(μ-Oxo)bis(μ-acetato)bis(tri-1-pyrazolylborato)diiron(III), [(HBpz$_3$)FeO(CH$_3$CO$_2$)$_2$Fe(HBpz$_3$)]: Model for the Binuclear Iron Center of Hemerythrin

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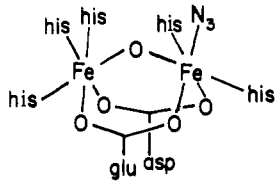
Structural studies[1,2] of the invertebrate respiratory proteins hemerythrin and myohemerythrin[3] in their azidomet forms revealed a binuclear, oxo-bridged diiron(III) center supported by



asp = aspartate; glu = glutamate; his = histidine

two additional glutamate and aspartate bridging ligands. Related bridged binuclear iron units are thought to occur in ribonucleotide reductase of *Escherichia coli*[4] and in purple acid phosphatases from various sources.[5] Although (μ-oxo)diiron(III) complexes have been intensively studied by inorganic chemists,[6] an exact replica of the (μ-oxo)bis(μ-acetato)diiron(III) core has not previously been obtained. Here we report the synthesis, X-ray crystal structure determination, and physical characterization of [(HBpz$_3$)FeO(CH$_3$CO$_2$)$_2$Fe(HBpz$_3$)] (**1**), a compound that faithfully mimics the geometric, magnetic, and electronic spectral properties of the diiron(III) center in the methemerythrin and metmyohemerythrin.

Compound **1** was prepared by "spontaneous self-assembly"[7] as follows. To a solution containing 9.98 g (18.7 mmol) of Fe(ClO$_4$)$_3$·10H$_2$O, 5.90 g (43.4 mmol) of NaOAc·3H$_2$O, and 200 mL of H$_2$O was added a solution of 5.10 g (21.6 mmol) of sodium tri-1-pyrazolylborate (NaHBpz$_3$) in 100 mL of water with rapid stirring. The resulting brown suspension was stirred for 10 h during which time it turned deep red. The solid was filtered from the reaction mixture, washed with water and acetonitrile to remove [Fe(HBpz$_3$)$_2$]$^+$ salts,[8] and dried in the air. Recrystallization from acetonitrile gave dark brown-green crystals of the acetonitrile solvate suitable for X-ray diffraction studies. Removal of the solvent in vacuo yielded 2.1 g (33%) of analytically pure **1**.[9]

The structure[10] of **1**, shown in Figure 1, consists of an oxo-bridged diiron(III) center linked by two additional acetate bridges.

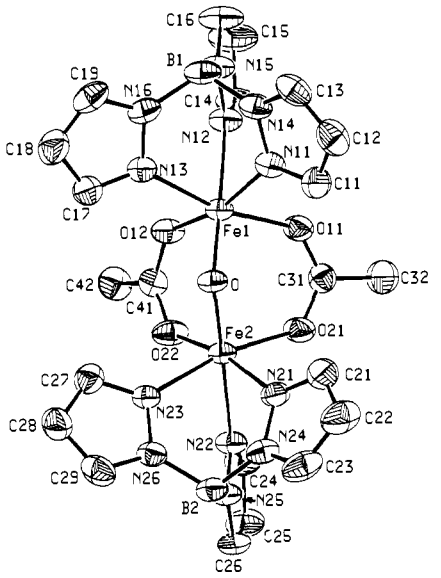


Figure 1. Structure of (μ-oxo)bis(μ-acetato)bis(tri-1-pyrazolylborato)diiron(III) (**1**) showing the 40% probability thermal ellipsoids and atom labeling scheme. The molecule has nearly perfect C_{2v} symmetry. Hydrogen atoms are omitted for clarity.

Table I. Structural Features of the Binuclear Iron(III) Centers of Azidomethemerythrin,[a] Azidometmyohemerythrin,[b] and the [(HBpz$_3$)FeO(O$_2$CCH$_3$)$_2$Fe(HBpz$_3$)] Model Compound (**1**)[c]

bond length, Å, or angle, deg[d]	azidomet-hemerythrin	azidometmyo-hemerythrin	**1**[e]
Fe(1)-O	1.89	1.80	1.783 (2)
Fe(2)-O	1.64	1.77	1.787 (2)
Fe(1)-O-Fe(2)	135	132	123.5 (1)
Fe(1)···Fe(2)	3.25	3.26	3.145 (1)
Fe(1)-O(11)	2.24	2.10	2.041 (3)
Fe(1)-O(12)	2.16	2.12	2.042 (2)
Fe(2)-O(21)	2.33	2.22	2.049 (3)
Fe(2)-O(22)	2.20	2.09	2.042 (2)
Fe(1)-N(11)	2.13	2.05	2.153 (3)
Fe(1)-N(12)	2.29	2.17	2.197 (3)
Fe(1)-N(13)	2.27	2.06	2.154 (3)
Fe(2)-N(21)	2.25	2.08	2.149 (3)
Fe(2)-N(22)	2.22	2.15	2.177 (3)
Fe(2)-N(23)	2.34	2.01	2.149 (3)

[a] Reference 1b. [b] Reference 2b. [c] This work. [d] Atoms are labeled as shown in Figure 1. For the proteins, N(11)-N(13) refer to His 77, His 73, and His 101 (or 106 for azidometmyohemerythrin, respectively; O(11), O(21) to Glu 58; O(12), O(22) to Asp 106 (111); N(21) and N(22) to His 54 and His 25, respectively; and N(23) to the azide nitrogen atom. [e] Numbers in parentheses are estimated standard deviations in the last digit listed. It is difficult to estimate the errors in the corresponding values for the two protein structure determinations. It should be noted, however, that they were refined with different restraints on metal-ligand distances.

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(9) Analytical and spectroscopic data. Anal. Calcd for $Fe_2C_{22}H_{26}B_2N_{12}O_5$ (**1**): C, 39.33; H, 3.90; N, 25.02; Fe, 16.63. Found: C, 39.95; H, 4.17; N, 25.18; Fe, 16.71. Electronic spectrum in chloroform: λ 262 nm (ϵ 6750 cm^{-1} M^{-1}), 339 (9270), 358 (sh), 457 (1010), 492 (920), 528 (sh), 695 (140), 995 (7). Proton NMR spectrum at 294 K in $CDCl_3$: δ -12.25 (br), -10.46 (br).

(10) X-ray analysis: The compound [(HBpz$_3$)FeO(O$_2$CCH$_3$)$_2$Fe(HBpz$_3$)]·4CH$_3$CN crystallizes in the monoclinic system, space group $P2_1/n$, with a = 13.236 (1) Å, b = 15.414 (2) Å, c = 21.697 (2) Å, β = 107.26(1)°, V = 4227.3 Å^3, ρ_{obsd} = 1.319 (9) g cm^{-3}, ρ_{calcd} = 1.313 g cm^{-3}, Z = 4. With the use of 4760 unique observed reflections collected with Mo Kα (λ = 0.7107 Å) radiation out to 2θ = 50° on a single-crystal X-ray diffractometer, the structure was solved by standard Patterson and difference Fourier methods and refined anisotropically to a current value for the discrepancy index R_1 of 0.042. Atomic positional and thermal parameters are provided as supplementary material. Full details will be reported elsewhere.

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Two tridentate tri-1-pyrazolylborate ligands cap the two ends of the cluster, resulting in a confacial bioctahedral structure that is nearly congruent with the diiron(III) core geometries of azidomet forms of hemerythrin and myohemerythrin (Table I). The Fe-N and Fe-O(acetate) bond lengths are those typical of high-spin iron(III)[11] while the Fe-O(oxo) distances also agree well with literature values for antiferromagnetically coupled oxo-bridged high-spin diiron(III) compounds.[6] The two equivalent Fe-O(oxo) bond lengths and the significantly larger Fe-N bond distances trans to the bridging oxo ligand in the model compound compare well with results for the azidometmyohemerythrin structure (Table I). The latter feature reflects the greater structural trans influence[12] of oxo compared with carboxylato oxygen donor ligands.

Magnetic susceptibility data for solid **1**, obtained by the Faraday method in the range 4.2 K $\leq T \leq$ 296 K, were fit to the expression[6,13] for χ_M vs. T derived from the spin exchange Hamiltonian, $H' = -2JS_1S_2$, with $S_1 = S_2 = {}^5/_2$. Antiferromagnetic behavior was apparent from the calculated J value of -122 cm^{-1}, which compares favorably with $J = -134$ cm^{-1} reported for metaquohemerythrin.[14] The effective room-temperature moment of 1.67 μ_B per iron for solid **1** agrees with the value of $\mu_{eff} = 1.71$ μ_B per iron measured by the Evan's method[15] at 294 K in 16 mM $CDCl_3$ solution. This result demonstrates that the bridged binuclear structure persists in solution. Especially noteworthy are the presence of 695 nm (ϵ 140 M^{-1} cm^{-1}) and ~990 nm (ϵ 7 M^{-1} cm^{-1}) ligand field bands in the solution optical spectrum of **1**,[9] features characteristic of oxy and all methemerythrin derivatives.[3,16] The proton NMR spectrum of a 16.1 mM $CDCl_3$ solution of **1** exhibits two broad resonances[9] tentatively assigned to the pyrazole ring protons H(4) and H(5). Paramagnetically shifted histidine proton resonances have not yet been identified in the ^{1}H NMR spectra of hemerythrin derivatives.[17]

In summary, the (μ-oxo)bis(μ-carboxylato)diiron(III) core of met- and metmyohemerythrin has been assembled. Its structural and physical properties provide valuable bench marks against which the features of hemerythrin derivatives may be judged. Moreover, the present study provides a foundation for further synthetic chemistry required to mimic the reversible oxygen binding of hemerythrin and to help characterize the diiron centers in ribonucleotide reductase, the purple acid phosphatases, and related nonheme iron proteins.

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Registry No. **1**·4CH$_3$CN, 86177-71-1.

Supplementary Material Available: Table of atomic positional and thermal parameters for compound **1** (2 pages). Ordering information is given on any current masthead page.

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Location of Internal Hydrogen Atoms in the Paradodecatungstate Polyanion by Neutron Diffraction

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The isopolyanion paradodecatungstate $[H_2W_{12}O_{42}]^{10-}$ has been studied by X-ray diffraction in six different compounds: (1) $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 10H_2O$ (orthorhombic),[1] (2) $(NH)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ (monoclinic),[2] (3) $Na_2(NH_4)_8[H_2W_{12}O_{42}]\cdot 12H_2O$ (orthorhombic),[3] (4) $(NH_4)_6H_4[H_2W_{12}O_{42}]\cdot 10H_2O$ (triclinic),[4] (5) $Mg_5[H_2W_{12}O_{42}]\cdot 38H_2O$ (triclinic),[5] (6) $Na_{10}[H_2W_{12}O_{42}]\cdot 20H_2O$ (triclinic).[6] The first full structure analysis by Allmann[1] firmly established the oxygen complement of the molecule ion as 42. The basicity of its salts commonly is 10 and has never been observed to exceed this value. It has long been suspected that the two nonreplaceable protons are located in some protected site within the molecule. Lunk et al.[7] have obtained direct evidence for the existence of these special protons from an NMR study of solid Na, K, and Li salts. They observed a line of medium breadth that does not shift but increases in intensity with dehydration and is distinct from the broad lines of intermolecular H_2O. From the line position, they calculate that the two protons within the molecule are separated by 2.22 (2) Å.

The Keggin-type, metadodecatungstic acid molecule $[H_2W_{12}O_{40}]^{6-}$ also contains two nonlabile H atoms, and these have been detected in similar fashion by Spicyn et al.[8] in solid Li, Na, and K salts. In solution, a sharp NMR signal for the nonlabile H atoms has been found in metadodecatungstic acid,[9,10] but no such signal can be detected for the paradodecatungstate[10] ion. These observations support the hypothesis that two H atoms are strongly bound internally in both the meta and para complexes but more strongly in the former than the latter.

The specific location of the H atoms in the paradodecatungstate molecule was first considered in detail by D'Amour and Allmann[2] in $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$. As with most X-ray structure determinations of such compounds, no direct evidence for the location of the two molecular H atoms could be obtained, but these authors inferred probable locations from an analysis of interatomic distances and bond-strength distributions in the molecule. Their argument leading to an association of H with an interior O atom triply shared with three W atoms is convincing, but their proposition that H lies nearly in line with another O atom to one side of the pseudomirror plane is more tenuous. Clearly, a neutron diffraction study is needed to settle the question of the H locations. We have carried out such a study, and report the results pertaining to this problem below. Full details of the structure analysis and

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