Some silatranes have beneficial biological actions, while others are toxic.[6] The biological properties of the new derivatives reported here are under investigation.

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Registry No. 3 (CC entry), 63344-73-0; **3** (silane entry), 31701-36-7; **4** (CC entry), 122722-12-7; **4** (silane entry), 122699-00-7; **5** (CC entry), 122699-04-1; **5** (silane entry), 122699-01-8; **6** (CC entry), 122699-05-2; **6** (silane entry), 122699-10-9; **7** (CC entry), 122699-06-3; **7** (silane entry), 122699-02-9; **8** (CC entry), 122699-07-4; **8** (silane entry), 122699-03-0; **9**, 122699-09-6.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters, bond lengths, torsion angles, general displacement expressions, and bond angles and a listing of ^1H and ^{13}C NMR data for **4-9**, an elemental analysis for **5**, and high resolution mass spectral data for **5** and **7-9** (9 pages); table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

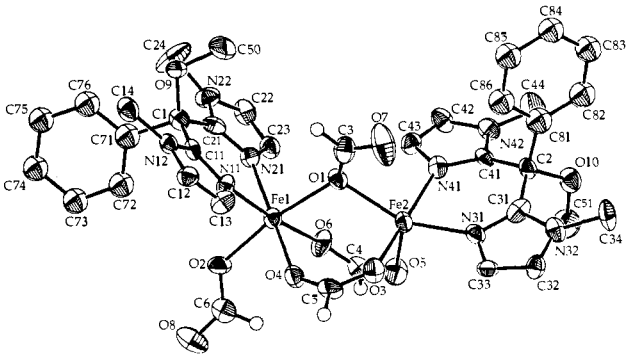

Figure 1. ORTEP drawing of $1 \cdot 1.5CH_2Cl_2$ showing the 55% probability thermal ellipsoids and atom labels for all non-hydrogen atoms (excluding CH_2Cl_2 solvate molecules). The hydrogen atoms on the formate ligands are included as isotropic spheres (B_{eq} = 1.0). Selected interatomic distances (Å) and angles (deg) are as follows: Fe1-O1, 2.168 (8); Fe1-O2, 2.045 (8); Fe1-O4, 2.132 (8); Fe1-O6, 2.16 (1); Fe1-N11, 2.14 (1); Fe1-N21, 2.13 (1); Fe2-O1, 2.129 (9); Fe2-O3, 2.09 (1); Fe2-O5, 2.07 (1); Fe2-N31, 2.104 (9); Fe2-N41, 2.13 (1); Fe1···Fe2, 3.585 (4); O1-Fe2-O5, 107.9 (4); O1-Fe2-O3, 88.8 (3); O1-Fe2-N41, 90.8 (4); O1-Fe2-N31, 147.3 (5); O3-Fe2-N41, 173.8 (4); Fe1-O1-Fe2, 113.1 (4).

Self-Assembly and Dioxygen Reactivity of an Asymmetric, Triply Bridged Diiron(II) Complex with Imidazole Ligands and an Open Coordination Site

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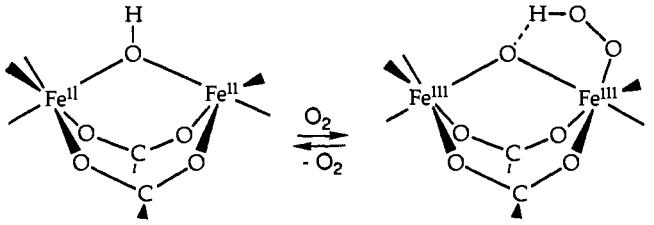
In the marine invertebrate respiratory protein hemerythrin (Hr), two dissimilar ferrous ions, one five- and the other six-coordinate, cooperate to bind dioxygen reversibly (eq 1).[1,2] An important

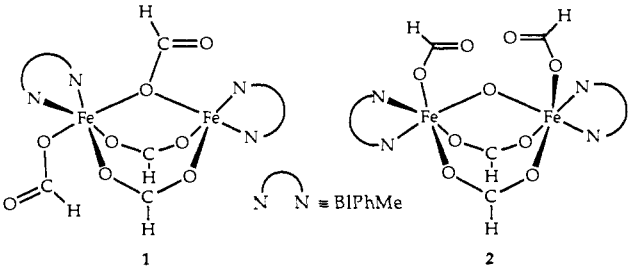


Deoxyhemerythrin Oxyhemerythrin

(1)

objective in the quest for model complexes that can mimic the biological activity of Hr, therefore, is the synthesis of an asymmetric diiron(II) complex[3] with an open terminal coordination position. Accurate spectroscopic and magnetic models of the diiron centers in the reduced and oxidized forms of Hr containing the $\{Fe_2(OR)(O_2CR')_2\}^+$ (R = H, Ph)[4] and $\{Fe_2O(O_2CR')_2\}^{2+}$ cores,[4b,5] respectively, are currently available. None of the diiron(II) compounds can model the molecular oxygen binding function of the protein, however, because they are capped by tridentate N-donor ligands and thus lack an open coordination site. By using bidentate instead of tridentate groups as terminal ligands on the diiron core, one can gain access to such a site.[6] Here we report the preparation by self-assembly of an asymmetric, triply bridged diiron(II) complex, **1**, from ferrous ions and biomimetic carboxylate and bis imidazole ligands, together with its X-ray crystal structure and Mössbauer and ESR spectra. Air oxidation of **1** yields the diiron(III) complex **2**, the oxo bridge of which is shown by resonance Raman spectroscopic experiments to derive from dioxygen.

Stirring of a 1:1 mixture of $Fe(O_2CH)_2 \cdot 2H_2O$[7] and bis(1-methylimidazol-2-yl)phenylmethoxymethane (BIPhMe)[8] in MeOH with strict exclusion of air for 0.5 h gave a colorless solution, which, upon workup, afforded $[Fe_2(O_2CH)_4(BIPhMe)_2]$ (**1**) as a colorless powder (91%). This formula is supported by



1 2

analytical data, the appearance of formate and BIPhMe vibrations in the FTIR spectrum, and an X-ray structure determination, performed on a crystal obtained from CH_2Cl_2/CH_3CN, which revealed an asymmetric molecule with an open coordination site

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(Figure 1).[9] Two Fe(II) atoms are bridged by one monodentate and two bidentate formate ligands. This triply bridged unit represents a new coordination geometry in diiron chemistry, to be contrasted with the known μ-oxo, μ-hydroxo, and μ-phenoxo diiron compounds containing supporting carboxylate bridges.[1,4,5,10] In **1**, a fourth formate ion is coordinated in monodentate fashion to one of the metal centers (Fe1), the octahedral coordination sphere of which is completed by ligation of two imidazoles from a BIPhMe molecule. In contrast, Fe2 is bonded to only five ligands, with a distorted trigonal-bipyramidal geometry.[11] An additional weak interaction occurs with O7 of the monodentate bridging formate [Fe2···O7, 2.74 (1) Å]. The latter is tilted toward Fe2, as reflected by the differing angles Fe1-O1-C3 [133.3 (9)°] and Fe2-O1-C3 [105.4 (7)°]. As expected from the lower coordination number, bonds to Fe2 are shorter than analogous bonds to Fe1 by 0.03-0.07 Å.

The zero-field Mössbauer spectrum of **1** measured at 4.2 K contains a broad, asymmetric doublet that could be nicely fit to a two-site model with δ_1 = 1.26 (3) mm s^{-1}, δ_2 = 1.25 (3) mm s^{-1}, ΔE_{Q1} = 2.56 (3) mm s^{-1}, and ΔE_{Q2} = 3.30 (3) mm s^{-1}. We ascribe the larger quadrupolar splitting to the pentacoordinate iron Fe2, which has the less symmetrical ligand environment. The X-band ESR spectrum at 7 K of a frozen, colorless solution of **1** prepared under N_2 in $CDCl_3$ (5 mM) contains a broad signal at $g \sim 16$ similar to that reported for a phenoxo-bridged diiron(II) complex[4c] and for deoxyHr azide.[2b] In addition, we observe a signal at g = 1.90, the origin of which is under investigation.

Exposure of solutions of **1** in $CHCl_3$ or CH_2Cl_2 to air results in the formation of a green-brown mixture from which green microcrystals of $[Fe_2O(O_2CH)_4(BIPhMe)_2]\cdot H_2O$ (**2**·H_2O) were isolated (~35%).[12] The same material forms upon mixing equimolar quantities of $Fe(O_2CH)_2\cdot 2H_2O$ and BIPhMe in $CHCl_3/CH_3CN$ (1:1) in air. An X-ray crystal structure determination revealed the presence of the now-familiar (μ-oxo)bis(μ-carboxylato)diiron(III) core in **2**, with the terminal metal coordination sites each occupied by two imidazoles from BIPhMe and a monodentate formate ligand cis to the oxo bridge.[13] The geometric parameters from the X-ray structure and the electronic, Mössbauer, IR, and resonance enhanced Raman spectroscopic data for **2** are analogous to those found for oxidized forms of Hr and for other complexes having similar cores.[1,4-6]

The source of the oxo bridge in **2** was determined to be dioxygen, rather than adventitious water, by exposing a solution of **1** in $CHCl_3$ to $^{18}O_2$ and monitoring the symmetric Fe-^{18}O-Fe stretch of the product by resonance enhanced Raman spectroscopy. By comparison to the spectrum of fully ^{18}O labeled **2**, prepared by exchange with $H_2{}^{18}O$, it was evident that ^{18}O incorporation from dioxygen had occurred. Further spectroscopic and mechanistic studies of the reaction of **1** with dioxygen are underway.

In conclusion, with the preparation of **1**, significant progress has been made toward modeling the geometric and spectroscopic properties as well as aspects of the dioxygen reactivity of diiron oxo proteins in their reduced forms. The uniquely bridged diiron(II) compound **1** contains only biomimetic imidazole and carboxylate ligands and a single open coordination site, features of deoxyHr heretofore unknown in synthetic complexes. While reversible dioxygen binding to **1** does not occur in solution at ambient temperature, an oxygen atom is incorporated upon exposure of **1** to air to give **2**. This chemistry is of likely relevance to the formation and/or functional activity of diiron oxo centers in the related proteins ribonucleotide reductase[14] and methane monooxygenase.[15]

Acknowledgment. This work was supported by U.S. Public Health Service Grant GM 32134 from the National Institute of General Medical Sciences. W.B.T. is grateful to the American Cancer Society for a postdoctoral fellowship. A.B. is on sabbatical leave from the Hebrew University of Jerusalem, Israel. We thank Dr. G. C. Papaefthymiou for assistance in obtaining Mössbauer data at the Francis Bitter National Magnet Laboratory, which is supported by the National Science Foundation. We also thank D. P. Bancroft, R. H. Beer, and J. G. Bentsen for assistance.

Supplementary Material Available: Spectroscopic and analytical data for BIPhMe, **1**, and **2**·H_2O, Mössbauer spectrum of **1**, ORTEP diagram and selected bond lengths and angles for **2**·MeOH·H_2O, and tables of atomic positional and thermal parameters for **1**·1.5CH_2Cl_2 and **2**·MeOH·2H_2O (15 pages). Ordering information is given on any current masthead page.

(9) Anal. ($C_{36}H_{40}N_8O_{10}Fe_2$): C, H, N; FTIR (KBr, cm^{-1}) 3122, 2955, 2940, 1609 (s), 1498, 1449, 1358, 1323, 1283, 1071, 988, 897, 762, 725, 702. Crystal data for **1**·1.5CH_2Cl_2 ($C_{37.5}H_{43}N_8O_{10}Cl_3Fe_2$, M_r = 983.86) at 194 K: size ca. 0.2 × 0.2 × 0.1 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 15.47 (1) Å, b = 15.940 (5) Å, c = 10.540 (3) Å, α = 98.72 (2)°, β = 105.38 (5)°, γ = 63.79 (5)°, V = 2246 (4) Å^3, Z = 2, ρ_{calcd} = 1.455 g cm^{-3}. For 3256 unique, observed reflections with $F^2 > 3\sigma(F^2)$ and 455 variable parameters, the current discrepancy indices are R = 0.080 and R_w = 0.100.

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(12) Anal. ($C_{36}H_{42}N_8O_{12}Fe_2$): C, H, N; FTIR (KBr, cm^{-1}) 3424, 3130, 2937, 2832, 1617 (sh), 1590 (s), 1500, 1449, 1356, 1310, 1283, 1070, 988, 900, 762, 725, 704; resonance Raman (λ 406.7 nm, 100 mW, ~0.03 M, $CHCl_3$, cm^{-1}) ν_{sym} (Fe-O-Fe) 518, ν_{sym} (Fe-^{18}O-Fe, by $H_2{}^{18}O$ exchange) 501; UV-vis ($CHCl_3$) [λ_{max}, nm (ϵ_M/Fe cm^{-1} M^{-1})] 329 (3400), 354 (sh, 2900), 448 (370), 478 (sh, 340), 520 (sh), 662 (70); Mössbauer (zero field, 4.2 K, mm s^{-1}) δ 0.54 (3), ΔE_Q 1.81 (3).

(13) Crystal data for **2**·MeOH·2H_2O ($C_{37}H_{48}N_8O_{14}Fe_2$, M_r = 940.53) at 194 K: size 0.20 × 0.15 × 0.15 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 15.215 (6) Å, b = 15.401 (6) Å, c = 10.133 (2) Å, α = 108.70 (3)°, β = 96.41 (2)°, γ = 74.32 (3)°, V = 2165 (3) Å^3, Z = 2, ρ_{calcd} = 1.443 g cm^{-3}, ρ_{measd} = 1.44 (1) g cm^{-3}. For 2629 unique, observed reflections with $F^2 > 3\sigma(F^2)$ and 456 variable parameters, the current discrepancy indices are R = 0.086 and R_w = 0.101. An ORTEP diagram of the complex is presented as supplementary material.

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Sequence-Selective Hydrolysis of Duplex DNA by an Oligonucleotide-Directed Nuclease

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The design of molecules capable of the efficient sequence-specific cleavage of large double-stranded DNAs would greatly facilitate the manipulation and mapping of genomic DNA. Current strategies for the selective cleavage of large duplex DNAs include the use of triple-helix formation[1] and DNA-binding proteins[2] to deliver oxidative cleaving agents to the sequence of interest. We report here the sequence-specific hydrolysis of supercoiled double-stranded DNA by a hybrid nuclease consisting of a short oligonucleotide selectively fused to staphylococcal nuclease.[3] Plasmid pUC19[4] was partially denatured in order to facilitate hybridization of the oligonucleotide-enzyme adduct[5] to DNA via D-loop formation[6] (Figure 1a). Both strands of the substrate were then efficiently hydrolyzed by the bound hybrid

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