Communication

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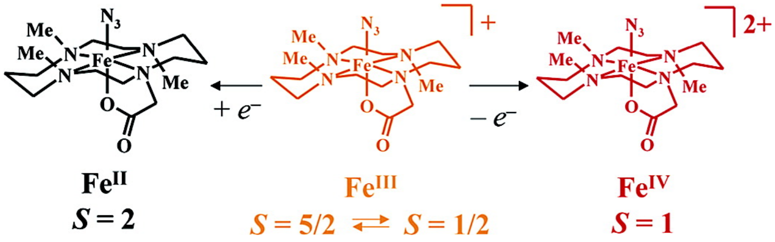
J. Am. Chem. Soc., **2005**, 127 (33), 11550-11551• DOI: 10.1021/ja052673t • Publication Date (Web): 29 July 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Octahedral Non-Heme Non-Oxo Fe(IV) Species Stabilized by a Redox-Innocent N-Methylated Cyclam−Acetate Ligand

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The coordination chemistry of high-valent iron is currently of considerable interest, due to the realization that such species play an important role in biological systems, that is, in metalloenzymes of the heme[1] or non-heme[2] variety. While most genuine examples of iron(IV)-containing species utilize bridging[3] or terminal[4] oxo ligands, high-valent complexes without these oxo groups are quite rare. In fact, to our knowledge, the only well-characterized mononuclear non-heme Fe(IV) complexes which do not contain an oxo ligand are the complexes of Collins with a macrocyclic tetra-anionic ligand,[5] a tetrahedral iron(IV) complex with phosphine donors and a terminal nitrido ligand,[6] and iron(IV) corrole species.[7] We have characterized ferryl oxo−iron(IV)[4a] as well as nitrido−iron(V)[8] species containing the macrocyclic ligand cyclam−acetate (**I**), which has also been utilized by Kaden[9] and Szulbinski.[10] Here, we report our preliminary results using a modification of **I**, in which three *N*-methyl groups have been introduced, namely, Me_3cyclam−acetate (**II**).

While many complexes of **I** are now known,[4a,10,11] the trimethylated ligand **II** has only been synthesized as its copper(II) complex[12] and has never been isolated in free form. We have prepared **II** in yields as high as 80% by reaction of **I**·4HCl in acidic formaldehyde solution, from which **II** was isolated as its HCl salt.[13] After in situ deprotonation of **II**, $[NEt_4][FeCl_4]$ is added to generate the iron(III) complex. Addition of NaN_3 and KPF_6 to the initial chloro species yields the azido complex $[(Me_3cyclam-acetate)FeN_3]PF_6$ (**1**) as a deep-red precipitate. Recrystallization from CH_3CN produces large red crystals of **1** in 30−40% yield.

The crystal structure[13] of **1** at 100 K has been obtained (Figure 1), and at first glance, appears to be similar to the complex employing the nonmethylated ligand **I** (i.e., $[(cyclam-acetate)FeN_3]PF_6$, **2**). Both complexes contain octahedrally coordinated iron having equatorial coordination of the cyclam ring with one axial position filled by the pendant-arm acetate and the other by an azido ligand. However, while the $Fe-N_{axial}$ and Fe−O distances of **1** (both 1.953(1) Å, as required by crystallographic symmetry[14]) are only slightly longer than those of 1.931(2) and 1.889(1) Å found in **2**,[4a] the average equatorial Fe−N distances of 2.145(2) Å in **1** are about 0.14 Å longer than the corresponding Fe−N distances in **2** (2.010(2) Å).[4a] It has been established that **2** is low spin with $S = {}^1/_2$,[4a] so the longer Fe−N bond distances in **1** indicate that **1** is high spin with $S = {}^5/_2$ at 100 K.

In fact, at room temperature, the effective magnetic moment of **1** of 5.6 μ_B is clearly indicative of five unpaired electrons, though at temperatures below 100 K, this value decreases steeply, indicative of a spin-crossover phenomenon. The temperature dependence of the ^{57}Fe Mössbauer spectra of **1** (isotopically enriched with 40% ^{57}Fe) in frozen MeCN solution is consistent with this, showing a broad asymmetric doublet with an isomer shift (δ) of 0.35 mm s^{-1} and a small quadrupole splitting (ΔE_Q) of 0.84 mm s^{-1} at 200 K, but at 80 K, a more complex spectrum is obtained, which can be deconvoluted and simulated as containing 60% high-spin Fe(III) and 40% low-spin Fe(III).[13] With respect to the high-spin species, similar Mössbauer parameters are found for the high-spin complex *cis*-$[(cyclam)Fe(N_3)_2]$ ($\delta = 0.46$ mm s^{-1} and $\Delta E_Q = 0.29$ mm s^{-1}).[15] The corresponding parameters found for the low-spin compound **2** ($\delta = 0.27$ mm s^{-1}, $\Delta E_Q = 2.53$ mm s^{-1})[4a] are in good agreement with those found for the low-spin species in **1** ($\delta = 0.33$ mm s^{-1}, $\Delta E_Q = 2.21$ mm s^{-1}).

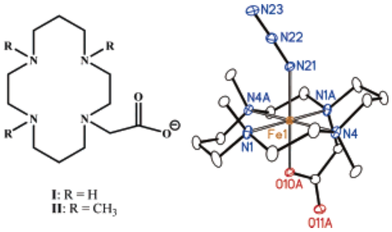

Figure 1. Diagram of the ligands **I** and **II** and thermal ellipsoid plot of the cation of **1** with ellipsoids drawn at the 30% probability level and hydrogen atoms removed.

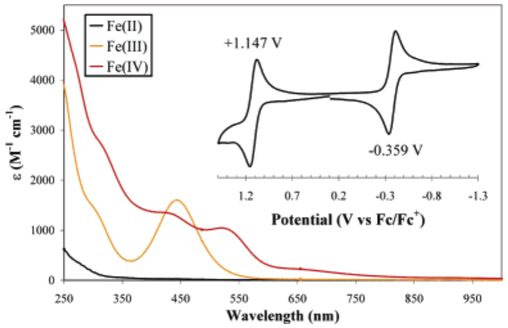

Figure 2. Electronic spectra of the Fe(II)-, Fe(III)-, and Fe(IV)-containing species **1red**, **1**, and **1ox** taken in CH_3CN solution. Inset: cyclic voltammogram of **1** in CH_3CN solution with 0.1 M NBu_4PF_6 supporting electrolyte at a scan rate of 100 mV/s. $E_{1/2}$ values are included next to the corresponding wave.

It is remarkable that N-alkylation of the cyclam−acetate ligand causes the resulting iron complex to be high spin at high temperatures because one may naively expect the electron-donating effects of the methyl groups to cause the ligand **II** to have a stronger ligand field strength than **I**. According to Meyerstein,[16] there are many competing effects which all play a role in the properties of complexes of tertiary amines versus those of secondary amines which result in a weaker ligand field strength in the former.

The most interesting difference between **1** and **2**, however, is in their electrochemical behavior. The cyclic voltammogram (CV) of **2** was reported previously in our group[4a] and consists of a reversible $Fe^{3+/2+}$ reduction wave at −750 mV versus Fc/Fc^+ and an *irreversible* oxidation wave at +990 mV. The CV of **1** is shown in the inset to Figure 2, and remarkable differences from the CV of **2** are readily observable. First, the reduction to iron(II) occurs at −360 mV versus Fc/Fc^+, denoting that the iron(II) species **1red**

10.1021/ja052673t CCC: $30.25

is thermodynamically more stable than **2red** by over 400 mV (or about 40 kJ mol^{-1})! The second notable feature in the CV is that the oxidation wave to iron(IV) at +1.15 mV is now *reversible*. Thus the one-electron oxidation product **1ox** is kinetically more stable than **2ox**, although its redox potential is less accessible. The thermodynamic stability of low-valent species and the kinetic stability of high-valent species are both effects which have been noticed by Meyerstein in the study of Ni and Cu complexes of N-alkylated macrocyclic ligands.[17]

Due to the stability of the reduced and oxidized species of **1**, they were generated in solution coulometrically and characterized spectroscopically. The electronic spectra of **1red**, **1**, and **1ox** are shown in Figure 2, where it can be seen that an increase in the oxidation state of the metal brings about an increase in the number and intensity of the various bands (likely LMCT in origin) in the spectrum. Thus, while the ferrous complex **1red** is colorless, ferric **1** is brilliant orange, and **1ox** is deep red. It should be noted that the low-energy band in **1ox** at 650 nm may have a similar origin to the bands in green ferryl complexes, typically observed at 650−850 nm.[18]

Oxidation and reduction of **1** were also monitored by IR spectroscopy since two intense bands corresponding to the N_3 stretch and the C═O stretch of the pendant carboxylate are in a region where the solvent and electrolyte do not absorb. Both of these bands show significant changes upon oxidation/reduction. In reoxidizing **1red** to **1** and re-reducing **1ox** to **1**, the original IR spectrum is quantitatively regenerated, demonstrating the reversibility of the process and showing that no ligands are removed during the coulometry. The C═O band becomes higher in energy as the oxidation state of the metal is increased (this band appears at 1633 cm^{-1} in **1red**, 1677 cm^{-1} in **1**, and 1732 cm^{-1} in **1ox**), denoting a stronger Fe−O bond with increased oxidation number, as would be expected from a purely electrostatic view. Such simple electrostatic arguments would not be expected to be useful in describing the N_3 stretch since π effects are undoubtedly important in describing the nature of the Fe−N_3 bond. In fact, both oxidation and reduction of **1** cause the azide stretch, originally at 2091 cm^{-1}, to move to lower frequencies (2063 and 2037 cm^{-1} in **1red** and **1ox**, respectively).

Electrochemically generated solutions of isotopically enriched samples (40% ^{57}Fe by weight) of **1red** and **1ox** were examined by Mössbauer spectroscopy[13] in order to demonstrate that the redox reactions are iron-centered in each case and to determine the spin state of the new species. The Mössbauer spectrum of **1red** at 80 K consists of a quadrupole doublet with $\delta = 1.08$ mm s^{-1} and a large value of ΔE_Q of 3.17 mm s^{-1}, both clear indications of high-spin ferrous iron and comparable to the parameters found in *cis*-[(cyclam)Fe$(N_3)_2$] ($\delta = 1.11$ mm s^{-1}, $\Delta E_Q = 2.84$ mm s^{-1}), which is also high spin.[15] The Mössbauer spectrum of **1ox** contains a well-resolved quadrupole doublet with a value of $\delta = 0.11$ mm s^{-1}, which is 0.2 mm s^{-1} lower than that of **1**, clearly identifying **1ox** as a genuine iron(IV) complex. The isomer shift value is comparable to those found in ferryl complexes ($\delta = 0.01-0.17$ mm s^{-1}),[4a] though higher than the value found in five-coordinate [Fe^{IV}(MAC*)Cl]$^-$ (−0.02 mm s^{-1}).[5] However, the ΔE_Q value of 1.92 mm s^{-1} found in **1ox** is larger than those found in either the ferryl species (which are all low spin, $S = 1$) or in Collins's five-coordinate species (high spin, $S = 2$), but the positive sign of ΔE_Q is consistent with a 3d$(xy)^2(xz,yz)^2$ configuration. Measurements with applied field have been obtained,[13] simulations of which assuming $S = 1$ yield the zero-field splitting parameter ($D = 24$ cm^{-1}) as well as the Fe hyperfine coupling tensor components ($A/g_N\beta_N$ = (−15.4, −17.8, and −2.3 T)). The data could also be fit to an $S = 2$ model, though the resulting A values are unrealistically small.

To summarize, because of N-methylation of the ligand **II**, the resulting iron(II) complex (**1red**) is stabilized and is high spin, its iron(III) analogue (**1**) is high spin at room temperature, but a significant amount of the compound is low spin at lower temperatures, and the iron(IV) species is stable at −25 °C for at least a few hours and low spin. Further work to obtain **1ox** as a solid is underway, and a general study of various six-coordinate iron(IV) species is now possible by exchanging the axial ligands in **1**, making it possible to study the electronic structure of this rare but important oxidation state of iron in great detail.

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support. J.F.B. thanks the Alexander von Humboldt Foundation for a postdoctoral fellowship.

Supporting Information Available: Synthetic procedures, crystallographic data for **1** in cif format, and Mössbauer spectra of **1red**, **1**, and **1ox**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) See Supporting Information.

(14) The iron atom in **1** is situated on a center of inversion in the space group $P2_1/n$, and therefore, the axial carboxylato and azido groups are disordered.

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JA052673T