Formation of Fe(III)Fe(IV) Species from the Reaction between a Diiron(II) Complex and Dioxygen: Relevance to Ribonucleotide Reductase Intermediate X  
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The reaction of m-terphenyl-based carboxylic acids with ferrous salts produces novel tetracarboxylate dinuclear clusters through an extraordinarily efficient self-assembly process. Recently, we reported the preparation of one such compound, [Fe2(μ-O2-CAR10)(O2-CAR10)]2(C6H8N4)] (1), and highlighted its unique reactivity with dioxygen. Efforts to explore this chemistry further were hampered by the poor solubility of 1 in nonpolar solvents, thus prompting the synthesis of new Ar Tol CO2 (4- tBuC5H4N)2 (2), that reacts with O2 to furnish [Fe2(μ-OH)2(μ-O2-CAR24)(O2-CAR18)(4-BuC6H4N)] (4). This process parallels the oxygenation reaction of 1, proceeding through a metastable green intermediate 3 that decays to afford 4 in isolated yields exceeding 75%. Studies with 2 have made possible the characterization and assignment of 3 as a mixture containing equimolar quantities of mixed-valent species FeIIFeIV and FeIIIFeIV. The formation of a high-valent diiron bridged complex from 2 and dioxygen mimics closely the purported mechanistic chemistry of certain diiron metalloenzymes. Additionally, the FeIIFeIV component in 3 represents a putative model for a key intermediate, X, in the reaction cycle of the R2 subunit of ribonucleotide reductase (RNR−R2).4,5 To the best of our knowledge, the formation of 3 is the first example of a process that utilizes dioxygen to access the FeIV oxidation state in synthetic model complexes.5

Neutral tetracarboxylate complex 2 was prepared upon treatment of [Fe2(μ2-O2-CAR10)]2(O2-CAR24)(THF)2 with 2 equiv of 4-tert-butylpyridine (Scheme 1). The structure of 2 reveals a dinuclear adduct in which four Ar Tol CO2− groups span the two metal centers (Figure S1). Each iron in 2 is square pyramidal and has a coordination geometry that closely resembles those of previously reported diiron(II) paddlewheel complexes.8

Scheme 1  

Oxygenation of a CH3Cl2 solution of 2 at −78 °C resulted in the irreversible generation of a deep green solution 3 with a broad visible absorption centered at ~670 nm (ε = 1700 M−1 cm−1). At low temperature, 3 is stable for >12 h, but it slowly decays upon warming above −65 °C to afford a yellow material (Figure S2). X-ray analysis established this product to be the bis(μ-hydroxo)diiron(III) complex 4 (Scheme 1 and Figures S3, S4). Compound 4 is structurally analogous to that obtained from oxidation of 1, having a short FeIII−FeII separation of ~2.8 Å due to the presence of four bridging ligands. A weak ferromagnetic interaction, J = 0.63(5) cm−1 with g = 2.00(1), was observed by SQUID susceptometry on solid samples of 4.

X-Band EPR spectra collected on frozen CH3Cl2 samples of 3 exhibited a strong isotropic g = 2 signal and a less intense absorption at g = 10 (Figure 1). Quantitation of these two species accounted for 70% of the total iron, the former signal contributing 40% and the latter 30%. The X-band signal at g = 2, with a width of ~28 G, originates from an S = 1/2 species which shows resolved g-anisotropy at Q-band (see inset). The two simulations overlaid on the data use the same parameter set of g = 1.986, 1.997, and 2.011. This g-anisotropy is similar to that of the RNR−R2 X (g = 1.994, 1.999, and 2.007) signal,8,9 which arises from the antiferromagnetically coupled FeIIFeIV core in this enzyme intermediate. The signals at g = 10 (X- and Q-band) and g = 4.3 and 2.8 (Q-band) originate from an S = 3/2 species and the simulations overlaid on the data were obtained with D = 1.2 cm−1, E/2 = 0.013, and g = 2.00. Both the S = 1/2 and S = 3/2 signals display Curie law behavior up to 150 K, indicating exchange interactions of |2J| > 200 cm−1 for the former and > 50 cm−1 for the latter.7 The similarity of the S = 1/2 EPR signal with that of a complex prepared by one-electron chemical oxidation of 2II leads us to assign it as the corresponding FeIIFeIII cation. The S = 3/2 spin state can result either from a ferromagnetic interaction between iron centers or by electron delocalization for which a double-exchange mechanism12 is dominant.

Figure 2 displays the Mössbauer spectra of a solid powder sample of 3 recorded at 4.2 K with a 50-mT magnetic field applied parallel (A) and perpendicular (B) to the γ-rays. The spectra may be deconvoluted into three major components. A central quadrupole doublet (marked by brackets) with apparent Mössbauer parameters of ΔE0 = 1.13 mm/s and δ = 0.54 mm/s is assigned

(7) H = −2S1/2S2.
(10) The resonances near g = 4 in Q-band for both parallel and perpendicular modes are from an intradoublet transition and are not included in the simulation. The g = 19 (X-band) and possibly the g = 29 (Q-band) signals are from the diiron(III) species, whereas the g = 16 signal (Q-band) and its simulation are from unreacted 2, which account for 20 and 10% of the total iron, respectively.
Figure 1. X-band (A, 9.4 GHz) and Q-band (B, 34.1 GHz) EPR spectra of a frozen CH₂Cl₂ solution of 3 for microwave fields parallel and perpendicular to the static field. Dashed lines are quantitative simulations for the S = 1/2 and S = 3/2 species discussed in the text. The inset is a magnified view of the Q-band g = 2 signal. Sample temperatures are ~12 K and relative signal gains are shown on the figure.

Figure 2. Mössbauer spectra of the solid powder sample of 3 recorded at 4.2 K with a 50-mT magnetic field applied parallel (A) and perpendicular (B) to the γ-rays. Spectrum C is a different spectrum of the spectra shown in A and B. The solid lines are theoretical simulations of the S = 1/2 species using the parameters listed in Table S1. The theoretical spectra are normalized to 36% of the total iron absorption.

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Supporting Information Available: Details of the synthetic procedures, X-ray crystallographic tables, physical characterization of 2 and 4 (PDF). An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Preliminary high-field Mössbauer data indicate this broad component to be a valence-delocalized S = 3/2 FeIIFeIII species, detailed characterization of which is currently in progress.


(15) In support of this putative reaction scheme, manometric measurements demonstrated that substoichiometric amounts of O₂ (0.75 ± 0.1) are consumed per mol of 2 to provide 3. At present, however, we have no apparent explanation for the formation of the diiron(III) species. It might be generated by a reaction between the FeIIFeIV and FeIIFeIII species or in a branching pathway involving 2 and dioxygen.

(16) A related model has been recently proposed for the generation of Y122 in RNR−R2, in which two functionally different diiron clusters are involved in the reaction with O₂; Miller, M. A.; Gobena, F. T.; Kauffmann, K.; Münck, E.; Que, L., Jr.; Stankovich, M. T. J. Am. Chem. Soc. 1999, 121, 1096–1097.

(17) The oxidizing ability of 3 was manifested by reactions with substituted phenols, 2,4,6-tri-tert-butylphenol and 2,4-di-tert-butylphenol, which provided the corresponding phenoxyl radical (10%) or biphenol coupled product (40%), respectively. Unpublished results.

(18) In this regard it is interesting to note that reaction of O₂ with a similar diiron(II) complex derived from 2,6-dimesitylbenzoic acid affords an EPR silent purple complex. This species has been assigned as a diiron(III) peroxide on the basis of an isotope-sensitive vibration at 885 cm⁻¹ in the resonance Raman spectrum: Hagadorn, J. R.; Que, L., Jr.; Tolman, W. B. J. Am. Chem. Soc. 1998, 120, 13531–13532.