Synthesis and Characterization of a New Class of Asymmetric Aqua−Acetate Bridged Dimers. Solid State Molecular Structures of the $[M_2(\mu\text{-}H_2O)((\mu\text{-}OAc)_2(OAc)_3(Py)_2]^-$ Anions (M = Mn(II), Fe(II), Co(II)). A Structural Model for the Fe_2 Site in Methane Monooxygenase

D. Coucouvanis,* R. A. Reynolds III, and W. R. Dunham

Department of Chemistry
The University of Michigan
Ann Arbor, Michigan 48109-1055

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Non-heme, non-sulfur, iron proteins that contain dinuclear iron sites are widely distributed in nature, and their function is mainly in the transport of oxygen, the oxygenation of various substrates, and the activation of dioxygen.[1] Representative examples of these proteins include the hemerythrins,[2] Hr, the methane monooxygenases,[3] MMO, and ribonucleotide reductase,[4] RRB2. The biological importance of bridged dinuclear iron structural units has stimulated extensive studies in the synthesis of analog complexes. A large number of complexes that contain diiron μ-oxo or μ-hydroxo dibridged or tribridged centers have been synthesized and characterized in detail.[5] The vast majority of the bridging units in these compounds contain μ-*O,O*-carboxylate ligands in addition to the μ-oxo or μ-hydroxo ligands. Rare among these "model" complexes are those that contain the reduced, diferrous−μ-aqua structural unit. Indeed, the $Fe_2(H_2O)(O_2CR)_4(tmen)_2$ complex (R = Me, Ph; tmen = *N,N,N′,N′*-tetramethyl-1,2-diaminoethane), a symmetric, neutral molecule, is the first example and was reported only recently.[6]

The structure of methane monooxygenase, MMO, from *Methylococcus capsulatus* has been determined at a 2.2 Å resolution[7] and reveals an asymmetric bis(μ-carboxylato)(μ-OH)Fe^{III}_2 dimer (Figure 1B).

With very few exceptions the known diiron, dibridged or tribridged, synthetic analog complexes are symmetric with the two iron subunits related by approximate (or real) mirror planes or 2-fold axes. The terminal ligand coordination of the iron atoms in many of these complexes is effected by tridentate chelates[8−10] such as 1,4,7-triazacyclononane,[8] TACN, tris-1-pyrazolylhydroborate), $[HB(pz)_3]^-$,[9] or tris(2-pyridylmethyl)-amine, tpa.[10] These tridentate ligands impart stability to the dimers; however, the thermodynamic stability associated with the chelate effect may preclude ligand dissociation or the potential for coordination unsaturation often important in function and chemical reactivity.

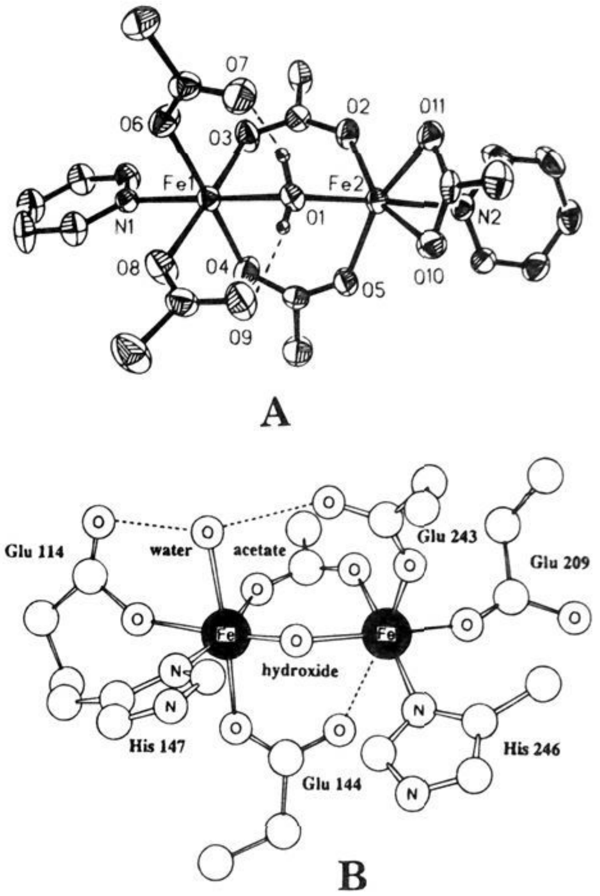

Figure 1. Structure and labeling of **A**, the anion in the $Et_4N[Fe_2(AcO)_5(H_2O)(py)_2]$ salt (the corresponding Mn and Co complexes are X-ray isomorphous and isostructural; thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces), and **B**, the active site in methane monooxygenase, MMO, recently reported in ref 7. Selected structural parameters for, respectively, **II**, **III**, and **IV**: (distances) M−M, 3.618(3), 3.577(2), and 3.548(2) Å; M−O (μ-H_2O), 2.252(7), 2.111(6); 2.206(6), 2.148(5); and 2.146(6), 2.111(5) Å; M−O (μ-OAc), 2.14(2,4), 2.09(2,4), and 2.06(1,4) Å; M−O (η^1-OAc), 2.141(8), 2.147(7); 2.110(5), 2.098(5); and 2.084(5), 2.068(6) Å; M−O (η^2-OAc), 2.259(7), 2.262(8); 2.195(6), 2.228(4); and 2.183(5), 2.181(6) Å; O (μ-OAc)−H (μ-H_2O), not observed; 1.68(7), 1.87(8); and 1.70(8), 1.82(6) Å; O (η^1-OAc)−O (μ-H_2O), 2.60(1), 2.547(10); 2.574(7), 2.615(8); and 2.573(8), 2.612(9) Å; M−N (py), 2.290(9), 2.314(8); 2.210(6), 2.222(6); and 2.167(6), 2.173(6) Å; (angles) M−O(H_2O)−M, 108.3(3), 110.5(2), and 112.9(2)°. The first number in parentheses represents the larger of the individual standard deviations or the standard deviation from the mean, $\sigma = [\sum_{i=1}^{N}(x_i - x)^2/N(N-1)]^{1/2}$; the second represents the number of chemically equivalent bonds averaged out.

Dinuclear Mn sites[10b] are present in the pseudocatalases from *Lactobacillus plantarum*[11] and *Thermus thermophilus*[12] where they catalyze the disproportionation of H_2O_2, and in certain ribonucleotide reductases (RR) where they catalyze the reduction of ribonucleotides to deoxyribonucleotides.[13] The coordination chemistry of oligomeric manganese complexes relevant to biological sites is extensive.[14,15] Among these complexes are included dimeric Mn(II) complexes represented by the symmetric $[Mn_2(F_5C_2COO)_4(H_2O)_3L_2]$[16] and the ($\mu$-aqua)bis($\mu$-carboxylato)$(L)_2Mn^{II}_2$ complexes.[17]

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Table 1. Summary of Interatomic Distances (Å) and Angles (deg) in $Et_4N[Mn_2(AcO)_5(H_2O)(py)_2]$ (**II**), $Et_4N[Fe_2(AcO)_5(H_2O)(py)_2]$ (**III**), and $Et_4N[Co_2(AcO)_5(H_2O)(py)_2]$ (**IV**)

	II	**III**	**IV**
		Distances (Å)	
M−M	3.618(3)	3.577(2)	3.548(2)
M−O (μ-H_2O)	2.252(7), 2.111(6)	2.206(6), 2.148(5)	2.146(6), 2.111(5)
M−O (μ-OAc)[a]	2.14(2,4)	2.09(2,4)	2.06(1,4)
M−O (η^1-OAc)	2.141(8), 2.147(7)	2.110(5), 2.098(5)	2.084(5), 2.068(6)
M−O (η^2-OAc)	2.259(7), 2.262(8)	2.195(6), 2.228(4)	2.183(5), 2.181(6)
O (μ-OAc)− H (μ-H_2O)	*b*	1.68(7), 1.87(8)	1.70(8), 1.82(6)
O (η^1-OAc)− O (μ-H_2O)	2.60(1), 2.547(10)	2.574(7), 2.615(8)	2.573(8), 2.612(9)
M−N (py)		2.210(6), 2.222(6)	2.167(6), 2.173(6)
		Angles (deg)	
M−O (H_2O)−M	108.3(3)	110.5(2)	112.9(2)

[a] The first number in parentheses represents the larger of the individual standard deviations or the standard deviation from the mean, $\sigma = [\sum_{i=1}^{N}(x_i - x)^2/N(N-1)]^{1/2}$; the second represents the number of chemically equivalent bonds averaged out. [b] The hydrogen atoms of the water molecule were not found in the electron density maps of this structure.

In this Communication we report the synthesis,[18] structural characterization, and spectroscopic properties of the isomorphous and isostructural Et_4N^+ salts of the $[py(\eta^1\text{-AcO})_2M(\mu\text{-}H_2O)(\mu\text{-}O,O\text{-AcO})_2M(\eta^2\text{-AcO})(py)]^-$ complexes (M = Mn, Fe, Co), a new class of asymmetric, μ-aqua, bis(μ-acetato) bimetallic complexes with divalent metal ions. The structures of these complexes have been determined.[19] The anions (Figure 1A) show an *asymmetric* dimeric core with two bridging acetate ligands and a bridging water molecule. Notwithstanding differences in the oxidation states of the Fe atoms and the nature of the carboxylate and single oxygen donor bridges the structure of the $[Fe_2(AcO)_5(H_2O)(py)_2]^-$ anion (**III**) is very similar to the structure of the Fe_2 site in MMO.[7]

A summary of bond distances and angles of **II**, **III**, and **IV** is shown in Table 1. The Fe−Fe distance in **III** compares with the Fe(II)−Fe(II) distances in $Fe_2(\mu\text{-}H_2O)(O_2CR)_4(tmen)_2$[6] (3.653(2) Å) and deoxyhemerythrin[20] (3.57 Å) and, as expected, is longer than the Fe(III)−Fe(III) in MMO (3.4 Å).[1f,7] In **II** the Mn−Mn distance is similar to distances reported for the $[Mn_2(F_5C_2COO)_4(H_2O)_3L_2]$ complex[16] and the (μ-aqua)bis(μ-carboxylato)$(L)_2Mn^{II}_2$ complexes,[17] respectively, at 3.739(2) Å and 3.5950(9) and 3.621(2) Å. The Co−Co distance in **IV** compares to distances in the $Co_2(\mu\text{-}OH_2)(COOR)_4(tmen)_2$ complexes[21] reported between 3.597 and 3.696 Å. In general the M−O and M−N distances in the complexes differ as expected for the differences in the ionic radii[22] of the six-coordinate, high-spin divalent metal ions in each dimer (Mn, 0.97 Å; Fe, 0.92 Å; Co, 0.89 Å). The M−O(H_2O)−M angle *increases* from Mn to Co. This reflects a change that minimizes M−M repulsions. The latter would be more pronounced if the dimers with the shorter M−μ-L bonds (**III** and **IV**) were to retain the more acute angle (108.3°) found in **II.** In the structures of **II**−**IV** the μ-H_2O ligand is hydrogen bonded to the monodentate acetate ligands (both bound to one of the two M atoms). In the structures of **III** and **IV** the hydrogen atoms were located and successfully refined.

The Mossbauer spectrum of **III** in the solid state at 125 K shows only one sharp quadrupole doublet (δ(Fe) =1.30(1) mm/s, ΔE_q = 2.00 mm/s, fwhm[23] = 0.15 mm/s). A single sharp quadrupole doublet also was obtained in frozen pyridine solution (δ = 1.18(1) mm/s, ΔE_q = 2.96 mm/s, fwhm [23] = 0.20 mm/s). The δ value for the solid **III** is similar to isomer shifts reported for the $Fe_2(H_2O)(O_2CR)_4(tmen)_2$ complex[6] MMO_{red}[1f] and $RRB2_{red}$[1d,g] at 1.25, 1.27, and 1.30 mm/s and 1.26 and 1.27 mm/s, respectively. The difference between the solid state and solution Mossbauer measurements suggests a change in the structural or even stoichiometric identity of **III** in pyridine solution.[24] The appearance of only one doublet in the solid state Mossbauer spectrum, unexpected for the asymmetric structure of **III**, reflects very similar electric field gradients at the two Fe sites. The magnetic moments of **II**, **III** and **IV** (μ_{eff}^{corr} (μ_B.) at 250 and 4.2 K) are 7.67 and 2.16, 7.62 and 4.37, and 6.76 and 4.72, respectively. Preliminary fits of the magnetic data have been obtained with exchange coupling constants *J* of −1, −0.2, and −0.2 cm^{-1}, respectively, for **II**, **III**, and **IV** ($H = -2JS_1S_2$). These results and saturation magnetization studies show that the metal ions in the dimers are only weakly antiferromagnetically coupled.[25] The EPR spectrum of **II** in pyridine solution shows a broad multiline signal (>25 lines) centered around g =2 with a principal splitting of 8.6 mT. Studies of the reactivities of **II**, **III**, and **IV** presently are under way in our laboratory. Interest in the chemistry of **III** derives from the need to understand the function of MMO and the possible structural similarity of this molecule to species present in the hydrocarbon-oxidizing Gif systems.[26] The latter use dioxygen or peroxide as oxidants and consist of mixtures of an iron source and carboxylic acids in pyridine solution.

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Supporting Information Available: Figures showing the EPR spectrum of **II** in pyridine solution at 84 K and the EPR spectra of the low-field regions of **II**, **III**, and **IV**, text describing the analytical, structural, and spectroscopic data and magnetic properties, and tables S1, S2, and S3 containing listings of positional parameters, thermal parameters, and selected distances and angles of **II**, **III**, and **IV** (35 pages); tables S4, S5, and S6 lisiting the calculated and observed structure factors for **II**, **III**, and **IV** (49 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(18) A typical synthetic procedure is as follows: To a solution of 2 mmol of $M^{II}(OAc)_2{\cdot}4H_2O$ (M = Mn, Fe, Co) in 35 mL of pyridine is added 1 mmol of $Et_4N(OAc){\cdot}4H_2O$. After standing for 1.5 h, the solution is filtered and 75 mL of diethyl ether is added to the filtrate. Upon standing, crystals of the $Et_4N[M_2(AcO)_5(H_2O)(py)_2]$ complexes form and are isolated in yields >80%. Satisfactory analytical data have been obtained for all of these complexes. These data and spectroscopic characterization data have been deposited as supporting information.

(19) **II**, **III**, and **IV** are X-ray isomorphous and isostructural. Unit cell dimensions for **III** are a = 18.085(6) Å, b = 10.955(4) Å, c = 18.273(7) Å, and β = 108.58(3). Exact unit cell dimensions for **II** and **IV** and details regarding data collection and refinement have been deposited as supporting information. At the conclusion of refinement, R = 0.059, 0.043, and 0.047, respectively, for **II**, **III**, and **IV**.

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(24) The electronic spectrum of **III** in CH_2Cl_2 solution (where most likely the anion retains the crystallographically determined structure) is featureless. The spectrum changes dramatically upon addition of even small amounts of pyridine and develops a new broad band centered around 375 nm (ϵ = ~4000).

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