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An Unsymmetrical, Doubly Bridged Diiron(II) Complex with Readily Accessible Coordination Sites

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The binding and activation of dioxygen at the diferrous centers of hemerythrin (Hr), ribonucleotide reductase (RR), and methane monooxygenase (MMO) are central to their biological functions.[1] The interaction of dioxygen with Hr and, presumably, other diiron proteins necessitates a vacant coordination site. In deoxyHr, five imidazoles from histidine residues are bound in an unsymmetrical arrangement to a (μ-hydroxo)bis(μ-carboxylato)diiron(II) core with an open coordination site at one iron available for dioxygen binding, which results eventually in an end-bound hydroperoxide ligand stabilized by internal hydrogen bonding.[2] The structures of both (μ-oxo)(μ-carboxylato)diiron(III) and bis(μ-carboxylato)diiron(II) forms of RR have been established by X-ray crystallography.[3] In the reduced state, both irons are five-coordinate and allow for a proposed μ-η^1, η^1 interaction of dioxygen with both metals.[1a] For MMO, the X-ray crystal structure of only the fully oxidized form has been determined;[4] however, Mössbauer spectroscopy has produced evidence of differing coordination numbers about the two iron centers in the reduced state.[5] In order to obtain a more complete description of the active site of binuclear proteins, it is desirable to model coordination number asymmetry. However, examples of binuclear model complexes that exhibit coordination number asymmetry are rare. These include binuclear iron compounds in which coordination number asymmetry was unexpectedly observed in the solid state,[6g,7] as well as recent examples where ligand design was used to influence structure in binuclear copper(II)[8,9] and mixed-valent iron complexes.[10] A number of binuclear iron(III) complexes have been prepared that mimic the spectroscopic properties of the fully oxidized state of these proteins.[1b−e,11] In contrast, only limited examples of binuclear iron(II) model complexes have been reported.[6] Although one example of coordination number asymmetry for iron(II) has been observed in the solid state,[6g] the use of ligand design to deliberately prepare such complexes has not been described. We report here the first example of an unsymmetrical, (μ-alkoxo)(μ-carboxylato)diiron(II) complex, **1**, that contains ferrous ions, benzoate, and an unsymmetrical multidentate ligand (HBMDP), which was described previously.[8,12] In addition, we have been able to demonstrate site-directed reactivity by the addition of the thiocyanate anion to produce a bis(thiocyanato)diiron(II) complex, **2**.

Yellow, air-sensitive $[Fe_2(BMDP)(OBz)(CH_3OH)_{1.5}(H_2O)_{0.5}]$-$[BF_4]_2$ (**1**) was prepared under nitrogen by the reaction of 2 equiv of $Fe(BF_4)_2\cdot 6H_2O$ with HBMDP[8a] in the presence of 2 equiv of sodium benzoate in methanol. The crystal structure[13] reveals that the cation (Figure 1) consists of two iron(II) ions, one bridging benzoate, a single BMDP ligand, and two tetrafluoroborate anions. The unsymmetrical ligand donates an aliphatic amine nitrogen to each iron, bridges the metal with

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(12) Abbreviations used: HBMDP = *N,N,N′*-tris(*N*-methyl-2-benzimidazolylmethyl)-*N′*-methyl-1,3-diamino-2-propanol; *N*-Et-HPTB = *N,N,N′,N′*-tetrakis(2-(1-ethylbenzimidazoyl))-2-hydroxy-1,3-diaminopropane; OAc = acetate; OBz = benzoate.

(13) Crystal data for **1**$\cdot 4CH_3OH\cdot 0.5H_2O$ ($C_{42.5}H_{59}B_2F_8Fe_2N_8O_3$, M_r = 1079.3) at 125 K: pale yellow needles, monoclinic space group $P2_1/n$, a = 17.023(3) Å, b = 13.312(2) Å, c = 22.942(5) Å, β = 104.77°, V = 5027(1) Å^3, Z = 4; R = 0.090, R_w = 0.095 for 2275 reflections with $F > 6\sigma_F$ and 307 parameters.

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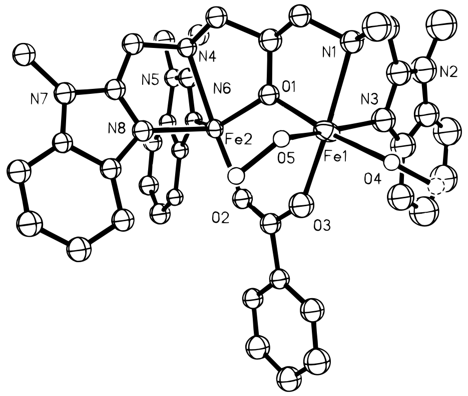

Figure 1. Structure of binuclear Fe(II) cation **1** with 30% thermal contours. Selected interatomic distances (Å): Fe1−O1, 2.028(13); Fe1−O3, 2.081(12); Fe1−N1, 2.327(18); Fe1−N3, 2.140(18); Fe1−O4 (solvent), 2.152(17); Fe1−O5 (solvent), 2.188(16); Fe2−O1, 1.968(10); Fe2−O2, 2.038(12); Fe2−N4, 2.299(16); Fe2−N6, 2.106(14); Fe2−N8, 2.078(16); Fe1···Fe2, 3.556(6). The dotted circle represents refinement for a carbon atom at 50% occupancy (0.5 MeOH). In addition, there is disorder in the phenyl ring of the benzoate group whereby two orientations are related by a 12° rotation. Set "B" has been omitted for clarity. (See Supporting Information).

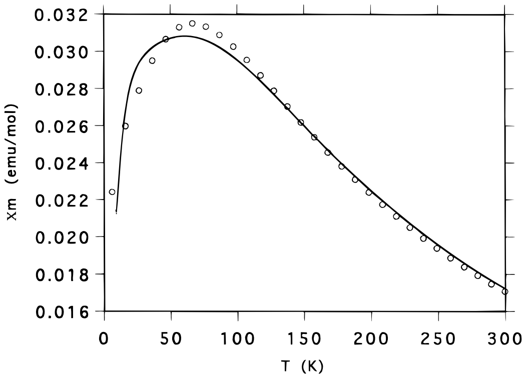

Figure 2. Temperature dependence of the corrected molar susceptibility for vacuum-dried $[Fe_2(BMDP)(OBz)(CH_3OH)_{1.5}(H_2O)_{0.5}][BF_4]_2$ (**1**) (6−300 K). The solid line is a least-squares fit for all data. Final parameter set for fit assuming an isotropic g value: $2J = -11.7(1)$ cm^{-1}, $g = 2.10(1)$, monomeric impurity level 0.018(1).

the alkoxo oxygen, and coordinates the three benzimidazoles in an unsymmetrical fashion: two to one iron atom and one to the other. The Fe···Fe separation is 3.556(6) Å, which is comparable to the 3.473(7) Å separation in $[Fe_2(N\text{-Et-HPTB})(OBz)][BF_4]_2$,[14] the symmetric analog of **1**. Fe2 is five-coordinate with distorted trigonal bipyramidal geometry where an amine nitrogen and a benzoate oxygen serve as axial ligands; the bridging alkoxo oxygen and two benzimidazole nitrogens complete the coordination about iron. Bond lengths and angles for Fe2 are similar to those found in $[Fe_2(N\text{-Et-HPTB})(OBz)][BF_4]_2$. Fe1 is six-coordinate with bonds to two benzimidazole groups, to the bridging alkoxide and benzoate group, to a methanol molecule, and to a site that modeled as shared by a methanol molecule and a water molecule. Thus, the asymmetry of the ligand has influenced the structure such that solvation occurs at the metal center that derives lower coordination from the ligand.

The magnetic properties of **1** in the solid state have been investigated at 1.0 T, over the temperature range of 6−300 K. The data are plotted as molar susceptibility (χ_{mol}) versus temperature in Figure 2. The maxima in the plot at ~70 K is indicative of antiferromagnetic coupling. The effective moment per iron at 300 K is 4.53 μ_B for **1**, which is comparable to the value found for $[Fe_2(N\text{-Et-HPTB})(OBz)][BF_4]_2$, ~4.4 μ_B. Fitting the data for **1** to the Heisenberg Hamiltonian $H = -2JS_1 \cdot S_2$,

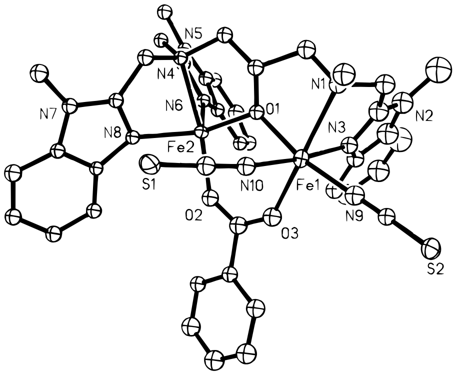

Figure 3. Structure of binuclear Fe(II) complex **2** with 30% thermal contours. Selected interatomic distances (Å): Fe1−O1, 2.021(7); Fe1−O3, 2.099(10); Fe1−N1, 2.365(12); Fe1−N3, 2.181(11); Fe1−N9, 2.115(10); Fe1−N10, 2.198(11); Fe2−O1, 1.948(8); Fe2−O2, 2.024(9); Fe2−N4, 2.306(10); Fe2−N6, 2.091(9); Fe2−N8, 2.111(10); Fe1···Fe2, 3.462(6).

where $S_1 = S_2 = 2$, we found $2J \sim -11.1(1)$ cm^{-1}.[15,16] However, because complicated energy level distributions arise when $|J| \leq |D|$, zero-field-splitting (D) terms should be included for a more complete analysis.

The potential to introduce accessible coordination site(s) at one metal is an important aspect of developing binuclear metal complexes with coordination number asymmetry. The reaction of **1** with the thiocyanate ion demonstrates site-directed reactivity. Thus, anaerobic treatment of **1** with 2 equiv of sodium thiocyanate in acetonitrile yields the yellow-orange, air-sensitive complex $[Fe_2(BMDP)(OBz)(SCN)_2]$ (**2**). The crystal structure[17] reveals that the neutral molecule (Figure 3) consists of two iron(II) ions, one bridging benzoate, a single BMDP ligand, and two thiocyanate anions. The overall coordination of the ligand and benzoate group remains unchanged. Both thiocyanate groups are bound through nitrogen donation to Fe1 and have displaced the methanol/water ligands. The original coordination number asymmetry in **1** is retained in **2**. It is interesting to note that reactivity has been influenced by the unsymmetrical ligand. Although Fe2 is pentacoordinate, and as such could be considered to be coordinatively unsaturated, thiocyanate binding does not occur at this metal center. Rather, the thiocyanate ligands have become bound to Fe1, the iron to which the BMDP ligand donates only three electron pairs. In addition, the isolation of **2** from acetonitrile corroborates ^{1}H NMR evidence that, for both complexes, the solid state structure remains intact in solution.

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Supporting Information Available: For complexes **1** and **2**, textual details of the preparations and physical measurements and full tables of structural parameters and refinement data, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (20 pages). Ordering information is given on any current masthead page.

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[17] Crystal data for $\mathbf{2}\cdot 2CH_3CN$ ($C_{44}H_{46}Fe_2N_{12}O_3S_2$, $M_r = 966.7$) at 125 K: yellow-orange prisims, monoclinic space group $P2_1/c$, $a = 14.043(2)$ Å, $b = 20.915(5)$ Å, $c = 15.440(3)$ Å, $\beta = 104.18$, $V = 4396.9(15)$ Å^3, $Z = 4$; $R = 0.0659$, $R_w = 0.0678$ for 2466 reflections with $F > 6\sigma_F$ and 273 parameters.