 , respectively. A simpler A→B kinetic model did not provide a satisfactory fit. The molar absorptivities ϵ_A , ϵ_B , and ϵ_C refer to species A, B, and C, and $[A]_0$ is the initial concentration of A.

$$\text{Abs}_{\lambda}(t)=[A]_0e^{-k_1t}(\epsilon_A - \epsilon_C)+\frac{k_1}{k_2 - k_1}[A]_0(e^{-k_1t} - e^{-k_2t})(\epsilon_B - \epsilon_C)+[A]_0\epsilon_C \quad (1)$$

Synthesis

[Fe₂(μ-O)(μ-OH)(R₃TPA)₂](ClO₄)₃ (**2**)

Two methods, 1 and 2, give analytically pure **2**. *METHOD 1*: The published procedure for [Fe₂(μ-O)(OH)(H₂O)(R₃TPA)₂](ClO₄)₃ (**1**),¹³ which was mischaracterized in the original report, yields a crude solid that was extracted into dichloromethane and filtered to remove an insoluble impurity. The organic filtrate was evaporated to dryness to afford **2** as a red powder (114 mg, 42%). *Note: The aquated derivative of **2**, compound **1**, has not been isolated in the solid state but can be generated by treatment of **2** with excess water at low temperature.

METHOD 2: R₃TPA (150 mg, 0.319 mmol) and Fe(ClO₄)₃·7.5H₂O (159 mg, 0.319 mmol; the number of water molecules was calculated based on the Fe content stated on the Aldrich Certification of Analysis) were dissolved in 3 mL of MeOH. The resulting red solution was stirred at room temperature for 2 h. A 0.96 mL solution of a 500 mM NaOH stock solution in MeOH was added via a syringe pump over the course of 1 h. The solution was further stirred for 24 h, resulting in the precipitation of a red solid. About 3 mL of water was added in a dropwise manner and the mixture was stirred for another 24 h. The pH of the solution was measured by a pH meter equipped with a glass electrode, giving a reading of ~5.5. The product was collected by filtration and washed with a 1:1 mixture of MeOH/H₂O. Yield: (231 mg, 75%). Red crystals suitable for X-ray crystallographic analysis were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of the compound. Crystals obtained from dichloromethane/diethyl ether were smaller than those grown from acetonitrile/diethyl ether. Note that hydrolysis of coordinated acetonitrile can occur to give [Fe₂(μ-O)(μ-CH₃CO₂)(R₃TPA)₂](ClO₄)₃; however, crystals of the acetate-bound diiron complex are yellow rather than red. Calcd for [Fe₂(μ-O)(μ-OH)(R₃TPA)₂](ClO₄)₃·4H₂O (C₅₄H₈₁N₈Cl₃Fe₂O₂₄): C, 44.91; H, 5.65; N, 7.76. Found: C, 45.24; H, 5.39; N, 7.85. ¹H NMR (CD₂Cl₂, 500 MHz): δ 4.70, 4.00, 3.89, 3.60, 3.42, 2.79, 2.24, 1.63 ppm. UV-vis (CH₂Cl₂): λ_{max} = 370, 550 nm. FT-IR (KBr): ν = 2950, 2863, 1599, 1575, 1478, 1456, 1402, 1385, 1292, 1267, 1095, 1080, 997, 875, 800, 623 cm⁻¹. ⁵⁷Fe Mössbauer (80 K, apiezon grease): δ = 0.44(2) mm/s; ΔE_Q = 1.46(2) mm/s; Γ_{L/R} = 0.47(2) mm/s. M.p. (decomp) = 190 °C.

[Fe₂(μ-O)(μ-CH₃CO₂)(R₃TPA)₂](ClO₄)₃ (**10b**)

Solid R₃TPA (200 mg, 426 μmol), Fe(ClO₄)₃·10H₂O (230 mg, 426 μmol), sodium acetate (17 mg, 213 μmol), and triethylamine (59 μL, 426 μmol) were dissolved in 2.0 mL of

CH₃OH and stirred at RT for 3 h. A solid precipitate was isolated by filtration and washed with MeOH to afford a pale yellow material (198 mg, 66%). Single crystals suitable for X-ray diffraction analysis were obtained from slow diffusion of diethyl ether into a solution of the compound in either acetonitrile or dichloromethane. ¹H NMR (CD₂Cl₂, 500 MHz): δ 3.91, 3.77, 3.67, 3.28, 2.92, 2.71, 2.44 ppm. UV-vis (CH₂Cl₂): λ_{max} = 332 (14,500 M⁻¹cm⁻¹), 374 (9,850 M⁻¹cm⁻¹), 454 (1,460 M⁻¹cm⁻¹), 504 (1,390 M⁻¹cm⁻¹), 700 (294 M⁻¹cm⁻¹) nm. FT-IR (KBr): ν = 2960, 1599, 1532, 1478, 1402, 1264, 1092, 994, 875, 801, 764, 623 cm⁻¹. ⁵⁷Fe Mössbauer (80 K, apiezon grease): δ = 0.44(2) mm/s; ΔE_Q = 1.49(2) mm/s; Γ_{L/R} = 0.38(2) mm/s. Anal. Calcd. for Fe₂C₅₆H₇₅N₈O₂₁Cl₃·(CH₃OH): C, 47.33; H, 5.51; N, 7.75; Found: C, 47.06; H, 5.32; N, 7.78. Mp (decomp) = 195 °C.

RESULTS AND DISCUSSION

Characterization of Diiron(III) Complexes of R₃TPA

Preparation of [Fe₂(μ-O)(OH)(H₂O)(R₃TPA)₂](ClO₄)₃ (**1**) was attempted according to the published procedure.¹³ Reaction of iron(III) perchlorate decahydrate, R₃TPA, and sodium hydroxide in methanol and water afforded a red powder as described. However, it was discovered that this bulk material can be a heterogeneous mixture. Initially, this conclusion was derived from simple solubility tests, in which only some of the red solid could be extracted into common organic solvents, such as dichloromethane or acetonitrile. The fact that this crude compound was red, rather than green like other [Fe₂(μ-O)(OH)(H₂O)(L)₂]³⁺ compounds, where L is a poly(*N*-donor) ligand, reported in the literature,^{7,20,21} was also unexpected.

The zero-field ⁵⁷Fe Mössbauer spectrum of the crude red powder was best fit to three quadrupole doublets (Figure 1A), giving parameters δ₁ = 0.44 mm/s, ΔE_{Q1} = 1.16 mm/s, Area 1 = 36%; δ₂ = 0.44 mm/s, ΔE_{Q2} = 1.66 mm/s, Area 2 = 28%; and δ₃ = 0.44 mm/s, ΔE_{Q3} = 0.71 mm/s, Area 3 = 36% (Table 1). If the material contained pure **1**, two quadrupole doublets would be expected because each of the two iron atoms has a distinct coordination environment. This was indeed the case for [Fe₂(μ-O)(OH)(H₂O)(5-Me₃-TPA)₂]³⁺, which exhibited two quadrupole doublets of equal area.⁹ The Mössbauer data for the crude red powder could then be interpreted as arising from at least two different complexes, accounting for the organic-soluble and -insoluble fractions. When the crude powder was extracted into dichloromethane, filtered, and evaporated to dryness, a slightly lighter red solid was obtained, hereafter referred to as compound **2**. As shown in Figure 1B, **2** exhibits a single quadrupole doublet having values of δ = 0.44 mm/s and ΔE_Q = 1.46 mm/s (Table 1). The Mössbauer parameters of **2** are most similar to those of site 2 in the crude material (Method 1 in the Experimental Section), suggesting that the dichloromethane extraction and filtration steps facilitated purification of the product.

For further comparison of the properties of the unpurified material to those of compound **2**, IR spectroscopy was employed. The IR spectra of the crude solid and **2** are shown in Figure 2A (black and red traces, respectively). As expected, both solids display intense bands at ~1100 cm⁻¹, characteristic of the perchlorate anion. The spectral envelope ranging from 500 to 1700 cm⁻¹ is essentially identical for the two samples (Table 1), with some slight variations in weak baseline features. These data suggest that the insoluble fraction either has few IR active features or has a composition similar to that of **2**.

In the course of our studies, we observed that the amount of insoluble material varied from batch to batch. We speculated that the amount of Fe(ClO₄)₃ in the reaction mixture and the addition rate of NaOH solution might play important roles in determining the quality of complex **2** that was obtained. In particular, the amount of water in the hygroscopic Fe(ClO₄)₃ salt depended on storage time and conditions and would therefore affect the

actual amount of iron added to the reaction mixture. By using a $\text{Fe}(\text{ClO}_4)_3$ salt with a known amount of water and adding the NaOH solution slowly via a syringe pump (Method 2 in the Experimental Section), we were able to reproducibly obtain samples of **2** containing a minimal amount of insoluble material.

Crystallization of **2** was attempted by slow diffusion of diethyl ether into a solution of the complex in acetonitrile. After several days, two different types of crystals were obtained, some red and others yellow. X-ray diffraction analysis of the red crystals revealed a diiron structure with an $\{\text{Fe}_2(\mu\text{-O})_2\}$ core (Figure 3, Table S1). The iron atoms are separated by 2.79 Å and have pseudo-octahedral coordination environments (Table 2). Each metal center is bound by a tetradentate R_3TPA ligand, with $\text{Fe-N}(\text{amine})$ and $\text{Fe-N}(\text{pyridyl})_{\text{ave}}$ distances of 2.18 and 2.14 Å, respectively. Two oxygen atoms bridge the iron centers, with Fe-O bond lengths of 1.88 and 1.93 Å. Because each diiron unit is associated with three perchlorate anions, charge balance considerations indicate that the oxygen atom bridges are best described as oxo and hydroxo ligands, giving the molecular formula $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$. Because the molecule is located on an inversion center, the Fe-O bond types are disordered, with distances that are an average of iron-oxo and iron-hydroxo bond lengths. The structural parameters of $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$ fall within the ranges exhibited by two isostructural diiron TPA complexes that differ only in their bridging oxygen atom protonation states, $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(6\text{-Me}_3\text{TPA})_2](\text{ClO}_4)_3$ ²² and $[\text{Fe}_2(\mu\text{-O})_2(6\text{-Me}_3\text{TPA})_2](\text{ClO}_4)_2$ ²³ (where 6-Me₃TPA = tris((6-methylpyridyl)-2-methyl)amine) (Table 2). Based on the similar spectroscopic properties of the red crystals compared to those of the red powder before crystallization, **2** is assigned as a $(\mu\text{-oxo})(\mu\text{-hydroxo})$ diiron(III) complex, $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$. Related (oxo)diiron(III) complexes supported by TPA, 5-Me₃-TPA, and 5-Et₃-TPA ligands, previously synthesized using a procedure analogous to that of Method 1 (see Experimental section),⁹ are green in color, not red as observed for the R_3TPA complex. Because the visible bands of these complexes arise from transitions of the $(\mu\text{-oxo})$ diiron(III) core, the difference in color most likely indicates a core structure having a different Fe-O-Fe angle.^{6,8,9} Indeed, the X-ray crystal structure of a complex containing 5-Et₃-TPA has the $[\text{Fe}_2(\mu\text{-O})(\text{OH})(\text{H}_2\text{O})(\text{L})_2]^{3+}$ core with an Fe-O-Fe angle of 136°.⁹ This result led some of us to assume, incorrectly, that the same core structure would be obtained in the case of R_3TPA .¹³ The R_3TPA ligand has one methoxy and two methyl substituents on each pyridine donor, compared to TPA, 5-Me₃-TPA, and 5-Et₃-TPA, which have at most one electron donating substituent on each pyridine ring. We conjecture that the more electron donating nature of R_3TPA stabilizes the $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})]$ core of **2**, allowing it to be crystallized.

The yellow crystals, which were obtained unexpectedly from crystallization of **2** in acetonitrile/diethyl ether, were also evaluated by X-ray crystallography (Figure 4, Table S1). The compound has a dinuclear structure with an Fe-Fe distance of 3.25 Å (Table S2). Each pseudo-octahedral iron atom is capped by a R_3TPA group, with $\text{Fe-N}(\text{amine})_{\text{ave}} = 2.20$ Å and $\text{Fe-N}(\text{pyridyl})_{\text{ave}} = 2.15$ Å, and is linked by two bridging ligands. One of the bridges is an oxo anion, as indicated by short Fe-O bond lengths of ~1.80 Å. A difference electron density map revealed that the second bridging ligand contains four non-hydrogen atoms arranged in a trigonal planar geometry. Assigning this group to an acetate moiety allowed the structure to refine to convergence, with Fe-O distances of 2.04 and 1.96 Å. The presence of an acetate moiety in this structure is surprising because no such anion was present during the preparation or crystallization of **2**. Because there are three perchlorate anions for each diiron unit, we assign the molecular formula as $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$ (**10a**). These results indicate that, although compound **2** is readily prepared in pure form, when dissolved in acetonitrile, **10** can form.

As expected, compounds **2** and **10a** display distinctive optical spectra (Figure S1). The absorption spectrum of **2** has λ_{max} values at 370 and 550 nm, which are characteristic of $(\mu\text{-oxo})(\mu\text{-hydroxo})\text{diiron(III)}$ rather than $\text{di}(\mu\text{-oxo})\text{diiron(III)}$ species.⁸ The visible band at 550 nm has been attributed to an oxo-to-iron(III) charge transfer. In contrast, **10a** exhibits optical bands at 332, 454, 492, and 700 nm. These features are identical to those reported for other $(\mu\text{-oxo})(\mu\text{-carboxylato})\text{diiron(III)}$ TPA species.⁶

The IR spectra of the red and yellow crystals of **2** and **10a**, respectively, were recorded (Figure 2A). Because of similarities in their molecular composition, **2** and **10a** share several prominent features in the spectral range between 500–1700 cm^{-1} . In addition to the vibrational modes present in the spectrum of **2**, however, **10a** displays peaks at 763 and 1540 cm^{-1} (Figure 2B). The former is ascribed to an asymmetric Fe–O–Fe stretching mode and the latter to an asymmetric C–O–O[−] vibration of the bridging acetate. From several comprehensive studies of synthetic oxo-bridged diiron(III) compounds^{20,8,24,25} it has been established that the Fe–O stretching frequency of an $\{\text{Fe}_2(\mu\text{-O})\}^{4+}$ unit is strongly correlated with its Fe–O–Fe angle. Because the Fe–O–Fe angle in **2** (94°) is significantly smaller than that of **10a** (130°), the $\nu_{\text{Fe-O}}$ stretching frequencies of **2** are expected to occur at higher energies than those in **10a**. Without further 18-O isotopic labeling studies, however, the Fe–O mode of **2** cannot be definitively assigned. Nevertheless, the IR data clearly show that **10a** contains a carboxylate group whereas **2** does not. These results are consistent with the formulation of **2** as $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$ and **10a** as $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$.

The ¹H NMR spectra of **2** and **10a** are indicative of paramagnetic species at room temperature. The spectrum of **2** shows several significantly broadened peaks at 4.70, 4.00, 3.89, 3.60, 3.42, 2.79, 2.24, and 1.63 ppm (Figure 5A), whereas those for **10a** appear at 3.92, 3.68, 3.28, 2.94, and 2.45 ppm (Figure 5B). Previous studies of iron TPA complexes have indicated that the β protons of its pyridine rings are highly sensitive to the electronic properties of the iron centers; no attempt was made to examine this property in the present work.⁸

To further confirm the identity of complex **10a**, particularly the assignment of acetate as its bridging ligand, efforts were made to prepare $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$ independently. Reaction of solid R₃TPA, iron(III) perchlorate decahydrate, sodium acetate, and triethylamine in a 2:2:1:2 ratio in a methanol solution afforded a yellow precipitate that was readily isolated by filtration. Single crystals of the compound were obtained by slow diffusion of diethyl ether into an acetonitrile solution. X-ray diffraction analysis of these yellow blocks showed two molecules of $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)(\text{R}_3\text{TPA})_2]^{3+}$ in the asymmetric unit (Figure S2), along with six perchlorate anions, five acetonitrile molecules, and one diethyl ether. The $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$ compound obtained from this preparation will hereafter be referred to as **10b**. Table S2 lists the metrical parameters of the structures of **10a** and **10b**. The two structures have essentially identical bond distances and angles, with deviations that are no greater than ~0.01 Å or ~1 deg., respectively. The small structural differences between **10a** and **10b** can be accounted for by crystal packing, for the two unit cells have different dimensions as a result of different numbers of solvent molecules in their lattices (Table S1). For discussion purposes, if the origin of the $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$ complex is unimportant, we hereafter refer to the compound as **10**, without an “a” or “b” annotation.

To obtain further evidence that **10a** and **10b** are indeed the same compound, ⁵⁷Fe Mössbauer spectra were recorded. Both display a single quadrupole doublet. The data for **10a** were fit with $\delta = 0.44$ mm/s and $\Delta E_{\text{Q}} = 1.47$ mm/s, whereas those for **10b** were fit with $\delta = 0.44$ mm/s and $\Delta E_{\text{Q}} = 1.49$ mm/s (Table 1). Although the two iron atoms in $[\text{Fe}_2(\mu\text{-O})$

$(\mu\text{-CH}_3\text{CO}_2)(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$ are not related by molecular symmetry, the similarity in their coordination environments make them indistinguishable by zero-field Mössbauer spectroscopy. These Mössbauer parameters are typical for iron in the +3 oxidation state and compare favorably with those of other $(\mu\text{-oxo})(\mu\text{-carboxylato})\text{diiron(III)}$ TPA compounds.⁶

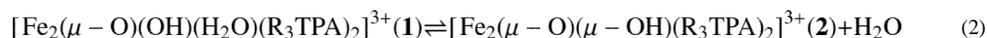
Finally, the UV-vis (Figure S1, blue) and ^1H NMR spectra of **10b** (Figure 5C) are identical to those of **10a** (Figure S1, yellow and Figure 5B, respectively). In sum, the evidence is unequivocal that the four-atom bridging ligand in **10a** is acetate.

Effect of Solvent, Temperature, and Water on the Stability of **2**

To examine the stability of the $(\mu\text{-oxo})(\mu\text{-hydroxo})\text{diiron(III)}$ core of **2** in solution, its absorption spectrum was recorded in different solvents at room temperature (Figure S3). The oxo-to-iron(III) charge transfer band at 550 nm is present when **2** is dissolved in either neat dichloromethane or acetonitrile. Dissolution of **2** in an equal mixture of dichloromethane and methanol, however, led to complete loss of this optical feature. The disappearance of the 550 nm band indicates that there is a change in the diiron core, perhaps resulting from a loss of one of the bridging ligands, conversion of the hydroxide to a methoxide bridge, or dissociation into mononuclear iron species. Although this behavior was observed only when methanol was introduced into dichloromethane, other protic solvents may have similar effects on **2**.

It has been documented that the $(\mu\text{-oxo})(\mu\text{-hydroxo})\text{diiron(III)}$ core can convert to a $(\mu\text{-oxo})(\text{hydroxo})(\text{aqua})\text{diiron(III)}$ unit through a temperature-dependent aquation reaction.^{8,21} When a solution of **2** in acetonitrile was cooled to $-30\text{ }^\circ\text{C}$ under ambient conditions, the prominent band at 550 nm decreased in intensity (Figure S4, red trace) and disappeared completely upon treatment with $\sim 8,000$ equiv of H_2O (green trace). When the solution was warmed to room temperature, the 550 nm band of **2** was partially restored (blue trace). It is likely that, upon cooling of **2** in solution, partial aquation from trace water in the solvent occurs to afford $[\text{Fe}_2(\mu\text{-O})(\text{OH})(\text{H}_2\text{O})(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$ (**1**). When H_2O was deliberately added to the solution at $-30\text{ }^\circ\text{C}$, **2** was completely converted to **1**. This equilibrium shifted back predominantly toward **2** when the solution was warmed to room temperature.

To obtain a quantitative measure of the affinity of **2** for H_2O at low temperature, the equilibrium constant for conversion between **1** and **2** was determined. As shown in Figure 6, titration of water to a solution of **2** resulted in disappearance of the 550 nm absorbance, indicating formation of **1**. From these data, a dissociation constant (K_d) of 0.0022(1) M was determined for the reaction shown in eq. 2.



This K_d value indicates that, for a 0.5 mM solution of **2**, having a water concentration of 50 mM would convert **2** to greater than 95% of the hydrated complex **1** at $-40\text{ }^\circ\text{C}$.

We also carried out resonance Raman experiments in an attempt to find support for the conclusion from UV-vis spectroscopy that **2** converts to **1** in acetonitrile solution. Unfortunately, we were unsuccessful in obtaining a Raman spectrum of **2** in the solid state or in frozen dichloromethane solution, conditions under which the characteristic red color of the $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})]$ core is retained. On the other hand, a Raman spectrum could be observed in a frozen acetonitrile solution. Upon freezing, however, the color of the solution turned from red to green, suggesting conversion of **2** to **1**. The coordinated water molecule in **1** formed in such a manner would have to derive from water trapped in the solid state lattice of **2**, which was precipitated from $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ during its preparation. Upon 457.9 nm excitation, two prominent resonance enhanced peaks appeared at 457 and 770 cm^{-1}

(Figure 7). These features are assigned, respectively, to the symmetric and asymmetric vibrational modes of the Fe–O–Fe moiety and exhibit the expected isotopic shifts upon ^{18}O labeling. Based on extensive studies of similar oxo-bridged diiron units,⁸ these $\nu_{\text{Fe–O–Fe}}$ values correspond to an Fe–O–Fe angle within the range of 130–143°, consistent with the Fe–O–Fe angle of 136° found in the X-ray structure of the (μ -oxo)(hydroxo)(aqua)diiron(III) complex supported by the 5-Et₃-TPA ligand.⁹ On the other hand, the (μ -oxo)(μ -hydroxo)diiron(III) core of **2** with an Fe–O–Fe angle of 94° (Table 2) would have been predicted to exhibit Raman bands at ca. 600 and 670 cm⁻¹, by analogy to the bands observed for [Fe^{III}₂(μ -O)(μ -OH)(6-Me₃TPA)₂]³⁺ and [Fe^{III}₂(μ -O)₂(6-Me₃TPA)₂]²⁺, which have Fe–O–Fe angles of 98.7° and 92.5°, respectively.⁸

Hydrolysis of Acetonitrile to Acetate

The yellow crystals of **10a** isolated from crystallization of **2** in acetonitrile could result either from a contaminant or through a chemical process that converts **2** to **10** under the conditions employed. Because no sources of acetate were used during the preparation of **2** and the results were verified by multiple independent experiments, the latter is more likely. Dimetallic complexes are known to promote the hydrolysis of organonitriles.^{26–28} As depicted in Scheme 2, it is possible that even at room temperature trace amounts of water in the solvent react with **2** to give **1**. A CH₃CN molecule can then displace the coordinated water in **1** to give the acetonitrile adduct **8**. In the first irreversible step, the hydroxide ligand bound to the other iron atom in **1** attacks the electrophilic nitrile group, affording a (μ -oxo)(μ -acetamido)diiron(III) species **9**. For most nitrogen-rich diiron compounds, the hydrolysis of CH₃CN does not proceed beyond the carboxamide.^{7,20} Because **10**, rather than **9**, was isolated from the crystallization of **2**, hydrolysis of the acetamide in **9** must occur to afford the acetate.

To obtain evidence for the complete hydrolysis of CH₃CN, the absorption spectrum of **2** in acetonitrile was recorded over the course of ~900 min. The reaction was performed with wet solvent in air at RT to reproduce the conditions under which **10a** was crystallized. Although the reaction is slow, spectral changes were observed between 340–380 nm as well as at 550 nm (Figure S5A). The kinetic data at 553 nm were fit satisfactorily to a two consecutive unimolecular reaction model, yielding rate constants of $k_1 = 2.04 \pm 0.16 \times 10^{-2} \text{ min}^{-1}$ and $k_2 = 1.98 \pm 0.06 \times 10^{-3} \text{ min}^{-1}$ (Figure S5B). These processes are tentatively attributed to conversion of **2** to **9** and of **9** to **10** (Scheme 2). A (μ -oxo)(μ -acetamido)diiron(III) complex **9** has not been isolated from the reaction mixture, but is a logical precursor to **10**.

Reaction of **2** with Hydrogen Peroxide

Because the diiron(III) R₃TPA complex can exist in two forms in solution, either as a (μ -oxo)(μ -hydroxo)diiron(III) (**2**) or a (μ -oxo)(hydroxo)(aqua)diiron(III) (**1**) species, it was of interest to determine whether both units are capable of generating the same high-valent diiron intermediates. When **2** was treated with H₂O₂ in anhydrous acetonitrile at -40°C, its absorption spectrum displayed a broad feature centered at ~705 nm (Figure 8). As previously reported,¹⁴ this spectrum corresponds to the diiron(IV) complex, [Fe^{IV}₂(μ -O)(OH)(O)(R₃TPA)₂]³⁺ (**4**) (Scheme 1). When **2** was treated with H₂O₂ in the presence of 50 mM H₂O, which essentially converts **2** to **1**, significantly greater amounts of the [Fe^{III}Fe^{IV}(μ -O)₂(R₃TPA)₂]³⁺ (**7**, $\lambda_{\text{max}} = 620 \text{ nm}$) side product were observed (Figure S6). Addition of deuterated D₂O₂/D₂O instead of H₂O₂/H₂O, however, afforded a greater yield of **4** (Figure 8). Although both complexes **1** and **2** yield **4** upon exposure to hydrogen peroxide, they react at significantly different rates. As shown by the time trace in Figure 9, when **2** was treated with H₂O₂ in dry solvent at -40°C, the reaction was complete in less than 100 s. In contrast, when the reaction was performed in the presence of 50 mM water, it took approx. 600 s to obtain the maximum yield of **4**. This result strongly suggests that

hydrogen peroxide reacts directly with **2** but not **1** and that water inhibits the formation of **4** by driving the solution equilibrium toward **1** (Scheme 3).

To eliminate the possible reaction of **2** with acetonitrile to afford the (μ -oxo)(μ -acetato)diiron(III) complex **10** in the course of H_2O_2 activation, the reaction of **2** with hydrogen peroxide was examined in other solvents. As indicated by the lack of an absorption band at 550 nm when **2** was dissolved in commercial grade acetone (Figure S7, dotted line), the complex was fully transformed to **1**, presumably due to the high content of water in the solvent. Because H_2O competes with H_2O_2 for reaction with **2**, the solution was treated with two equiv of H_2O_2 , instead of one, to favor the formation of high-valent diiron species (Figure S7). After ~30 s, the absorption spectrum showed a feature at 705 nm, corresponding to **4**. After ~1000 s, a prominent band at 620 nm had fully developed, indicating that the mixed-valent diiron(III,IV) species **7** is the final product. When **2** was dissolved in a CH_2Cl_2/CH_3CN (3:1) mixture, the (μ -oxo)(μ -hydroxo)diiron(III) core of **2** remained intact (Figure S8). Upon treatment with one equiv of H_2O_2 , **2** had converted mostly to **4**, together with a small amount of **7**. Although formation of **4** from **2**/ H_2O_2 occurs most cleanly in anhydrous acetonitrile, the fact that it also forms in solvents other than CH_3CN demonstrates that acetonitrile hydrolysis is not involved in H_2O_2 activation by **2**.

CONCLUSION

Through a combination of spectroscopic and crystallographic investigations, the diiron(III) complex prepared from iron(III) perchlorate, sodium hydroxide, and tris((3,5-dimethyl-4-methoxy)pyridyl-2-methyl)amine (R_3TPA) was determined to have the composition $[Fe_2(\mu-O)(\mu-OH)(R_3TPA)_2](ClO_4)_3$ (**2**) rather than $[Fe_2(\mu-O)(OH)(H_2O)(R_3TPA)_2](ClO_4)_3$ (**1**). Conversion of **2** to **1** is favored in the presence of water and at low temperature in solution. To date, compound **1** has not been isolated in pure form in the solid state. Prolonged dissolution of **2** in wet acetonitrile at room temperature led to complete hydrolysis of the nitrile group of CH_3CN to CH_3COO^- . This transformation is unusual in that similar reactions mediated by iron(III) complexes do not typically proceed beyond the formation of acetamide.^{7,20} Further reactivity studies demonstrate that the (μ -oxo)(μ -hydroxo)diiron(III) core of **2** reacts readily with H_2O_2 , but that the (μ -oxo)(hydroxo)(aqua)diiron(III) core of **1** does not. In fact, the addition of water to **2** retards the formation rate of high-valent diiron intermediates, suggesting that **1** does not lie along the reaction pathway to the (μ -oxo)(hydroxo)(oxo)diiron(IV) complex (**4**). Activation of hydrogen peroxide by **2** also occurs in non-nitrile containing solvents, although the yield of **4** is much lower than when the reaction is performed in acetonitrile. This work has led to a better understanding of the nature of the diiron species supported by the electron-rich R_3TPA ligand and the requirements for generating high-valent diiron(IV) complexes of possible relevance to carboxylate-bridged diiron enzymes that activate dioxygen.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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REFERENCES

1. Feig AL, Lippard SJ. Chem. Rev. 1994; 94:759–805.
2. Wallar BJ, Lipscomb JD. Chem. Rev. 1996; 96:2625–2658. [PubMed: 11848839]

3. Du Bois J, Mizoguchi TJ, Lippard SJ. *Coord. Chem. Rev.* 2000; 200–202:443–485.
4. Que L Jr, Tolman WB. *Nature.* 2008; 455:333–340. [PubMed: 18800132]
5. Friedle S, Reisner E, Lippard SJ. *Chem. Soc. Rev.* 2010; 39:2768–2779. [PubMed: 20485834]
6. Norman RE, Yan S, Que L Jr, Backes G, Ling J, Sanders-Loehr J, Zhang JH, O'Connor CJ. *J. Am. Chem. Soc.* 1990; 112:1554–1562.
7. Hazell A, Jensen KB, McKenzie CJ, Toftlund H. *Inorg. Chem.* 1994; 33:3127–3134.
8. Zheng H, Zang Y, Dong Y, Young VG Jr, Que L Jr. *J. Am. Chem. Soc.* 1999; 121:2226–2235.
9. Dong Y, Fujii H, Hendrich MP, Leising RA, Pan G, Randall CR, Wilkinson EC, Zang Y, Que L Jr, Fox BG, Kauffmann K, Münck E. *J. Am. Chem. Soc.* 1995; 117:2778–2792.
10. Hsu H-F, Dong Y, Shu L, Young VG Jr, Que L Jr. *J. Am. Chem. Soc.* 1999; 121:5230–5237.
11. Shu L, Nesheim JC, Kauffmann K, Münck E, Lipscomb JD, Que L Jr. *Science.* 1997; 275:515–518. [PubMed: 8999792]
12. Tinberg CE, Lippard SJ. *Acc. Chem. Res.* 2011; 44:280–288. [PubMed: 21391602]
13. Xue G, Wang D, De Hont R, Fiedler AT, Shan X, Münck E, Que L Jr. *Proc. Natl. Acad. Sci. U.S.A.* 2007; 104:20713–20718. [PubMed: 18093922]
14. Xue G, Fiedler AT, Martinho M, Münck E, Que L Jr. *Proc. Natl. Acad. Sci. U.S.A.* 2008; 105:20615–20620.
15. Xue G, De Hont R, Münck E, Que L Jr. *Nat. Chem.* 2010; 2:400–405. [PubMed: 20414242]
16. Xue G, Pokutsa A, Que L Jr. *J. Am. Chem. Soc.* 2011; 133:16657–16667. [PubMed: 21899336]
17. Sheldrick, GM. SADABS: Area Detector Absorption Correction. Göttingen, Germany: University of Göttingen; 2001.
18. Sheldrick GM. *Acta Cryst., Sect. A.* 2008; A64:112–122. [PubMed: 18156677]
19. Spek, AL. PLATON, A Multipurpose Crystallographic Tool. Utrecht, The Netherlands: Utrecht University; 2000.
20. Wilkinson EC, Dong Y, Que L Jr. *J. Am. Chem. Soc.* 1994; 116:8394–8395.
21. Poussereau S, Blondin G, Cesario M, Guilhem J, Chottard G, Gonnet F, Girerd J-J. *Inorg. Chem.* 1998; 37:3127–3132.
22. Zang Y, Pan G, Que L Jr, Fox BG, Münck E. *J. Am. Chem. Soc.* 1994; 116:3653–3654.
23. Zang Y, Dong Y, Que L Jr, Kauffmann K, Münck E. *J. Am. Chem. Soc.* 1995; 117:1169–1170.
24. Sanders-Loehr J, Wheeler WD, Shiemke AK, Averill BA, Loehr TM. *J. Am. Chem. Soc.* 1989; 111:8084–8093.
25. Kurtz DM Jr. *Chem. Rev.* 1990; 90:585–606.
26. Curtis NJ, Hagen KS, Sargeson AM. *J. Chem. Soc., Chem. Commun.* 1984:1571–1573.
27. Kukushkin VY, Pombeiro AJL. *Chem. Rev.* 2002; 102:1771–1802. [PubMed: 11996549]
28. Borriello C, Centore R, Roviello G. *Inorg. Chem. Commun.* 2005; 8:755–758.
29. Praneeth VKK, Näther C, Peters G, Lehnert N. *Inorg. Chem.* 2006; 45:2795–2811. [PubMed: 16562937]

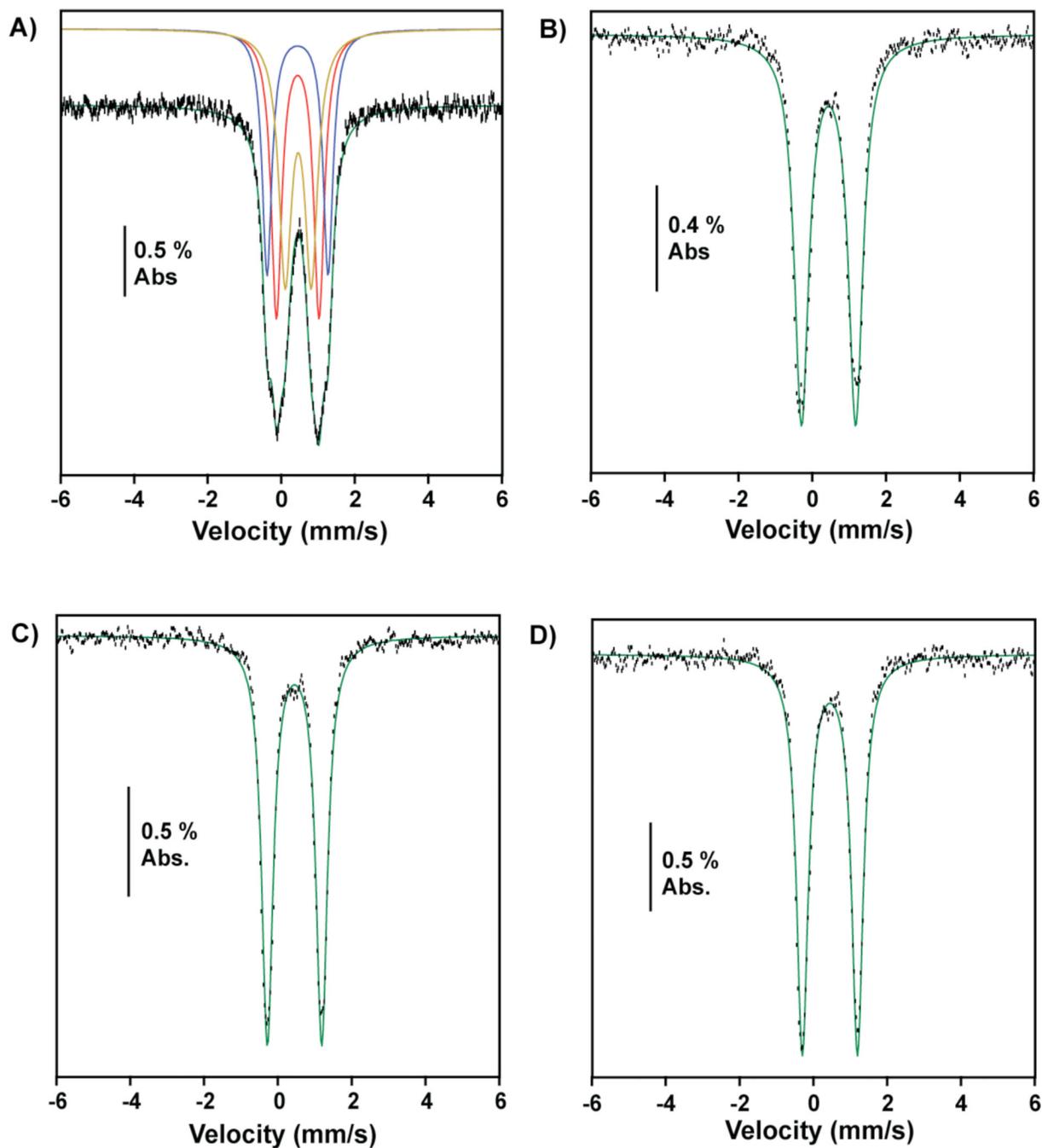


Figure 1. Zero-field Mössbauer spectra (80 K) of A) crude material isolated from reaction of iron(III) perchlorate, sodium hydroxide, and R₃TPA; B) compound **2**; C) compound **10a**; and D) compound **10b**. Spectrum A was best fit to three quadrupole doublets, whereas those of B, C, and D were adequately modeled with one-site fits. Raw data are in black, simulated fits are in green, and individual sites are in blue, yellow, and red.

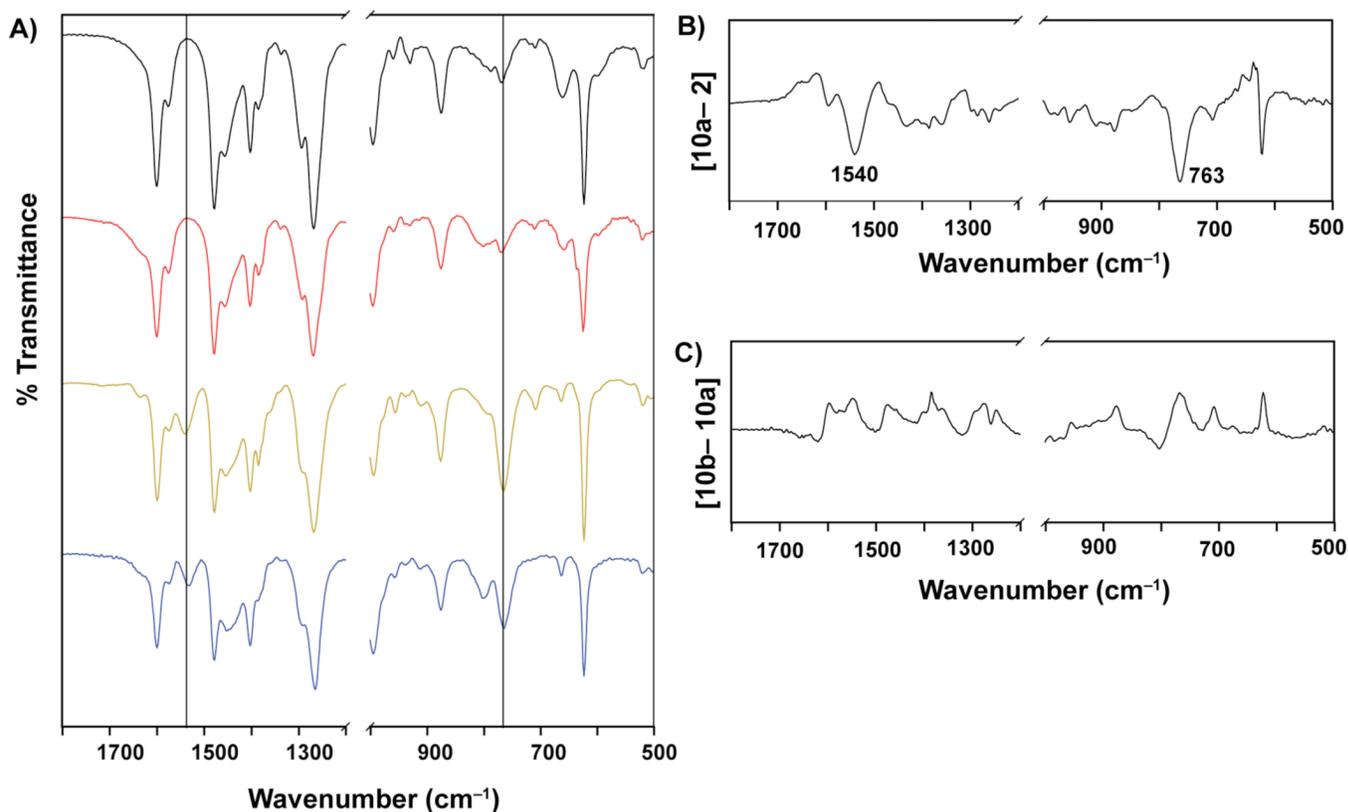


Figure 2. Stack plots of the FTIR spectra (KBr pellets) of the crude material from reaction of iron(III) perchlorate, sodium hydroxide, and R₃TPA (black line), compound **2** (red line), compound **10a** (yellow line), and compound **10b** (blue line) (panel A). The difference spectra of **2/10a** (panel B) and **10a/10b** (panel C) are shown. The spectrum of **10a**, compared to that of **2**, displays two new peaks at 763 and 1540 cm⁻¹. No significant differences were observed in the spectrum of **10a** compared to that of **10b**. The spectral region from 1000–1200 cm⁻¹ exhibits strong absorption from the perchlorate anion and has been omitted for clarity.

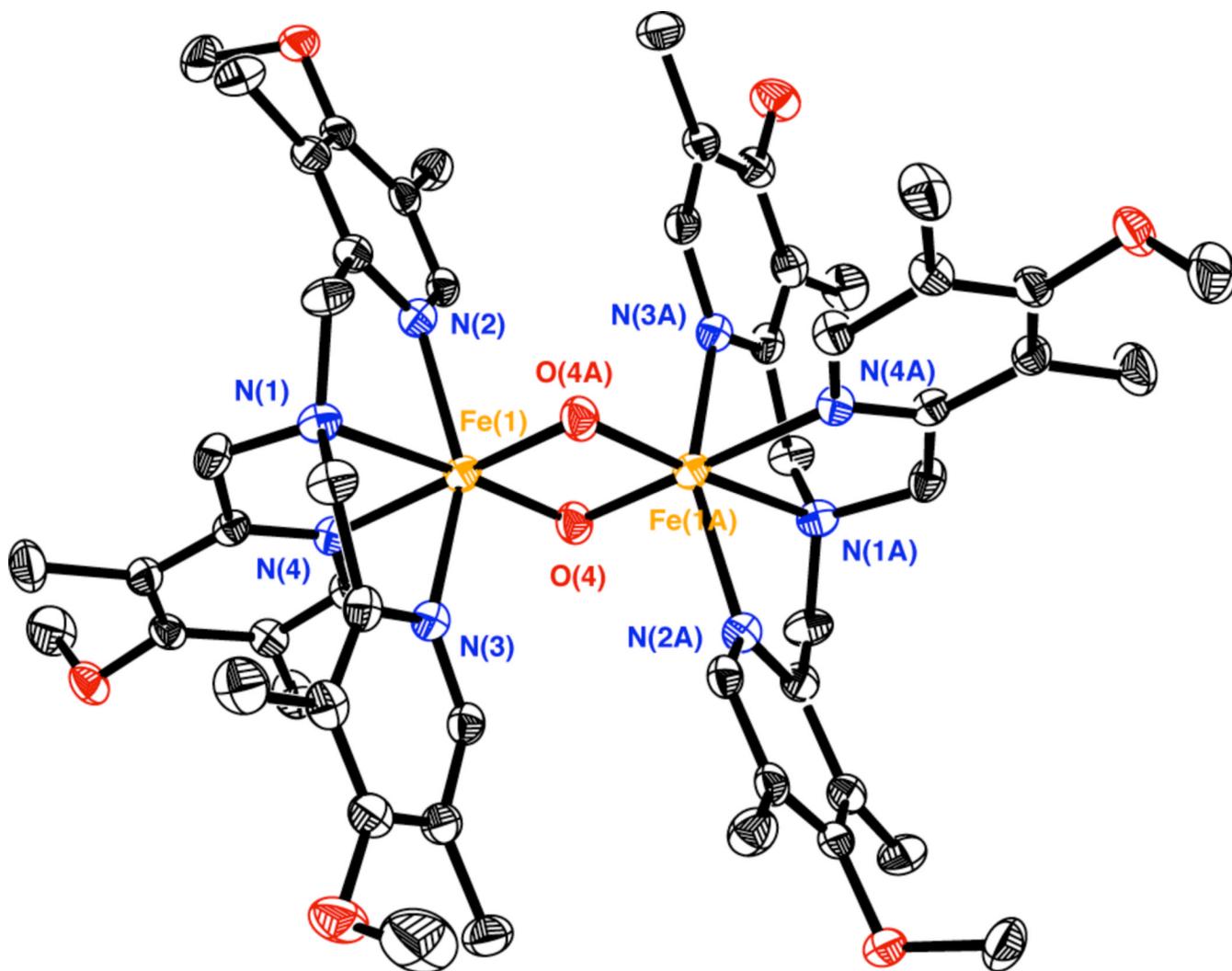


Figure 3.

A thermal ellipsoid (50%) diagram of the X-ray structure of $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3 \cdot (\text{CH}_3\text{CN})_4$ (**2**). Hydrogen atoms, solvent molecules, and perchlorate anions are omitted for clarity. Color scheme: iron, orange; oxygen, red; nitrogen, blue; carbon, black. See Table S1 and Table 2 for the data refinement and structural parameters of **2**, respectively.

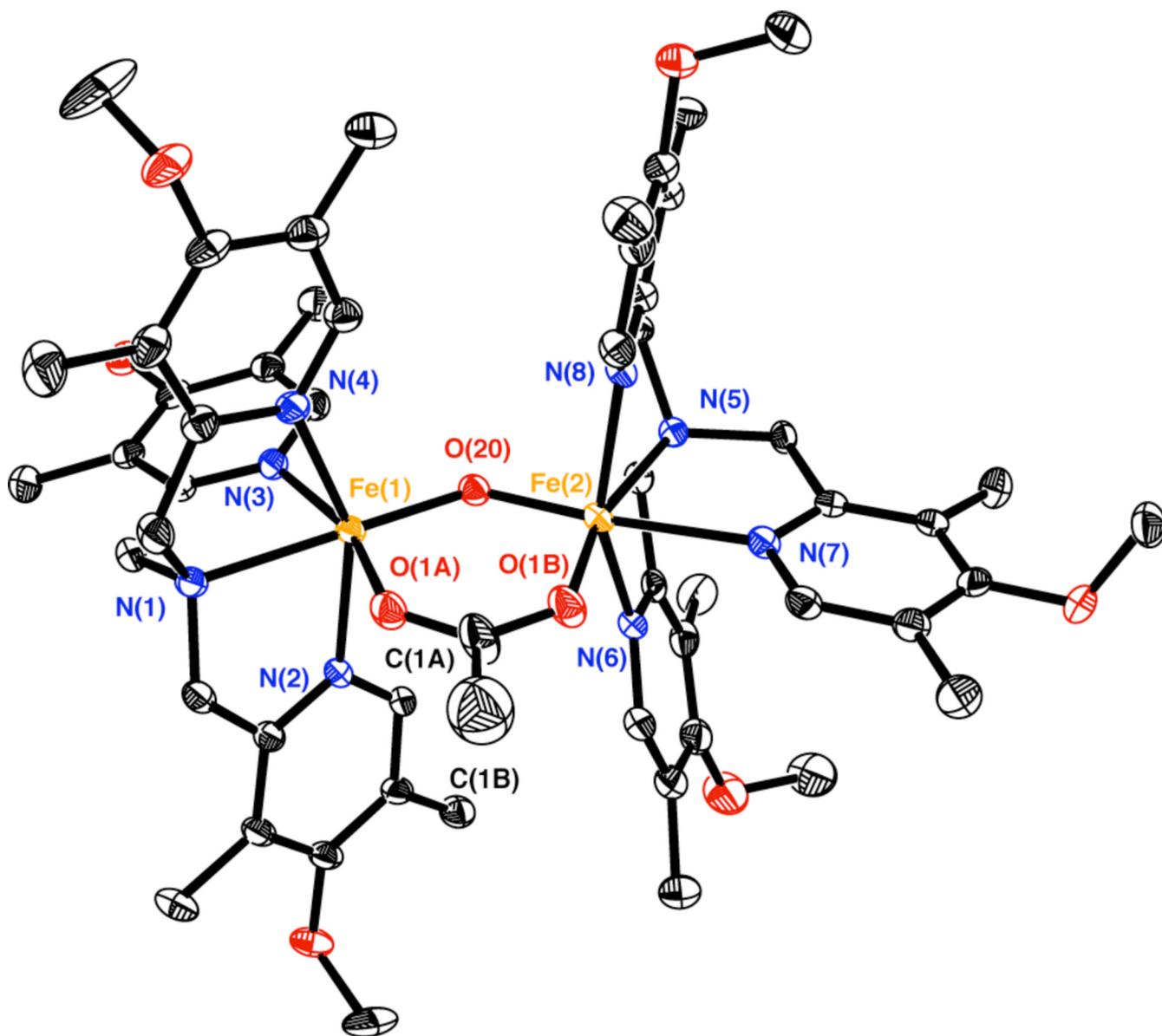


Figure 4. A thermal ellipsoid (50%) diagram of the X-ray structure of $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3 \cdot (\text{CH}_3\text{CN})_2$ (**10a**). Hydrogen atoms, solvent molecules, and perchlorate anions are omitted for clarity. Color scheme: iron, orange; oxygen, red; nitrogen, blue; carbon, black. See Table S1 and Table S2 for the data refinement and structural parameters of **10a**, respectively.

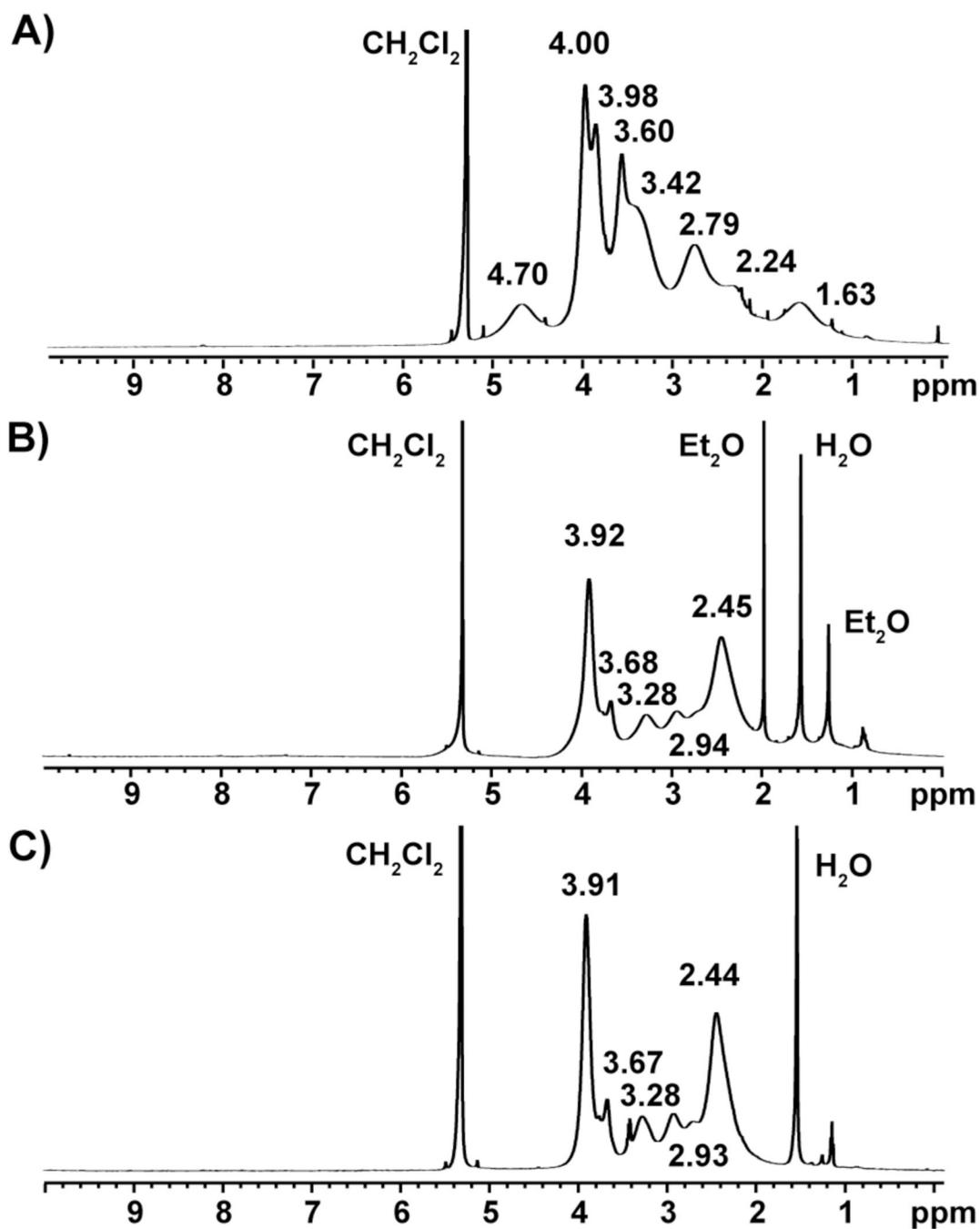


Figure 5. ^1H NMR spectra (CD_2Cl_2 , 500 MHz) of A) complex **2**, B) complex **10a**, and C) complex **10b** recorded at RT.

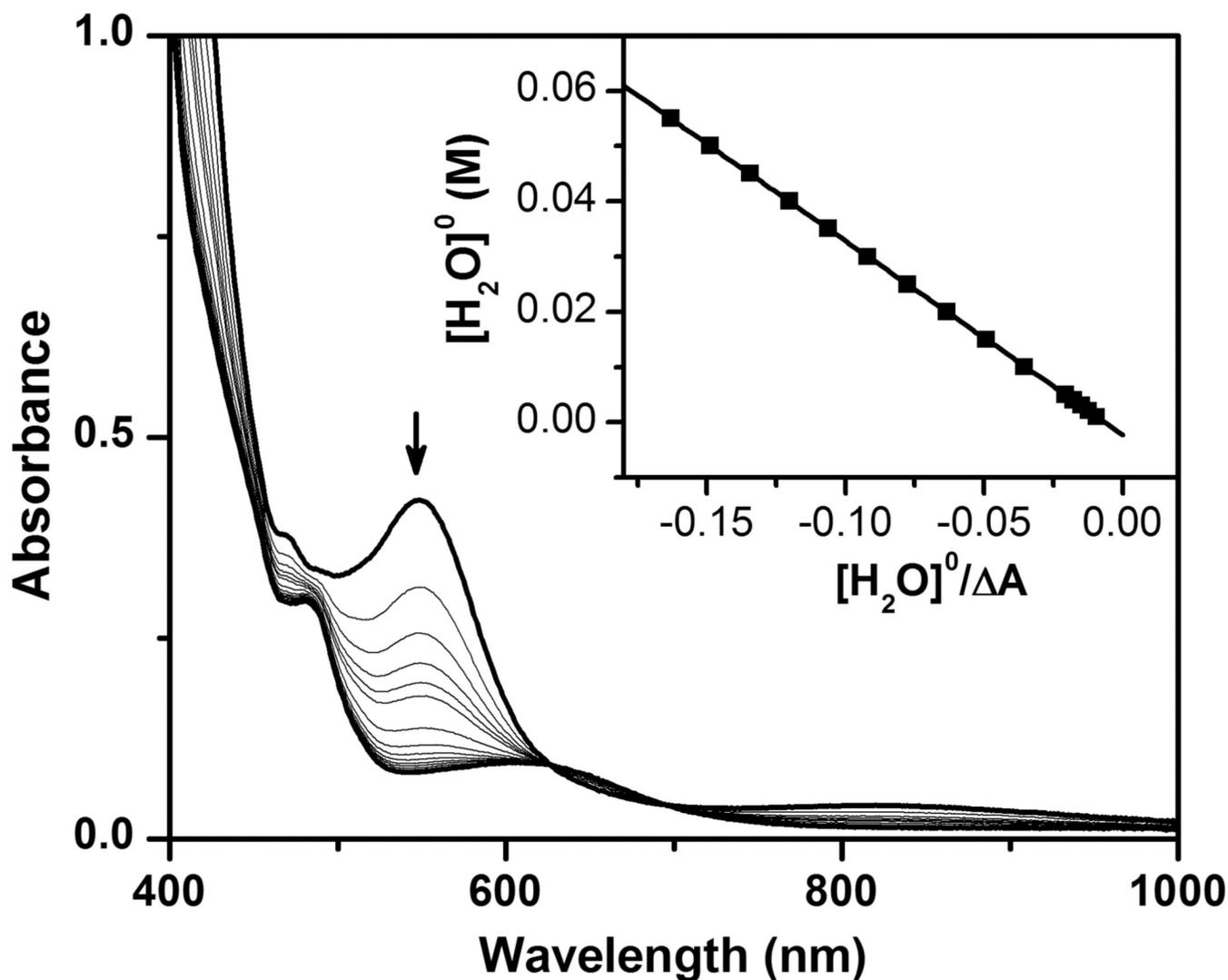


Figure 6.

UV-vis spectra of a 0.5-mM solution of complex **2** in CH₃CN at -40 °C upon titration with water. Inset: plot of the [H₂O]⁰ (total added water concentration) versus [H₂O]⁰/ΔA (absorbance change at 550 nm), from which a dissociation constant of water (K_d) in the hydrated form of **2** (complex **1**) is determined to be 0.0022(1) M. Upon addition of 50 mM H₂O, [1]/[2] = [H₂O]/ K_d = 22, meaning that over 95% of the iron complex is in the hydrated form. The K_d value was determined from these optical data using a model described previously.²⁹

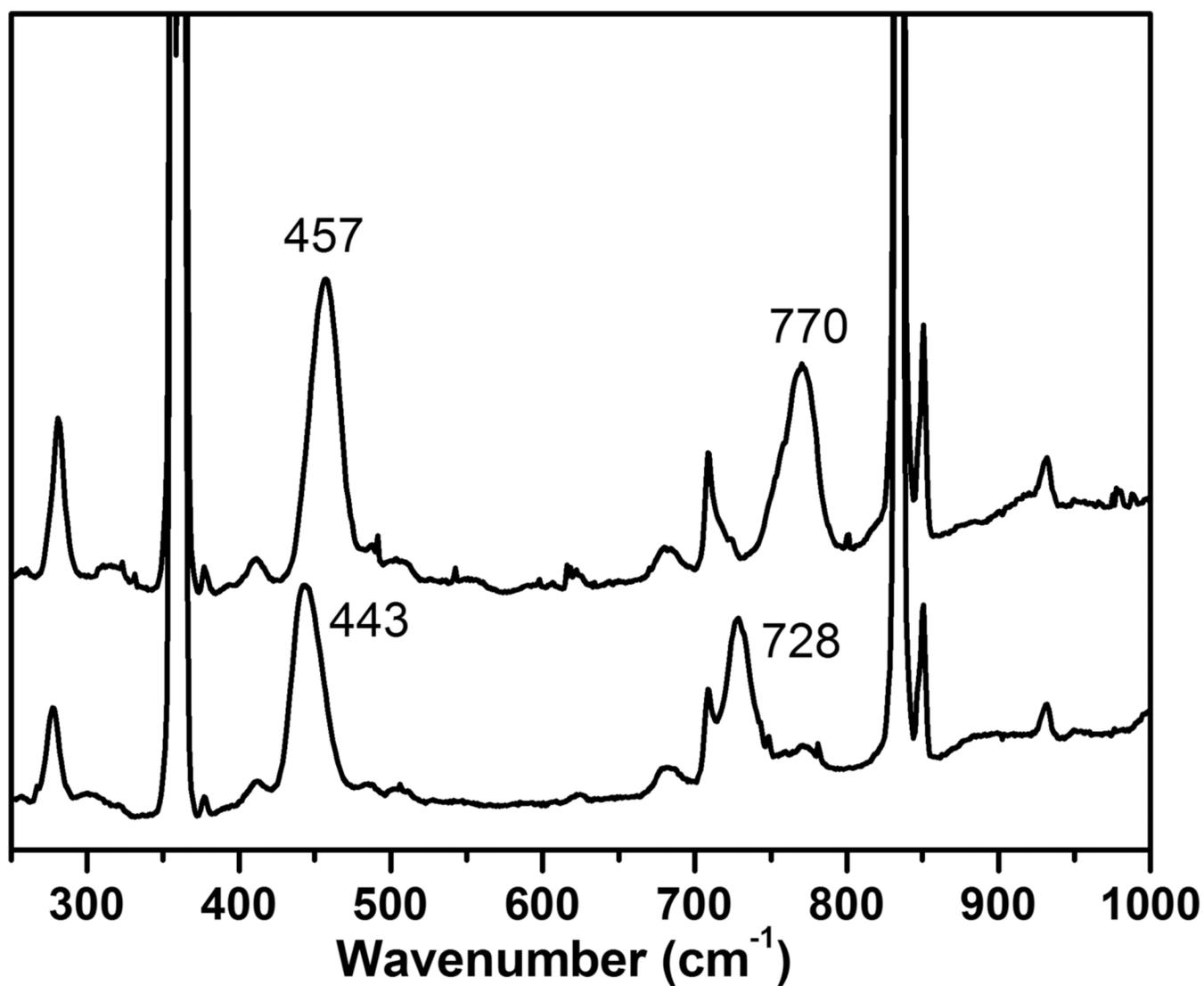


Figure 7. Raman spectra of 10 mM ¹⁶O- (top) and ¹⁸O-labeled (bottom) **2** in frozen CH₃CN-*d*₃ (77 K). Excitation: 457.9 nm. The peaks at 457 cm⁻¹ and 770 cm⁻¹ arise from the symmetric and asymmetric vibration modes of the Fe–O–Fe unit, respectively.

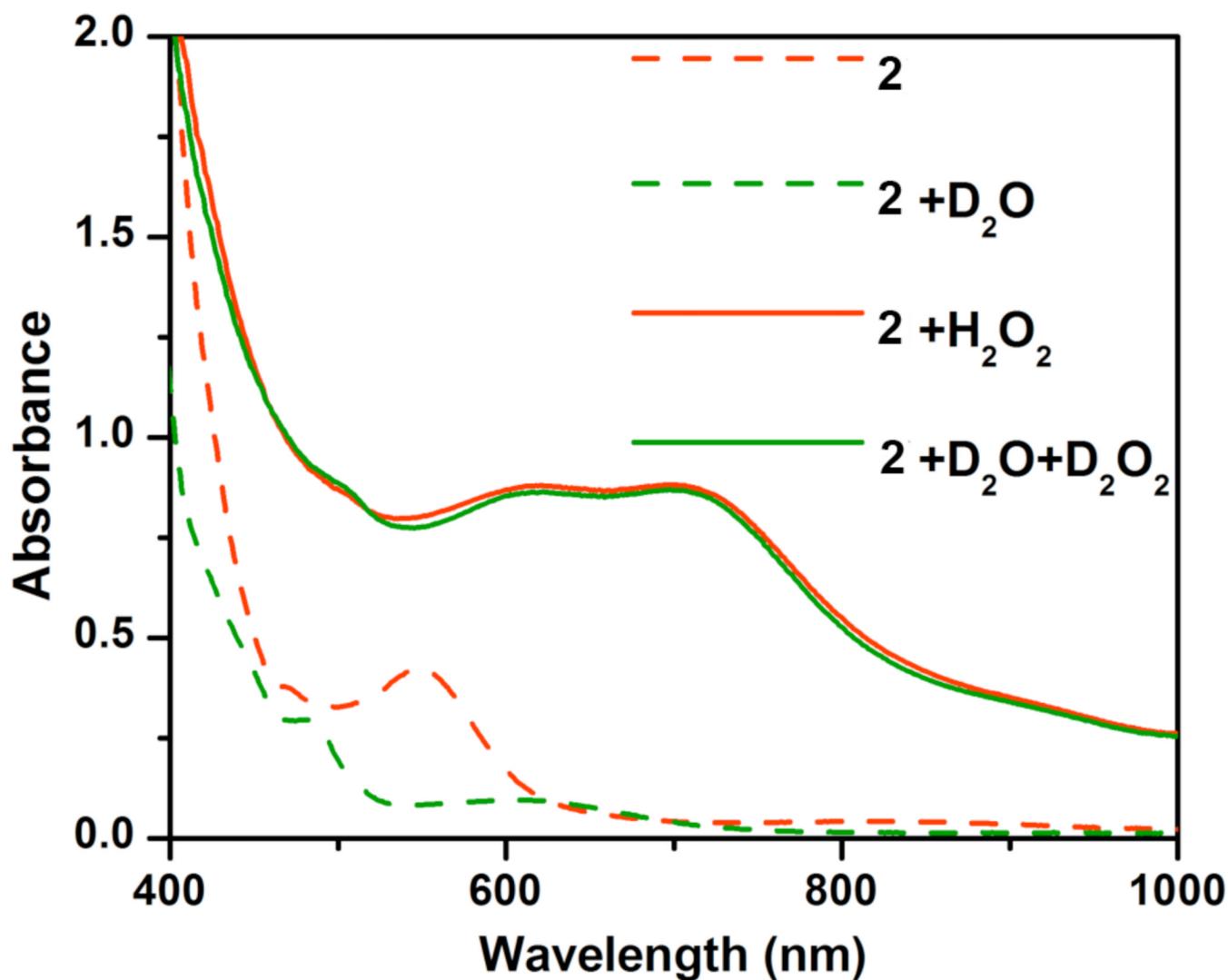


Figure 8. UV-vis spectra of 0.5 mM **2** in anhydrous CH₃CN (red dashed line) and after reaction with 0.5 mM H₂O₂ (red solid line), as well as 0.5 mM **2** in CH₃CN with 50 mM D₂O (green dashed line) and after reaction with 0.5 mM D₂O₂ (green solid line). All spectra were measured at -40 °C. These data show that both **1** and **2** react with H₂O₂ to generate the [HO-Fe^{IV}-O-Fe^{IV}=O]³⁺ (**4**) product in the same yield (~70% with respect to **2**).

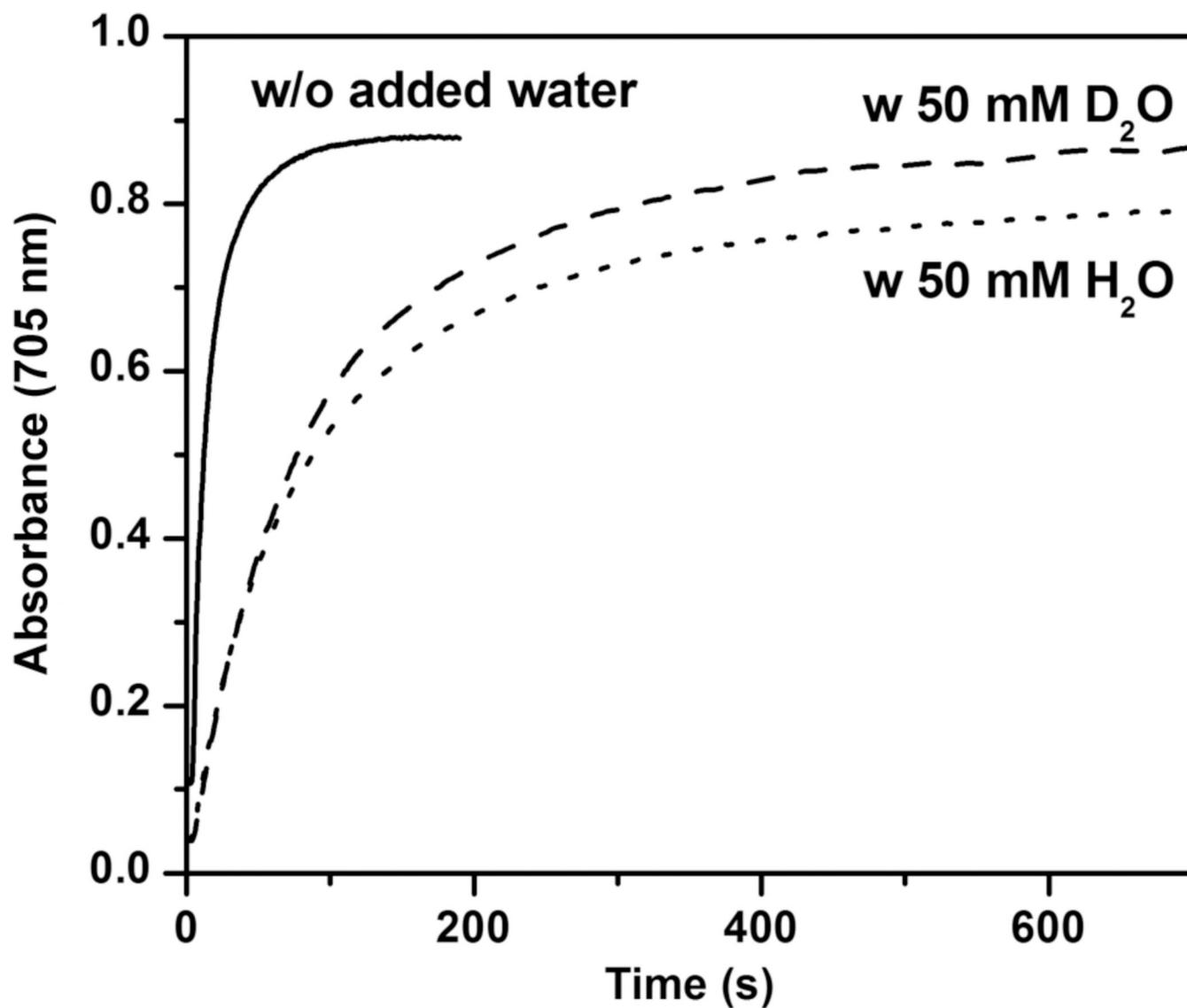
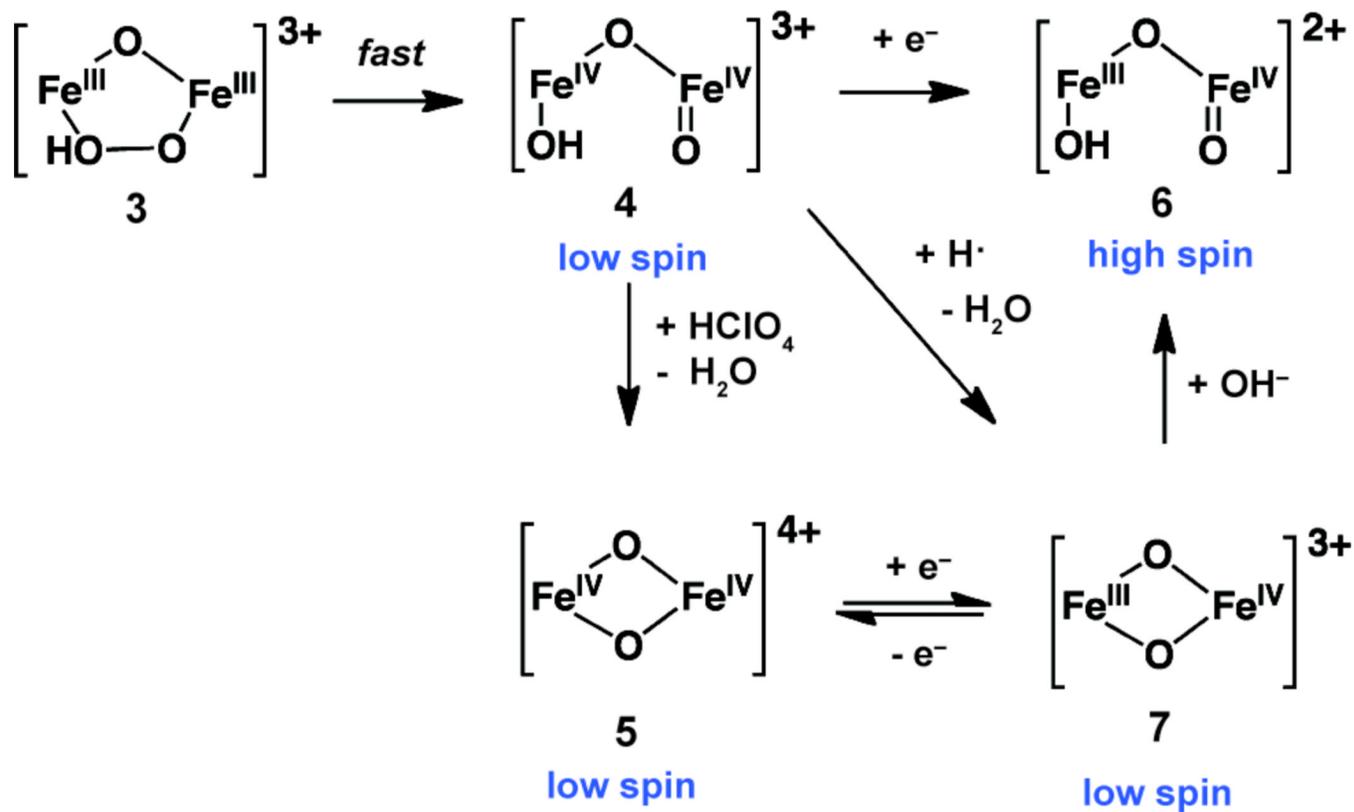
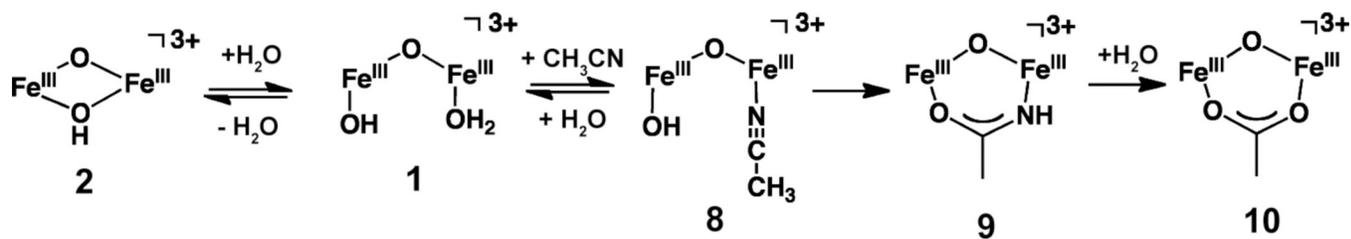


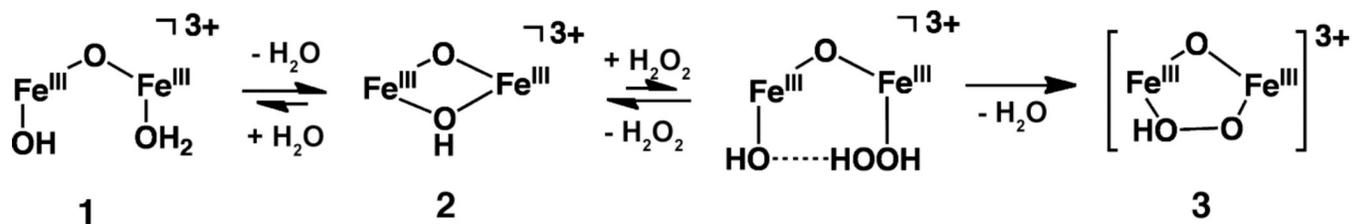
Figure 9. Time traces showing different rates for reactions of **2** with hydrogen peroxide in the absence (solid line) or presence of 50 mM added water [$\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (dotted line) or $\text{D}_2\text{O}_2/\text{D}_2\text{O}$ (dashed line)] in CH_3CN at -40°C .

**Scheme 1.**

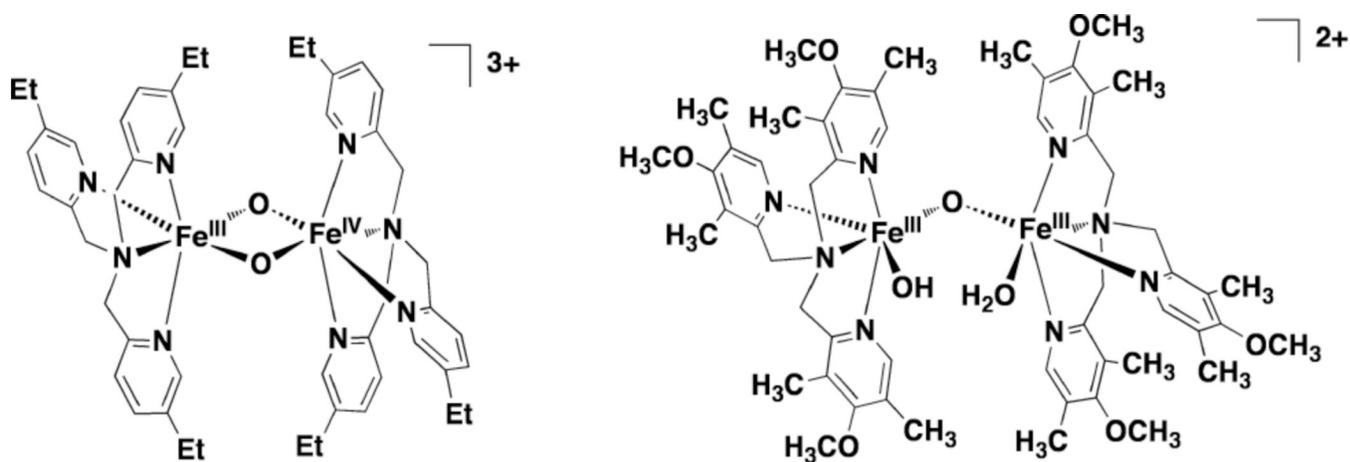
Reactions of a $[\text{Fe}^{\text{III}}_2(\mu\text{-O})(\mu\text{-OOH})(\text{R}_3\text{TPA})_2]^{3+}$ species (3) leading to formation of high-valent diiron(IV) and diiron(III,IV) units.

**Scheme 2.**

Proposed pathway for the complete hydrolysis of acetonitrile to acetate mediated by a $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{R}_3\text{TPA})_2]^{3+}$ (2) complex.

**Scheme 3.**

Hydrogen peroxide reacts directly with **2**, not **1**. This scheme is revised from that previously reported.

**Chart 1.**

The $[\text{Fe}_2(\mu\text{-O})_2(5\text{-Et-TPA})_2]^{3+}$ complex (left) was the first di(μ -oxo)diiron(III,IV) species structurally characterized by X-ray crystallography. The $[\text{Fe}_2(\mu\text{-O})(\text{OH})(\text{H}_2\text{O})(\text{R}_3\text{TPA})_2]^{3+}$ (**1**, right) compound was reported to be a versatile starting material for generating diiron(IV) species.

Table 1

Summary of Spectroscopic Data.

	Crude Solid			2	10a	10b
	Site 1	Site 2	Site 3			
Mössbauer^a						
δ (mm/s)	0.44	0.44	0.44	0.44	0.44	0.44
ΔE_Q (mm/s)	1.16	1.66	0.71	1.46	1.47	1.49
Γ (mm/s)	0.35	0.32	0.40	0.47	0.38	0.38
	36%	28%	36%			
UV-visible^b				370, 550	450, 490, 690	454, 504, 700
λ_{\max} (nm)						
Infrared^c						
ν (cm ⁻¹)	2945	2947		2947	2927	2960
	1600	1599		1599	1598	1599
	1575	1575		1575	1576	1570
	1478	1478		1478	1478	1478
	1456	1455		1455	1450	1450
	1401	1402		1402	1402	1402
	1384	1384		1384	1384	
	1293	1292		1292	1292	1291
	1267	1268		1268	1267	1264
	1077	1076		1076	1091	1092
	1096					
	995	995		995	994	995
	874	874		874	875	875
		800 (w)		800 (w)		800
	768(w)	763(w)		763(w)	765	764
	660	657(w)		657(w)		
	623	624		624	623	623
¹H NMR^d						
δ (ppm)				4.70, 4.00, 3.89, 3.60, 3.42, 2.79, 2.24, 1.63	3.92, 3.68, 3.28, 2.94, 2.45	3.91, 3.67, 3.28, 2.93, 2.44

^a Polycrystalline samples recorded at 80 K.

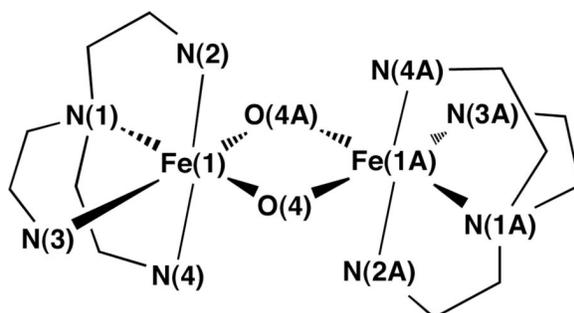
^b Recorded in dichloromethane at RT.

^c Measured as KBr pellets; IR peaks designated with a "w" indicate weak intensity.

^d Recorded in chloroform-*d*₁.

Table 2

Selected Structural Parameters of $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(\text{R}_3\text{TPA})_2](\text{ClO}_4)_3$ (**2**), $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(6\text{-Me}_3\text{TPA})_2](\text{ClO}_4)_3$, and $[\text{Fe}_2(\mu\text{-O})_2(6\text{-Me}_3\text{TPA})_2](\text{ClO}_4)_2$.



	2	$[\text{Fe}_2(\mu\text{-O})(\mu\text{-OH})(6\text{-Me}_3\text{TPA})_2](\text{ClO}_4)_3^b$	$[\text{Fe}_2(\mu\text{-O})_2(6\text{-Me}_3\text{TPA})_2](\text{ClO}_4)_2^c$
Bond Distances (Å)^a			
Fe(1)–Fe(1A)	2.7920(9)	2.95(1), 2.94(1)	2.716(2)
Fe(1)–O(4)	1.883(3)	1.906(8), 1.91(1)	1.844(3)
Fe(1)–O(4A)	1.934(2)	1.981(8), 1.960(9)	1.916(4)
Fe(1)–N(1)	2.183(3)	2.174(9), 2.18(1)	2.194(4)
Fe(1)–N(2)	2.147(3)	2.239(9), 2.28(1)	2.255(4)
Fe(1)–N(3)	2.151(3)	2.194(9), 2.196(9)	2.279(4)
Fe(1)–N(4)	2.134(3)	2.188(9), 2.18(1)	2.244(4)
Bond Angles (deg)^a			
Fe(1)–O(4)–Fe(1A)	94.01(11)	98.7(4), 98.7(6)	92.5(2)
O(4)–Fe(1)–O(1A)	85.99(11)	81.3(4), 81.3(6)	87.5(2)
N(1)–Fe(1)–N(2)	76.24(10)	77.2(3), 76.0(5)	75.7(1)
N(1)–Fe(1)–N(3)	76.24(10)	81.2(4), 81.5(4)	74.7(2)
N(1)–Fe(1)–N(4)	79.74(10)	75.1(3), 75.6(4)	79.0(2)
N(1)–Fe(1)–O(4)	176.66(10)	170.6(4), 168.7(4)	175.1(2)
N(1)–Fe(1)–O(4A)	96.12(10)	89.4(4), 88.0(5)	87.8(2)

^a A generalized numbering scheme, depicted in the above cartoon representation, is used. These atom labels do not necessarily correspond to those assigned in their respective X-ray structures.

^b Previously reported (ref. 22). Each asymmetric unit contains two independent molecules.

^c Previously reported (ref. 23).