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Inorganic Chemistry

Communications

A General Method for Assembling (μ-Oxo)bis(μ-carboxylato)diiron(III) Complexes with Labile Terminal Sites Using a Bridging Dicarboxylate Ligand

Structural and spectroscopic models of the (μ-oxo)bis(μ-carboxylato)diiron(III) center found in the marine invertebrate respiratory protein hemerythrin (Hr)[1] have been synthesized with a variety of facially coordinating tridentate ligands.[2] In order to mimic the functions of Hr and the related diiron proteins ribonucleotide reductase (RR)[3] and methane monooxygenase (MMO),[4] new model complexes are required having vacant or labile terminal coordination sites. These positions are necessary to bind or otherwise react with dioxygen. One synthetic approach to such compounds is to use bidentate, rather than tridentate, ligands to coordinate to the terminal positions of the triply bridged core. Early attempts to apply this tactic in self-assembly syntheses yielded only tetranuclear complexes, specifically $[Fe_4O_2(O_2CCH_3)_7(H_2B(pz)_2)_2]^-$,[5] $[Fe_4O_2(O_2CCH_3)_7B_2]^+$ (B = bpy, 4,4′-Me$_2$bpy, TMEDA),[6,7] and $[Fe_4O_2(O_2CPh)_4(BICO)_2(BICOH)_2]^{2+}$.[8,9] More recently, however, $[Fe_2O(O_2CCH_3)_2(bpy)_2Cl_2]$ was successfully prepared by cleavage of $[Fe_4O_2(O_2CCH_3)_7(bpy)_2](ClO_4)$ in the presence of excess bipyridine and Et_4NCl.[7]

In the present communication we describe a general synthetic route for assembling $[Fe_2O(MPDP)B_2M_2]$ complexes having terminal bidentate (B) nitrogen donors and labile monodentate (M) ligands. The key to this chemistry is the bridging dicarboxylate ligand *m*-phenylenedipropionate (MPDP^{2-}),[10] which was designed such that the distance between the β-methylene carbon atoms matches the 6-Å span between acetate methyl groups in $[Fe_2O(O_2CCH_3)_2(HBpz_3)_2]$ (**1**)[11] (Chart I). The bidentate ligands, B, include 4,4′-Me$_2$bpy, BIPhMe,[12] and TMICMe[13] (Chart I). The latter two polyimidazole ligands afford a more accurate representation of the histidine environment found in Hr,[14] RR,[15] and MMO.[16]

Chart I

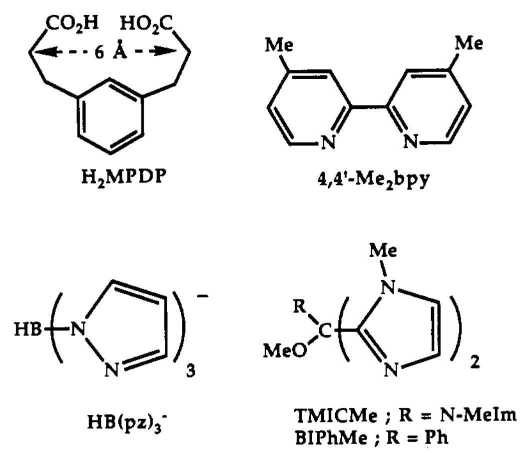

Table I. Selected Interatomic Distances (Å) and Angles (deg) for Compounds **2**–**4** and metN$_3$myoHr

structural properties[a]	**2**	**3**	**4**	metN$_3$-myoHr[b]
Fe–O	1.797 (4)	1.771 (3)	1.783 (5)	1.77
	1.793 (5)	1.774 (3)	1.790 (4)	1.80
Fe–Cl		2.358 (2)	2.428 (2)	
		2.376 (2)	2.413 (2)	
Fe–O–Fe	123.4 (3)	124.0 (2)	125.9 (2)	130
Fe⋯Fe	3.161 (1)	3.130 (1)	3.183 (2)	3.23
Fe–N$_{cis}$(av)	2.135 (7)	2.155 (4)	2.119 (5)	2.13
Fe–N$_{trans}$(av)	2.211 (7)	2.200 (4)	2.159 (6)	2.24
Fe–O$_{COO}$(av)	2.053 (5)	2.100 (4)	2.077 (5)	2.10
Fe–O$_{COO\ trans}$(av)		2.177 (4)	2.109 (5)	2.18
Fe–O$_{COO\ cis}$(av)		2.025 (3)	2.045 (5)	2.05

[a] Fe–N$_{cis/trans}$ designates iron–nitrogen bonds situated, respectively, cis or trans to the bridging oxo ligand. Fe–O$_{COO\ cis/trans}$ designates a carboxylate oxygen atom positioned adjacent or opposite to a terminal chloride. [b] Reference 14a.

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(9) Abbreviations used: bpy, 2,2′-bipyridine; 4,4′-Me$_2$bpy, 4,4′-dimethyl-2,2′-bipyridine; $H_2B(pz)_2^-$, dihydrobis(1-pyrazolyl)borate; TMEDA, *N,N′,N″,N‴*-tetramethylethylenediamine; BICOH, 2,2′-bis(1-methylimidazolyl)hydroxymethane; H$_2$MPDP, *m*-phenylenedipropionoic acid; $HB(pz)_3^-$, hydrotris(1-pyrazolyl)borate; BIPhMe, 2,2′-bis(1-methylimidazolyl)phenylmethoxymethane; TMICMe, 2,2′,2″-tris(1-methylimidazolyl)methoxymethane.

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Table II. Comparison of Spectroscopic and Magnetic Properties of **2–5** and metClHr

physical data	**2**	**3**	**4**	**5**	metClHr
		Electronic Spectral Data			
λ_{max}, nm (ϵ/Fe, cm^{-1} mol^{-1} L[a])	341 (4600) 365 (sh) 460 (440) 493 (400) 533 (sh) 698 (60)	328 (sh) 365 (sh) 462 (450) 483 (400) 535 (sh) 655 (70)	341 (3000) 360 (sh) 483 (400) 525 (sh) 682 (90)	335 (3220) 356 (sh) 475 (380) 485 (350) 530 (sh) 684 (60)	329 (3300)[b] 380 (3000) 490 sh (375) 656 (90)
		Vibrational Spectroscopic Data			
ν_s(Fe–O–Fe), cm^{-1} [c]	526	532	522	524	507[d]
		Magnetic[e] and Mössbauer[f] Data			
$-J$, cm^{-1}	[g]	119	122	124	134 (metHr)[h]
δ, mm s^{-1}	0.53	0.51	0.52	0.54	0.59 (0.50)[i]
ΔE_Q, mm s^{-1}	1.66	1.66	1.94	1.78	2.12 (2.04)

[a] Reported for $CHCl_3$ solutions. [b] Reference 21a. [c] Spectra of **2** and **3** in CH_2Cl_2 were collected with 514.5-nm Ar^+ laser excitation. Spectra of **4** and **5** were collected with 356.4-nm Kr^+ laser excitation in DMF and $CHCl_3$, respectively. [d] Freier, S. M.; Duff, L. L.; Shriver, D. F.; Klotz, I. M. *Arch. Biochem. Biophys.* **1980**, *205*, 449. [e] Magnetic measurements and analyses were performed as described in ref 11. [f] Mössbauer parameters were obtained at 4.2 K. [g] For **1**, the J value is -121 cm^{-1}.[11] [h] Dawson, J. W.; Gray, H. B.; Koenig, H. E.; Rossman, G. R.; Schredder, J. M.; Wang, R. H. *Biochemistry* **1972**, *11*, 461. [i] Mössbauer parameters for metClHr obtained at 4.2 K (77 K).[22]

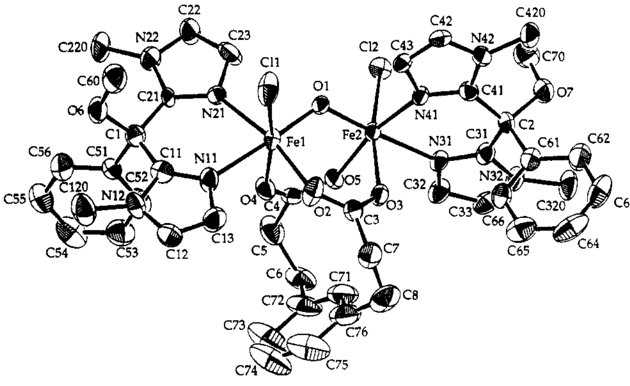

Figure 1. ORTEP drawing of **4**, showing the 65% probability thermal ellipsoids and atom labels for all non-hydrogen atoms. Selected interatomic distances and angles are given in Table I.

Compounds $[Fe_2O(MPDP)(HB(pz)_3)_2]$ (**2**), $[Fe_2O(MPDP)(4,4'\text{-}Me_2bpy)_2Cl_2]$ (**3**), $[Fe_2O(MPDP)(BIPhMe)_2Cl_2]$ (**4**), and $[Fe_2O(MPDP)(TMICMe)_2Cl_2]$ (**5**) were prepared by the self-assembly method described previously.[11] In a typical synthesis, an equimolar mixture of Na_2MPDP and $(Et_4N)_2[Fe_2OCl_6]$[17] was stirred in CH_3CN for 10–15 min. To the red-brown heterogeneous mixture was added a solution of the desired ligand (2 equiv) in either CH_3CN, CH_2Cl_2, or $CHCl_3$. The compounds were isolated as powders or crystalline solids upon workup of the resulting green solutions (yields 50–59%).[18] Importantly, although $[Fe_2O(MPDP)B_2M_2]$ complexes could be obtained in this manner, it has not been possible to synthesize analogues in which the bridging dicarboxylate ligand $MPDP^{2-}$ is replaced by acetates or other monoacid anions.

Compounds **2–4** were characterized by single-crystal X-ray diffraction.[19] The geometry of **2** is nearly identical with that of **1**,[11] a satisfying result since the dicarboxylate ligand was designed to be compatible with the $\{Fe_2O(O_2CR)_2\}^{2+}$ core structure. As illustrated in Figure 1 for **4** and in Table I, compounds **3** and **4** have essentially the same (μ-oxo)bis(μ-carboxylato)diiron(III) core as in **2** and other previously structurally characterized model compounds.[2,8] The chloride ligands are coordinated cis to the bridging oxo ligand, as observed for the exogenous ligand binding site in Hr.[2,14a,b] The Fe–N bonds trans to the oxo bridge are elongated as in previous complexes.[2,11] In addition, the Fe–O_{COO} (COO = carboxylate) bonds trans to the Fe–Cl bonds are lengthened. The same effect is observed for the carboxylate oxygen atom trans to the azide nitrogen atom in the X-ray structure of $metN_3Hr$.[14a,b] A comparison of the structures of **3** and **4** reveals interesting differences between pyridine and imidazole ring nitrogen coordination. The slightly shorter Fe–N bond lengths of 2.113 (5) –2.169 (6) Å in **4** reflect tighter binding of BIPhMe to the core compared with 4,4'-Me_2bpy (Fe–N = 2.151 (4)–2.210 (4) Å). Stronger coordination of BIPhMe is also manifest by significantly longer Fe–Cl and Fe–O_{oxo} bonds and small increases in the Fe···Fe distance and Fe–O–Fe bond angle in the structure of **4**.

Spectroscopic and magnetic data for compounds **2–5** are reported in Table II along with comparative information for Hr. The energy of the ligand field transition at 655 nm in **2** is remarkably similar to that found in metClHr (656 nm).[20] Resonance Raman spectra of **2–5** all show enhanced bands in a narrow frequency range (522–532 cm^{-1}), assigned to the ν_s(Fe–O–Fe) stretch.[11,21] Variable-temperature solid-state magnetic suscep-

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(18) Satisfactory elementary analyses were obtained for the compounds as follows: **2** ($C_{30}H_{32}N_{12}B_2O_5$), C, H, N.; **3** ($C_{36}H_{36}N_4O_5Cl_2Fe_2$), C, H, N, Cl, Fe; **4**·H_2O ($C_{44}H_{50}N_8O_8Cl_2Fe_2$), C, H, N, Cl; **5**·$H_2O$ ($C_{40}H_{50}N_{12}O_8Cl_2Fe_2$), C, H, N, Cl. Analytical and IR data for **2–5** are provided as supplementary material.

(19) Crystal data for **2**·$5CHCl_3$ ($C_{35}H_{37}N_{12}O_5B_2Cl_{15}Fe_2$), M_r = 1370.9, space group $P\bar{1}$, at 298 K: a = 12.878 (1) Å, b = 20.301 (2) Å, c = 11.906 (2) Å, α = 96.282 (1)°, β = 106.96 (1)°, γ = 74.33 (1)°, V = 2865 (1) $Å^3$, Z = 2. For 4823 unique, observed reflections with $I > 3\sigma(I)$ and 682 variable parameters, the current discrepancy indices are R = 0.060 and R_w = 0.066. Crystal data for **3**·$2CH_3CN$ ($C_{40}H_{42}N_6O_5Cl_2Fe_2$), M_r = 869.41, space group $P\bar{1}$, at 298 K: a = 10.941 (1) Å, b = 11.328 (1) Å, c = 18.781 (2) Å, α = 100.34 (1)°, β = 95.66 (1)°, γ = 115.56 (1)°, V = 2025 (1) $Å^3$, Z = 2. For 4153 unique observed reflections with $I > 3\sigma(I)$ and 496 variable parameters, R = 0.047 and R_w = 0.048. Crystal data for **4**·$3CHCl_3$·CH_3CN ($C_{49}H_{54}N_9O_7Cl_{11}Fe_2$), M_r = 1382.70, space group $P\bar{1}$, at 197 K: a = 15.446 (2) Å, b = 16.077 (2) Å, c = 12.453 (2) Å, α = 95.41 (1)°, β = 100.68 (1)°, γ = 93.17 (1)°, V = 3017 (1) $Å^3$, Z = 2. For 5307 unique, observed reflections with $I > 3\sigma(I)$ and 703 variable parameters, R = 0.053 and R_w = 0.065. Atomic positional and thermal parameters are provided in the supplementary material. Full crystallographic details will be published elsewhere.

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