Communication

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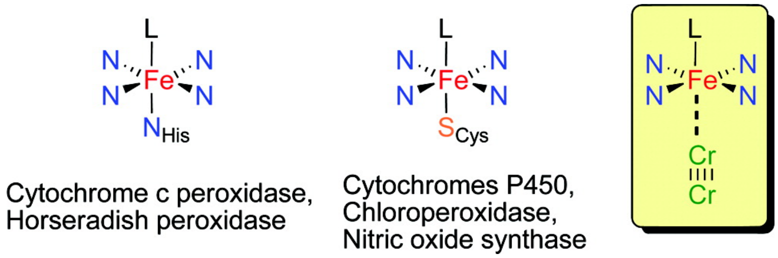
J. Am. Chem. Soc., **2007**, 129 (42), 12684-12685• DOI: 10.1021/ja076337j • Publication Date (Web): 27 September 2007



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Introducing a Metal−Metal Multiply Bonded Group as an "Axial Ligand" to Iron: Synthetic Design of a Linear Cr−Cr⋯Fe Framework

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Axial interactions are known to be important in regulating reactivity of iron-porphyrin containing (heme) enzymes.[1] For example, heme groups with axial N-donor atoms (histidine, **I** in Chart 1) act as peroxidases, whereas replacement of the histidine moiety for the stronger σ donating thiolate (cysteine, **II**) ligand allows the heme groups to catalyze oxidations of saturated hydrocarbons as in cytochromes P450,[2] as well as other reactions such as oxidation of nitrogen and sulfur compounds, reductions, isomerizations, and dehydrations.[3]

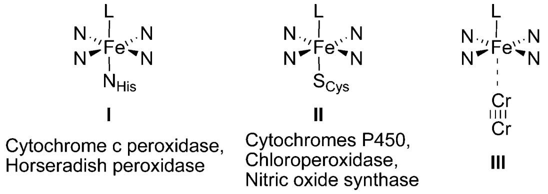
Prompted by these observations, we have sought to regulate reactivity of iron in a new way using axial interactions from electron-rich metal−metal multiply bonded units as in **III** (Chart 1). Reported here is our first synthetic step toward this goal: the synthesis of a new heterotrinuclear complex with a linear Cr≣Cr⋯Fe connectivity, $\mathrm{CrCrFe(dpa)_4Cl_2}$ (**1**) (dpa = 2,2′-dipyridylamide), with all three metal ions present in their divalent states.[4,5]

We have chosen to use the ligand dpa in our syntheses because it is well-known to stabilize linear trimetallic chains, particularly those with unsymmetrical M−M⋯M structures.[4] Our strategy is to use an unsymmetrical M−M⋯M complex as a precursor to new M−M⋯M′ species. In this connection, it should be noted the dpa ligand was recently used by Peng et al. to synthesize a novel CoPtCo complex.[5a] The reported synthesis relies on self-assembly of the complex from $\mathrm{CoCl_2}$ and $\mathrm{PtCl_2}$ starting materials, which results in low overall yield (∼30%).[5a] In contrast to this method, we report here a rationally designed preparative route that can be broadly and systematically applied to a number of M−M⋯M′ systems (Scheme 1).

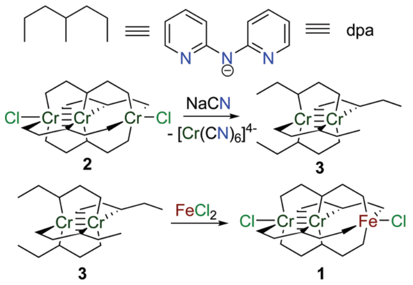
The unsymmetrical homotrinuclear compound $\mathrm{Cr_3(dpa)_4Cl_2}$ (**2**)[6] reacts with an excess of NaCN, resulting in extraction of one Cr(II) ion to form the binuclear complex $\mathrm{Cr_2(dpa)_4}$ (**3**) in >60% yield.[7] Reaction of **3** with anhydrous $\mathrm{FeCl_2}$ (1.1 equiv) in refluxing THF furnishes **1**, which precipitates from the reaction mixture and can be recrystallized from $\mathrm{CH_2Cl_2}$ solutions (crystalline yield: 82%). Large, dark yellow-orange single crystals of **1·Et$_2$O** or **1·CH$_2$Cl$_2$** (space groups $P2_1/c$ and $Pnn2$, respectively) were obtained by crystallization from $\mathrm{CH_2Cl_2}$ and either $\mathrm{Et_2O}$ or hexanes. The structure of the etherate is shown in Figure 1. Similar to **2**,[6] the metal atom positions in **1** are disordered, having equal occupancy of Cr≣Cr⋯Fe and Fe⋯Cr≣Cr orientations.[8]

Although it is not possible to distinguish Cr from Fe using X-ray crystallographic data, the assignment of the Cr and Fe positions may be made based upon known Cr−Cr distances for quadruply bonded $\mathrm{Cr_2}$ pairs (2.25 Å in **2·CH$_2$Cl$_2$**[6] and 1.94 Å in **3**[7a,b]). The assigned Cr−Cr and Cr⋯Fe distances are 2.028(5) and 2.712(6) Å and 2.029(6) and 2.697(7) Å for the two crystallographically independent orientations in **1·Et$_2$O** and 2.025(2) and 2.715(2) Å in **1·CH$_2$Cl$_2$**, which are in gratifyingly good agreement with each other, though it should be mentioned that the Cr≣Cr distance in **1** is significantly shorter (0.22 Å) than that in **2**. Notably, the Cr⋯Fe distance of ∼2.70 Å is too long to be considered a formal bond, but not too long to preclude the possibility of Cr(d_{z^2})−Fe(d_{z^2}) orbital overlap. In fact, the longer $\mathrm{Cr_2}$⋯Fe distance in **1** (∼2.70 Å) compared to the $\mathrm{Cr_2}$⋯Cr distance in **2** (∼2.48 Å) is likely a result of the population of the antibonding Fe d_{z^2} orbital in the former case, whereas in the latter compound, the Cr d_{z^2} orbital is empty.

Chart 1



Scheme 1



The coordination geometry of the Fe atom may be described as distorted octahedral, if the σ orbital of the quadruply bonded $\mathrm{Cr_2}$ unit is seen as a "ligand" to the iron center. The Fe−N bond lengths range from 2.13 to 2.16 Å and the mean Fe−Cl bond distance is 2.308(3) Å. Notably, the Fe center lies significantly (∼0.40 Å) above the plane formed by the four N atoms away from the Cr atoms.

The presence of Fe in **1** is definitively established by ESI mass spectrometry (characteristic isotope pattern for $[\mathrm{M} - \mathrm{Cl}]^+$ at m/z = 875 amu)[8] and elemental analysis (% Fe: calcd for **1·CH$_2$Cl$_2$** 5.60; found 5.52). Also, the electronic absorption spectrum of **1** features a band at ∼700 nm that is tentatively assigned to an iron-centered d−d transition.[9]

Variable-temperature magnetic susceptibility (χ) measurements on **1** reveal the existence of four unpaired electrons ($\chi \cdot T$ at room temperature = 3.90 emu K mol^{-1}; $\mu_{\mathrm{eff}} = 5.59\ \mu_{\mathrm{B}}$).[8] The g value of 2.28 and the zero-field splitting value, $|D|$, of 8.3 cm^{-1} derived from spin-Hamiltonian analysis of the $\chi \cdot T$ versus T curve[8] are well within the expected range of values for high-spin Fe(II) ions,[10] in good agreement with the formulation of **1** as containing a diamagnetic quadruply bonded $\mathrm{Cr_2}$ center attached to a high-spin Fe(II) ion (d^6, $S = 2$).

The axially appended $\mathrm{Cr_2}$ unit in **1** endows the iron center with unique redox properties. The dominant feature of the cyclic

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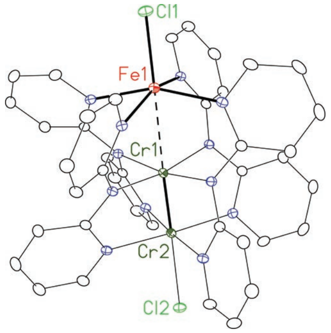
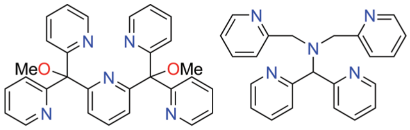


Figure 1. Thermal ellipsoid plot of **1** from **1·Et$_2$O** drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity, and only one orientation of the disordered metal atoms is shown.

Chart 2



IV **V**

voltammogram of **1** is a reversible one-electron oxidation wave ($E_{1/2}(CH_2Cl_2) = -236$ mV, $E_{1/2}(CH_3CN) = -173$ mV; potentials referenced versus ferrocene/ferrocenium (Fc/Fc^+)) and one irreversible oxidation at higher potential ($E(CH_2Cl_2) = 538$ mV, $E(CH_3CN) = 512$ mV).[8] To investigate the nature of the reversible oxidation wave, **1** was oxidized with ferrocenium triflate. The EPR spectrum of the oxidized species shows a high effective *g* value of 5.82 that is characteristic of a high-spin Fe(III) center with large axial zero-field splitting.[8] The second oxidation is irreversible and may be tentatively assigned to an iron-centered oxidation, producing an Fe(IV) complex that is unstable on the time scale of cyclic voltammetry. The wave is not assigned to the oxidation of the Cr_2 quadruply bonded unit because the $Cr_2^{4+/5+}$ redox couple is typically reversible in corresponding trimetallic compounds.[6]

It is useful to compare the redox properties of **1** with analogues of **I** (model complexes of **II** with pyridine donor ligands are as yet unknown), such as the high-spin Fe(II) chloro complexes of the ligands **IV** and **V** that have been studied by the groups of Stack and Que (Chart 2), whose Fe−N(equatorial) and Fe−Cl distances (2.218(5) and 2.316(2) Å, respectively) are slightly longer than those in **1**.[11,12]

Figure 2 shows the redox potentials reported[11,12] for the $Fe^{2+/3+}$ redox couple in complexes of **IV** and **V** (left and middle columns, respectively) compared to the analogous $Fe^{2+/3+}$ wave in **1**. Complexes of **IV** having an axial pyridine ligand *trans* to the chloride have the highest oxidation potentials, ∼400 mV vs Fc/Fc^+. Exchanging the axial pyridine donor in **IV** for the axial tertiary amine donor in **V** makes the redox wave more accessible by ∼200 mV, as expected for the increased σ donor strength of the tertiary amine ligand. The $Fe^{2+/3+}$ redox wave for **1** is significantly lower than either of these two species (by 400−600 mV!), signifying greater thermodynamic stability of the Fe(III) species. Moreover, it should be emphasized that, in contrast to the chloro complexes of **IV** and **V** in which no $Fe^{3+/4+}$ waves were observed, a wave assignable to the $Fe^{3+/4+}$ couple in **1** is observable but irreversible. Though the reasons for the dramatically increased stability of higher oxidation states in **1** may involve differences in charge or geometry in the compounds, we are currently exploring the possibility that this stability may also be regulated by $Cr_2\cdots Fe$ interactions. The nature of this interaction is the subject of current spectroscopic and computational work in our lab.

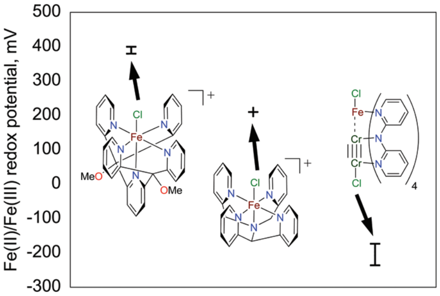


Figure 2. Redox potentials of the Fe(II)/Fe(III) redox couple in [(**IV**)FeCl]$^+$ (left), [(**V**)FeCl]$^+$ (middle), and **1** (right) scaled to the Fc/Fc^+ reference. Bars represent a range of measured values, whereas + represents a single measurement.

Acknowledgment. J.F.B. is grateful to the University of Wisconsin for providing generous startup funds. We thank Dr. Ilia Guzei for assistance with the crystallography, Dr. Eckhard Bill for obtaining the magnetic susceptibility data, and Prof. Shannon Stahl for helpful discussions.

Supporting Information Available: Synthetic procedures, crystallographic information, ESI and MALDI mass spectra, EPR spectrum of $\mathbf{1}^{ox}$, and magnetic susceptibility measurements of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA076337J