Inorg. Chem. **1992,** *31,* 3342-3343

Synthesis and Molecular Structures of Diferrous Complexes Containing a Bis(hydroxo) or a Hydroxo Carboxylato Bridge

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Received March 30, 1992

Hemerythrin (Hr) is a dioxygen-transport protein for some marine worms.[1] DeoxyHr contains an asymmetric μ-hydroxo bis(μ-carboxylato) diferrous site. Dioxygen is terminally bound to the five-coordinate iron, resulting in a unique hydroperoxo adduct, as indicated below in Scheme I.[2] Although a number of μ-oxo bis(μ-carboxylato) diferric complexes have recently been reported as structural analogues for metHr,[3] only a few diferrous complexes are known.[4-7] These include an asymmetric diferrous complex having a tris(carboxylato) bridge reported by Lippard et al.[5] and an alkoxo-bridged complex reported by Que et al.[6] Both of these complexes possess open coordination sites and react with dioxygen. However, formation of a hydroperoxo species as in Hr cannot be mimicked with these complexes, since they do not contain a hydroxo bridge. The sole example of a diferrous complex containing a hydroxo bridge[7] is coordinatively saturated, and formation of a dioxygen adduct was not observed.

We recently reported a monomeric ferrous complex Fe(OBz)-(HB(3,5-iPr$_2$pz)$_3$) (**1**), which binds dioxygen reversibly.[8] When **1** was treated with aqueous NaOH, formation of a bis(μ-hydroxo) complex [Fe(HB(3,5-iPr$_2$pz)$_3$)]$_2$(OH)$_2$ (**2**) was noted. In a typical experiment, 420 mg of **1** was stirred in toluene (10 mL) with NaOH (0.5 N, 7 mL) under an argon atmosphere for 1 h. After removal of the aqueous phase, the toluene was evaporated to dryness. To the resulting solid was added 5 mL of MeCN. The insoluble portion of the solid was collected by filtration and dried under vacuum. Recrystallization of the solid from pentane at -20 °C afforded **2** as colorless crystals solvated with pentane (ca. 30% yield).[9] The X-ray analysis of **2**$\cdot$2C$_5$H$_{12}$ indicated that each asymmetric unit contains two independent molecules of **2**, each of which sits on a center of symmetry. The structure of one molecule is presented in Figure 1. The other molecule has an essentially identical structure. The Fe–OH distances found in **2** are typical for this type of bond.[7]

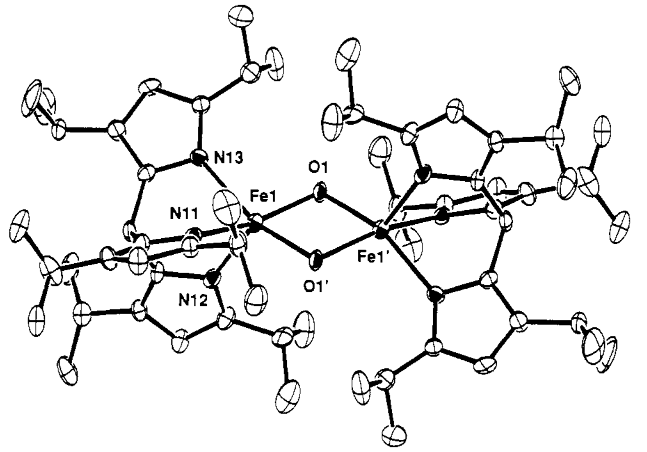
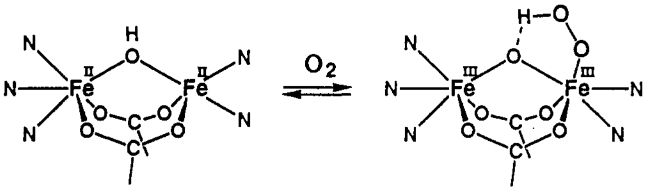


Figure 1. ORTEP view of [Fe(HB(3,5-iPr$_2$pz)$_3$)]$_2$(OH)$_2$ (**2**) (30% probability). The molecule sits on a center of symmetry. The n-C$_5$H$_{12}$ molecules of crystallization were omitted for clarity. Selected bond distances (Å) and angles (deg): Fel–O1, 2.016 (9); Fel–O1', 2.04 (1); Fel–N11, 2.19 (1); Fel–N12, 2.10 (2); Fe–N13, 2.22 (1); Fel–O1–Fel', 103.3 (5); O1–Fel–O1', 76.7 (5); Fel- -Fel', 3.179 (5). The structural parameters of the other crystallographically independent molecule are comparable (see the supplementary material).

Scheme I



The reaction of **2** with 1 equiv of benzoic acid in toluene gave [Fe(HB(3,5-iPr$_2$pz)$_3$)]$_2$(OH)(OBz) (**3**) quantitatively.[10,11] Single

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(9) Satisfactory elemental analysis was obtained for **2** dried under vacuum. Anal. Calcd for C$_{54}$H$_{94}$N$_{12}$O$_2$B$_2$FE$_2$: C, 60.24; H, 8.80; N, 15.61. Found: C, 60.50; H, 8.99; N, 15.27. IR (KBr; cm^{-1}): ν(BH) 2533. The ν(OH) band was not observed clearly. ^{1}H-NMR (toluene-d_8, 25 °C; δ, ppm): -14.4 (4 H), -2.2 (36 H), 4.9 (36 H), 13.5 (6 H), 49.2 (6 H). **2**$\cdot$2C$_5$H$_{12}$ (C$_{64}$H$_{118}$N$_{12}$O$_2$B$_2$Fe$_2$; fw 1221.04) crystallized in the triclinic space group $P\bar{1}$ with a = 14.576 (5) Å, b = 22.508 (4) Å, c = 14.140 (5) Å, α = 93.18 (3)°, β = 126.28 (2)°, γ = 97.99 (3)°, V = 3648 (2) Å^3, and Z = 2. The data ($2° < 2\theta < 40°$) were collected at -50 °C. The refinement based on 3531 reflections ($F_o > 6\sigma(F_0)$) converged to the current R (R_w) factor of 6.3% (6.9%).

(10) Anal. Calcd for C$_{61}$H$_{98}$N$_{12}$O$_3$B$_2$Fe$_2$: C, 62.05; H, 8.37; N, 14.23. Found: C, 61.88; H, 8.40; N, 14.33. IR (KBr; cm^{-1}): ν(OH) 3647, ν(BH) 2524, ν(C=C) 1593, ν(COO) 1531. ^{1}H-NMR (toluene-d_8, 25 °C; δ, ppm): -6.6 (2 H), -1.6 (36 H), 4.2 (36 H), 9.6 (5 H), 10.0 (6 H), 46.6 (6 H). **3**$\cdot$3MeCN (C$_{67}$H$_{107}$N$_{15}$O$_3$B$_2$Fe$_2$; fw 1304.00) crystallized in the monoclinic space group $P2_1$ with a = 17.928 (11) Å, b = 12.523 (3) Å, c = 17.313 (6) Å, β = 96.55 (4)°, V = 3862 (3) Å^3, and Z = 2. The current R (R_w) value is 5.8% (3.8%) for 3714 reflections ($2° < 2\theta < 45°$, $F_o > 6\sigma(F_o)$) collected at -65 °C.

(11) The reaction of **2** with 1 equiv of acetic acid gave [Fe(HB(3,5-iPr$_2$-pz)$_3$)]$_2$(OH)(OAc), whose X-ray structure was determined. The core structure is essentially identical to that of **3**. The details will be published elsewhere.

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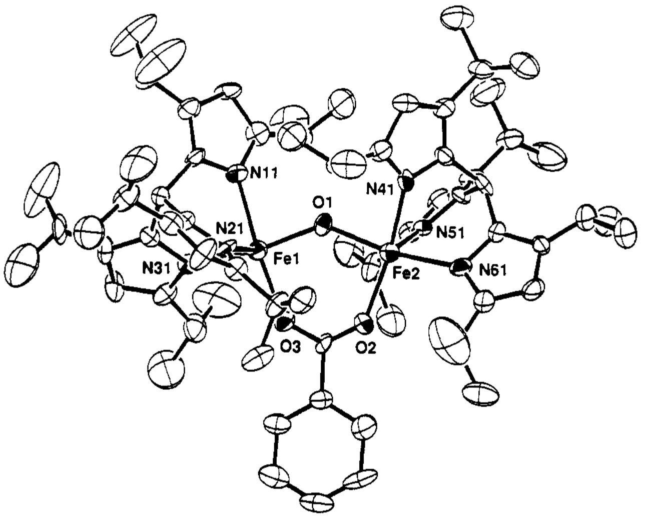

Figure 2. ORTEP view of [Fe(HB(3,5-iPr$_2$pz)$_3$)]$_2$(OH)(OBz) (3) (50% probability). The MeCN molecules of crystallization were omitted for clarity. Selected bond distances (Å) and angles (deg): Fe1–O1, 1.964 (5); Fe1–O3, 2.102 (5); Fe1–N11, 2.218 (6); Fe1–N21, 2.077 (7); Fe1–N31, 2.126 (6); Fe2–O1, 1.993 (5); Fe2–O2, 2.071 (5); Fe2–N41, 2.234 (7); Fe–N51, 2.157 (8); Fe1–N61, 2.102 (7); Fe1–O1–Fe2, 137.0 (3); Fe1- -Fe2, 3.681 (3).

crystals of $3\cdot 3$MeCN were obtained by recrystallization from MeCN at –20 °C. Given in Figure 2 is the ORTEP view of **3**, representing a novel μ-hydroxo μ-carboxylato diferrous core.[12] The Fe–OH distances of 1.96 and 1.99 Å are comparable to the average Fe–OH distances reported for deoxyHr (2.02 Å) on the basis of the 2.0-Å resolution X-ray analysis,[13] while the Fe–OH–Fe core in deoxyHr is asymmetric (Fe–OH: 2.15 (4) and 1.88 (3) Å). The Fe–Fe separation (3.68 Å) and Fe–O–Fe angle (137°) of **3** are considerably different from those of deoxyHr (3.32 Å and 111° from the X-ray structure; although the Fe–Fe separation estimated by EXAFS is 3.57 Å[14]). This structural inconsistency may be associated with more steric flexibility of the μ-hydroxo μ-carboxylato bridge than of the μ-hydroxo bis(μ-carboxylato) bridge, in conjunction with the highly steric hindrance of HB-(3,5-iPr$_2$pz)$_3$. Several diferric complexes containing a μ-oxo μ-carboxylato bridge are known.[15] The Fe–Fe separations in these complexes are in the range of 3.2–3.3 Å. The shorter Fe–Fe separations found in the μ-oxo diferric complexes than that in **3** reflect the short Fe–O distances (ca. 1.8 Å). The resting coordination sites of the irons in **3** are occupied by the pyrazolylborate ligand, constructing five-coordinate geometries about the irons. The geometry around each iron may be described as square-pyramidal with the apical ligands being N21 and N51 for Fe1 and Fe2, respectively. Thus, each iron possesses an open coordination site and these sites are oriented trans to each other.

Complex **2** is extremely oxygen sensitive. When a solution of **2** in pentane was treated with 1 atm of O$_2$ at –78 °C, the color immediately changed to dark green and was further converted into brownish orange within a few minutes. The reaction of **3** with O$_2$ at –78 °C gave a moderately stable dark green solution, which was noted to decompose irreversibly to a dark orange complex when warmed to –40 °C. These observations may implicate the formation of dioxygen adducts, while the adduct of **2** is apparently much more unstable than that of **3**.

The reactivities of **2** and **3** under O$_2$ were explored; if the dioxygen adducts are hydroperoxo species, such complexes are expected to be highly reactive for oxo-transfer reactions.[16] When 10 equiv of PPh$_3$ was stirred with **2** under 1 atm of O$_2$ for 1 h at –78 °C, formation of OPPh$_3$ was noted in 39% yield based on **2**. The same reaction with **3** yielded 17% OPPh$_3$. No epoxidation of cyclohexene, however, proceeded with oxygenated **2** or **3**. Thus, the oxygenated species formed from **2** or **3** may be effective for oxo-transfer reactions, although the reactivities are not markedly high.

The detailed magnetic properties of **2** and **3** and the structures and reactivities of the oxygenated products of **2** and **3** are now under investigation.

Acknowledgment. This research was supported in part by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, and Culture (03241106).

Supplementary Material Available: A textual presentation of the X-ray experimental details for $2\cdot 2C_5H_{12}$, figures showing the atomic numbering of $2\cdot 2C_5H_{12}$ and $3\cdot 3$MeCN, and tables giving atomic coordinates, anisotropic thermal parameters, and bond distances and angles for $2\cdot 2C_5H_{12}$ and $3\cdot 3$MeCN (32 pages); listings of observed and calculated structure factors for $2\cdot 2C_5H_{12}$ and $3\cdot 3$MeCN (51 pages). Ordering information is given in any current masthead page.

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