proton of **1** and the C-terminal carbonyl oxygen of **2**, (2) a hydrogen bond between the dinitrobenzoyl amide proton of **2** and the carbonyl oxygen of **1**, and (3) a π-donor–acceptor interaction between the naphthyl system of **1** and the dinitrobenzoyl system of **2**. The complex derived from the (S) thioester cannot achieve all of these bonding interactions simultaneously and is consequently of lesser stability. This model is supported by a recently reported study of intermolecular nuclear Overhauser effects in a closely related system.[4b,c]

The effects of solvent and temperature are easily rationalized by the complexation model. Polar solvents decrease the extent of complexation by providing competitive solvation of the uncomplexed species. Not surprisingly, the extent of complexation increases as the temperature is lowered.

In addition to differential complexation, interconversion of the enantiomers is requisite for deracemization. Both diazabicyclooctane (Dabco) and triethylamine are sufficiently basic to promote the interconversion of thioester enantiomers; pyridine is not. The amidine bases 1,5-diazabicyclo[4.3.0]non-5-ene and 1,8-diazabicyclo[5.4.0]undec-7-ene, still stronger bases, induce decomposition of the dinitrobenzoyl portion of the thioester, thus precluding their use for deracemization of the ester and amide analogues of **2**. These fail to undergo deracemization with triethylamine owing to insufficient acidity of their α-hydrogens.

In summary, we have demonstrated a highly selective deracemization process in which the mechanism of differentiation is similar to that which occurs in analogous chiral HPLC processes. Further applications of chromatographic data to the development of first-order asymmetric transformation processes are in progress.

Models for Iron–Oxo Proteins: A Mixed-Valence Iron(II)–Iron(III) Complex

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Mixed-valence iron clusters in the active sites of metal–oxo proteins are characterized by EPR signals with $g_{av} \sim 1.7$–1.8 which arise from the antiferromagnetic coupling of high-spin Fe(II) and Fe(III) ions.[1–4] Such sites have been found in the semimet forms of hemerythrin[1] and the reduced forms of purple acid phosphatases[2] and may also be present in methane monooxygenase[3] and the early stages of ferritin core formation.[4] Efforts to model such sites by one-electron reduction of analogues for methemerythrin which have (μ-oxo)bis(μ-carboxylato)diiron(III) core structures have been unsuccessful because of the instability of the Fe(II)–Fe(III) core.[5] A strategy for circumventing the instability problem is the use of a binucleating ligand to hold the two metal centers together. One such Fe(II)–Fe(III) complex has been characterized by elemental analyses, near-IR spectroscopy, and magnetic susceptibility measurements from 80 to 300 K.[6] We have also adopted the binucleating ligand strategy to model the mixed-valence forms of iron–oxo proteins and report herein the properties of the Fe(II)–Fe(III) complex of N,N′-(2-
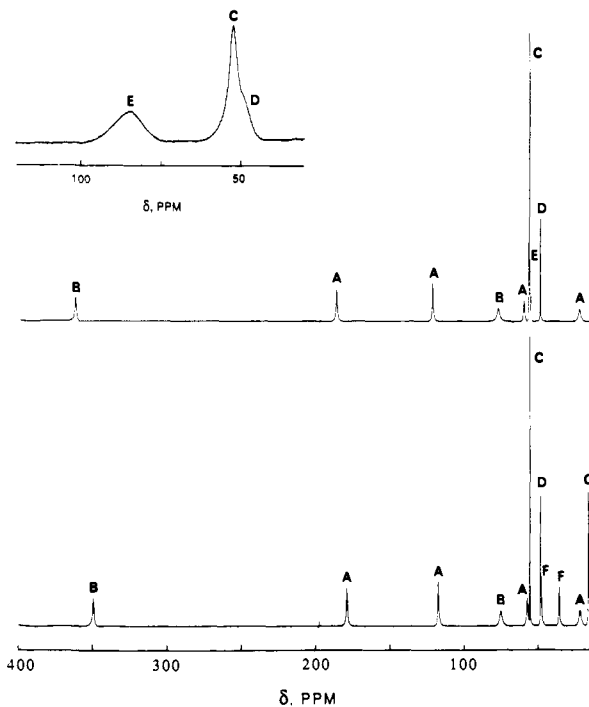
Figure 1. NMR spectra of [Fe^{II}Fe^{III}(HXTA)(OAc)$_2$]$^{2-}$ (top), [Fe^{II}Fe^{III}(HXTA)(OPr)$_2$]$^{2-}$ (bottom), and [Fe^{III}Fe^{III}(HXTA)(OAc)$_2$]$^-$ (insert) in CD$_3$OD with 0.050 M NaO$_2$CR/HO$_2$CR. Assignments (integration): (A) NCH$_2$COO$^-$ (2); (B) ArCH$_2$N (2); (C) p-ArCH$_3$ (3); (D) m-ArH (2); (E) $^-$OAcCH$_3$ (6); (F) $^-$OPrCH$_2$ (2); (G) $^-$OPrCH$_3$ (6).

hydroxy-5-methyl-1,3-xylylene)bis[N-(carboxymethyl)glycine] (HXTA).[7]

The diferric complex [Me$_4$N][Fe$_2$(HXTA)(OAc)$_2$] (**1**) has been crystallographically characterized to have a (μ-phenoxo)bis(μ-acetato)diiron(III) core structure.[8] Cyclic voltammetry of **1** in DMF shows a reversible wave centered at −286 mV vs SCE, which corresponds to the Fe(III)Fe(III)/Fe(II)Fe(III) couple.[9] Thus the treatment of a methanolic solution of **1** in the presence of 50 mM NaOAc/50 mM HOAc[8] with β-mercaptoethanol and excess Me$_4$NCl under nitrogen results in a one-electron reduction of **1** and yields a dark crystalline complex, [Na][Me$_4$N][Fe$_2$-(HXTA)(OAc)$_2$]·3H$_2$O (**2**).[10]

The electronic absorption spectrum of **2** exhibits a broad band at 470 nm (ε 800 M^{-1} cm^{-1}) which corresponds to phenolate-to-Fe(III) charge-transfer transitions. Two additional features are observed at 840 nm (ε 190 M^{-1} cm^{-1}) and 1275 nm (ε 200 M^{-1} cm^{-1}), which have extinction coefficients that are significantly higher than those normally expected for ligand field transitions.[11] We assign these bands as predominantly intervalence charge-transfer transitions between the two iron centers. These results suggest that **2** is a type II mixed-valence complex in the Robin–Day classification.[12]

As illustrated in Figure 1, the NMR spectra of **2** and its propionate derivative (**3**) exhibit sharp well-resolved signals which span 400 ppm in chemical shift. The significant decrease in the

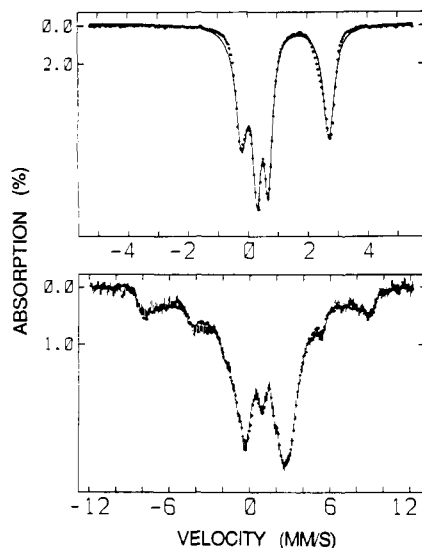(1) Wilkins, R. G.; Harrington, P. C. *Adv. Inorg. Biochem.* **1983**, *5*, 51–85.
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(10) Elemental Anal. Calcd for C$_{25}$H$_{41}$Fe$_2$N$_3$NaO$_{14}$: C, 38.78; H, 5.35; Fe, 14.42; N, 5.42. Found: C, 38.73; H, 4.97; Fe, 14.70; N, 5.48. We have also isolated the corresponding propionate derivative, [Me$_4$N]$_2$[Fe$_2$-(HXTA)(OPr)$_2$]. Anal. Calcd for C$_{31}$H$_{51}$Fe$_2$N$_4$O$_{13}$: C, 46.57; H, 6.44; N, 7.00. Found: C, 46.21; H, 6.69; N, 7.15.
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Figure 2. Mössbauer spectra of ^{57}Fe-enriched $[Fe_2(HXTA)(OAc)_2]^{2-}$ in methanol with 0.050 M HOAc/NaOAc at 55 K in zero applied field (top) and at 4.2 K in parallel (crosses) and transverse (hatchmarks) applied fields of 50 mT (bottom).

line width relative to that found in **1** is consistent with the presence of a fast-relaxing high-spin Fe(II) center in the mixed-valence complex.[13,14] The sharpness of the spectra allows us to observe all the protons in **2** and **3**, and we have assigned them by atom substitution experiments.[15,16] The HXTA ligand retains its twofold symmetry, indicating that electron transfer between the metal centers in the complex is fast on the NMR time scale. The bound acetate protons, found at 56 ppm, are in slow exchange with the free acetate in solution, and substitution of acetate with propionate results in CH_2 signals which are diastereotopic.[17] Both observations suggest that the carboxylates bridge the two iron centers; hence the triply bridged diiron structure found in **1** is retained in the mixed-valence form.

The Mössbauer spectrum of **2** at 55 K (Figure 2, top) consists of two quadrupole doublets of equal intensity with isomer shifts of 1.23 and 0.50 mm/s and quadrupole splittings of 2.87 and 0.37 mm/s, respectively, consistent with a high-spin Fe(II)–Fe(III) formulation.[18] The observation of discrete quadrupole doublets for this complex indicates that intervalence electron transfer is slow on the Mössbauer time scale at 55 K. Studies at 110 K show some line broadening, suggesting the onset of intermediate electron exchange. At 4.2 K the Mössbauer spectra (Figure 2, bottom) exhibit magnetic hyperfine interactions, even in zero applied magnetic field, implying a system with half-integer spin.[19] The spectra recorded in parallel (crosses) and transverse (hatchmarks) fields are essentially the same. This suggests a Kramers doublet with uniaxial magnetic properties; such systems produce, at best, only weak EPR signals. Indeed, except for a minor signal at g = 4.3 (<0.05 spin/Fe) which can be attributed to iron(III) from the decomposition of the complex in solution, **2** does not exhibit an EPR signal, even at 2 K. A preliminary analysis of the Mössbauer data suggests a coupled Fe(III)–Fe(II) system where the Fe(II) zerofield splitting and the antiferromagnetic coupling

between the metal centers are of similar magnitudes. Zerofield splittings for high-spin ferrous centers in non-heme environments are in the range of 10 cm^{-1},[20] while the J value for the complex is estimated to be ca. -5 ± 2 cm^{-1}[21] from the temperature dependence of the NMR isotropic shifts.[22] Further magnetic susceptibility studies on **2** are in progress.[23]

The Mössbauer and EPR properties of **2** recall those of the reduced uteroferrin–phosphate complex, which is also EPR silent despite Mössbauer data indicating a half-integer spin state;[24] **2** thus serves as a potential model for the magnetic properties of this complex. We are currently investigating the properties of Fe(II)–Fe(III) complexes of other binucleating ligands in an effort to understand how ligand environments influence the spectroscopic properties of mixed-valence iron complexes.

Note Added in Proof: We have recently become aware of a paper[25] reporting the electrochemical reduction of $[(Me_3TACN)_2Fe_2O(OAc)_2]^{2+}$, where Me_3TACN is 1,4,7-trimethyl-1,4,7-triazacyclononane. The one-electron reduction of this complex in solution yields a mixed-valence species with EPR features at g < 2.0, which are similar to those found in mixed-valence forms of iron–oxo proteins.

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Synthesis and Reactions of Anionic Metallocarboxylates of Iron

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Interest in both metallocarboxylic acids and their conjugate bases derives from their proposed intermediacy in metal carbonyl catalyzed water gas shift (WGS) reactions.[1] However, few of the acids[2] and fewer of the anionic metallocarboxylate complexes[3] have been characterized. Syntheses of the anionic complexes have resulted from either direct carbonation of a metal anion or deprotonation of a metallocarboxylic acid; in only a few cases has isolation been possible. We report here the isolation and characterization of M[FeCp(CO)(PPh$_3$)(CO$_2$)] (M = Li and K; Cp = η-C$_5$H$_5$), their behavior toward electrophiles, and their thermolysis reactions.

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