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Syntheses, Crystal Structures, and Properties of Unsymmetrical (μ-Oxo)diiron(III) Complexes Containing Polyimidazole Ligands

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Non-heme diiron(III) proteins such as hemerythrin,[1] ribonucleotide reductase,[2] and methane monooxygenase[3] are known to have μ-oxo/hydroxo- and μ-carboxylato-bridged core structures assembled in a manner that produces chemically distinct iron coordination sites.[4] There have been several attempts at modeling the asymmetry of the iron coordination sites in non-heme diiron proteins using tridentate[5] and tetradentate[6] amine ligands and, more recently, with unsymmetrical polydentate chelates.[7] However, only the sterically constrained Me_3tacn[5] ligand has been used to prepare oxo-bridged diiron(III) complexes containing two different chelating ligands.

We have found that the sterically hindered polyimidazole ligand temima[8] reacts with $(Et_4N)_2[Fe_2OCl_6]$[9] to form the monosubstituted product (temima)Fe(Cl)OFeCl$_3$ (**1**).[10] Apparently the temima chelate is bulky enough to retard the addition of a second ligand to the $FeCl_3$ fragment of **1**. Interestingly, Jameson *et al.*[11] have reported that hexadentate polybenzimidazole chelates react with $FeCl_3$, forming structurally related $[N5FeOFeCl_3]^+$ complexes; however, there has been no indication that these complexes react further with other ligands to form stable oxo−iron complexes.

Compound **1**, on the other hand, reacts readily with other tetradentate polypodal ligands, L, in the presence of NaOAc and $NaClO_4$ to form unsymmetrical compounds of the general type $[Fe_2O(temima)(L)(OAc)]^{3+}$.[12] In this study, L represents the tetradentate amine ligand tmima,[13,14] but we have established that other tetradentate ligands, such as tpa,[13,15] also react with **1** to form $[Fe_2O(temima)(L)(OAc)]^{3+}$ complexes, thus providing direct evidence of a general stepwise procedure for preparing unsymmetrical (μ-oxo)diiron(III) complexes. It is important to note that tmima has been found[16] to stabilize only symmetric (μ-oxo)diiron(III) complexes, due to its smaller size and less bulky shape. Therefore the unsymmetrical structure observed for $[Fe_2O(temima)(tmima)(OAc)](ClO_4)_3$ (**2**) (*vide infra*) appears to be directly related to the steric interactions between the temima and the tmima ligands and the stepwise procedure used to prepare **2**. In this report, we describe the syntheses of compounds **1** and **2** and their characterizations by X-ray crystallography, by UV−vis and ^1H NMR spectroscopies, and by magnetic methods.

The X-ray crystal structure of **1**[17] (Figure 1) shows the complex has a bent (μ-oxo)diiron(III) core, with an Fe(1)−O(1)−Fe(2) angle of 154.7(3)° and an Fe−Fe separation of 3.456(2) Å. The core parameters of **1** are consistent with those found for related $[N5FeOFeCl_3]^+$ complexes.[11] Fe(1) is octahedrally coordinated to the bridging oxo ligand, a chloride ligand, and four nitrogen atoms of temima. The $Fe-N_{amine}$ bond ($Fe(1)-N(1) = 2.366(7)$ Å) trans to the oxo bridge is characteristically longer than the three cis $Fe-N_{im}$ bonds (average $Fe-N = 2.105(7)$ Å) due to the trans influence of the oxo group.[4] Fe(2), on the other hand, is tetrahedrally coordinated to the bridging oxo ligand and three chloride ligands. The Fe(1)−O(1) and Fe(2)−O(1) distances are 1.790(5) and 1.750-

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(8) A complete description of the synthesis of tris[(1-ethyl-4-methylimidazol-2-yl)methyl]amine (temima) will be published elsewhere. Anal. Calcd for temima·H_2O, for $C_{21}H_{35}N_7O$: C, 62.84; H, 8.73; N, 24.44. Found: C, 63.07; H, 8.67; N, 24.48. ^1H NMR ($CDCl_3$): δ 6.51 (s, 3 H), 3.77 (s, 6 H), 3.21 (q, 6 H), 2.16 (s, 9 H), 0.99 (t, 9H). ^{13}C NMR ($CDCl_3$): δ 144.17, 136.22, 115.55, 48.64, 39.74, 16.10, 13.49.

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(10) An ethanol solution (3 mL) containing temima (102 mg, 0.266 mmol) was added slowly with stirring to an acetone solution (3 mL) of $(Et_4N)_2[Fe_2OCl_6]$[9] (160 mg, 0.266 mmol), producing a yellowish orange precipitate (160 mg, 92%). Anal. Calcd for **1**·C_2H_5OH, $C_{23}Cl_4Fe_2H_{39}N_7O_2$: C, 39.51; H, 5.58; N, 14.03. Found: C, 39.79; H, 5.56; N, 14.35.

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(12) To an acetonitrile solution (5 mL) of **1** (151 mg, 0.228 mmol) were added with stirring 69 mg (0.228 mmol) of tmima and 19 mg (0.228 mmol) of NaOAc in 5 mL of methanol followed by 98 mg (0.80 mmol) of $NaClO_4$ in methanol. The solution volume was reduced, and ethanol was added to induce precipitation. *Caution! Although no problems were encountered in the preparation and purification of compound **2**, suitable precautions should always be followed in handling perchlorate salts.* The yield of **2** was 227 mg (84%). Anal. Calcd for **2**, $C_{38}Cl_3Fe_2H_{57}N_{14}O_{15}$: C, 39.08; H, 4.92; N, 16.78. Found: C, 39.04; H, 4.91; N, 16.80.

(13) Tmima = tris[(1-methylimidazol-2-yl)methyl]amine and tpa = tris(2-pyridinylmethyl)amine. The syntheses of the tmima[14] and tpa[15] have been reported elsewhere.

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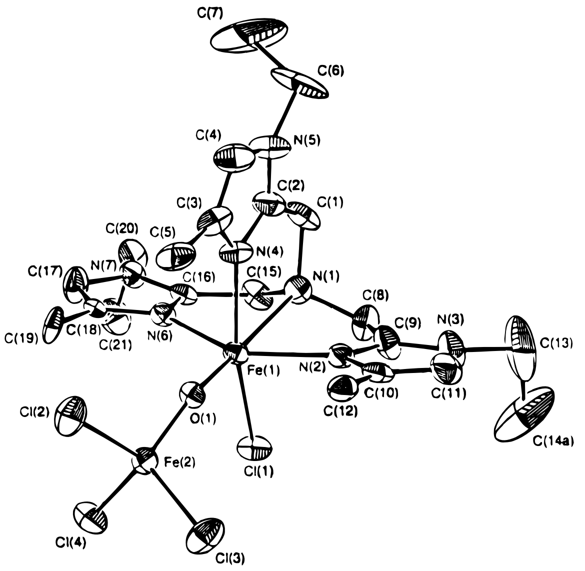

Figure 1. ORTEP plot of compound **1** showing a partial numbering scheme. The hydrogen atoms are omitted. Selected bond distances (Å) and angle (deg): Fe(1)−Fe(2) = 3.456 (2), Fe(1)−O(1) = 1.790(5), Fe(2)−O(1) = 1.750(5), Fe(1)−N(1) = 2.366(7), Fe(1)−N(2) = 2.098(7), Fe(1)−N(4) = 2.126(7), Fe(1)−N(6) = 2.091(7), Fe(1)−Cl(1) = 2.379(2), Fe(2)−Cl(2) = 2.231(3), Fe(2)−Cl(3) = 2.224(3), Fe(2)−Cl(4) = 2.225(3), Fe(1)−O(1)−Fe(2) = 154.7(3).

(5) Å, respectively, and are consistent with those of other iron−oxo complexes,[4] while the Fe−Cl bonds are typical of high-spin iron(III) complexes.[18]

The crystal structure of **2**[19] is shown in Figure 2 and reveals a (μ-oxo)(μ-carboxylato)diiron(III) core with two different tetradentate amine ligands. The doubly bridged core restricts the Fe−O−Fe angle to 129.9(5)°, and the Fe−Fe separation is 3.236(3) Å. The iron−oxo distances are slightly different (Fe(1)−O(1) = 1.806(8), Fe(2)−O(1) = 1.765(8) Å) as observed in the unsymmetrical complex $[Fe_2O(TPA)_2(OAc)](ClO_4)_3$.[6b] The iron atoms in **2** have different octahedral coordination environments, and the bridging oxo ligand bonds trans to the tertiary amine nitrogen of tmima on Fe(2) and cis to the tertiary amine nitrogen of temima on Fe(1). This results in significantly different $Fe-N_{amine}$ bond lengths for tmima (Fe(2)−N(8) = 2.38(1) Å) and temima (Fe(1)−N(1) = 2.27(1) Å). Two imidazole nitrogen atoms of temima and three imidazole nitrogen atoms of tmima bond cis to the bridging oxo ligand (average Fe(2)−N = 2.08(1) and Fe(1)−N = 2.14(1) Å), while the third imidazole pendant of temima bonds trans to the bridging oxo ligand (Fe(2)−N(13) = 2.14(1) Å).

The UV−vis spectrum of **1** in acetonitrile exhibits transitions with maxima near 328, 374 (sh), and 400 (sh) nm which are assigned to both oxo → Fe^{III} and $Cl^- \rightarrow Fe^{III}$ charge-transfer transitions. Similar spectral features have been reported for the structurally related $[N5FeOFeCl_3]^+$ complex.[11] Compound **2**, on the other hand, displays more intense oxo → Fe(III) charge-transfer transitions in the UV−vis region at 320, 332 (sh), 410 (sh), 480 (sh), and 590nm. The maxima of the transitions of **2** fall between those observed for the structurally related complexes $[Fe_2O(tmima)_2(OAc)]^{3+}$ [15] and $[Fe_2O(temima)_2(OAc)]^{3+}$.[21]

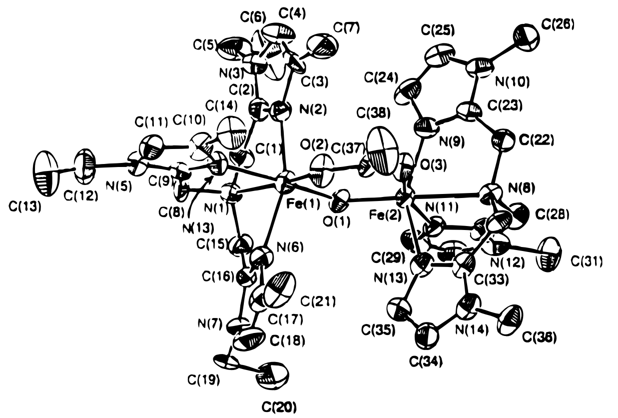

Figure 2. ORTEP plot of compound **2** showing a partial numbering scheme. The hydrogen atoms are omitted. Selected bond distances (Å) and angle (deg): Fe(1)−Fe(2) = 3.236 (3), Fe(1)−O(1) = 1.806(8), Fe(1)−O(2) = 1.982(9), Fe(2)−O(1) = 1.765(8), Fe(2)−O(3) = 2.039(8), Fe(1)−N(1) = 2.27(1), Fe(1)−N(2) = 2.11(1), Fe(1)−N(4) = 2.17(1), Fe(1)−N(6) = 2.15(1), Fe(2)−N(8) = 2.38(1), Fe(2)−N(9) = 2.08(1), Fe(2)−N(11) = 2.08(1), Fe(2)−N(13) = 2.14(1), Fe(1)−O(1)−Fe(2) = 129.9(5).

The ^1H NMR spectrum of compound **2** displays proton signals between 0 and 28 ppm (Supporting Information), indicating that the iron(III) ions are strongly antiferromagnetically coupled. Variable-temperature magnetic susceptibility measurements were made on compounds **1** and **2**. Data (Supporting Information) for both compounds were fit using a model for an isolated Heisenberg dimer $H = -2JS_1 \cdot S_2$, where S_1 and $S_2 = {}^5/_2$. The exchange parameters (J) for compounds **1** and **2** are −116.1 and $-115.7\ cm^{-1}$, respectively, consistent with other strongly antiferromagnetic coupling (μ-oxo)diiron(III) complexes.[4c]

In summary, we have developed a general stepwise synthetic procedure for preparing unsymmetrical (μ-oxo)diiron(III) complexes by exploiting the steric properties of a new tetradentate polyimidazole ligand. $[Fe_2O(temima)(tmima)(OAc)](ClO_4)_3$ (**2**) is the first example of a (μ-oxo)(μ-carboxylato)diiron(III) complex containing two different polyimidazole ligands and displays many of the structural and physical properties reported for non-heme diiron proteins.

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Supporting Information Available: Text giving experimental details, tables of crystallographic data, atomic parameters, anisotropic thermal parameters, complete bond distances and angles, magnetic susceptibility data, and ^1H NMR data, ORTEP drawings, ^1H NMR spectra, UV−vis spectra, μ_{eff} vs T plots, and a scheme showing the stepwise synthesis for **1** and **2** (31 pages). Ordering information is given on any current masthead page.

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(17) Crystals of **1** were grown from acetonitrile solutions layered with diethyl ether. Crystal data for $\mathbf{1} \cdot C_2H_5OH$: orange block, orthorhombic, space group $P\ 2_12_12_1$ (No. 19), a = 14.228(3) Å, b = 18.386(4) Å, c = 13.085(2) Å, V = 3423.0(10) $Å^3$, $D_{calcd} = 1.35\ g\ cm^{-3}$ Z = 4. For 3263 unique, observed reflections with $I > 3\sigma(I)$ and 362 parameters, the discrepancy indices are R = 0.049 and R_w = 0.055.

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(19) Crystals of **2** were isolated from an acetonitrile solution layered with diethyl ether. Crystal data for **2**: dark green block, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 21.581(6) Å, b = 24.030(7) Å, c = 10.137(3) Å, V = 5256(2) $Å^3$, $D_{calcd} = 1.48\ g\ cm^{-3}$, Z = 4. For 2716 unique, observed reflections with $I > 3\sigma(I)$ and 649 parameters, the discrepancy indices are R = 0.057 and R_w = 0.060.

(20) $[Fe_2O(temima)_2(OAc)](ClO_4)_3$ was prepared by reacting appropriate quantities of temima and NaOAc with $Fe(ClO_4)_3 \cdot 9H_2O$ in ethanol. Crystal data: dark green block, monoclinic, space group Pn (No. 7), a = 14.404(2) Å, b = 10.373(3) Å, c = 20.847(5) Å, β = 92.04(2)°,V = 3112(1) $Å^3$. The discrepancy indices are R = 0.058 and R_w = 0.059.