(7bβ,12bα,14cα)-7b,12b,13,14c-tetrahydro-1,3,6-trihydroxy-14*H*-benzo[*c*]naphtho[2,1,8-*mna*]xanthen-14-one.

The biogenetic pathway to **1** in *P. ohioense* apparently involves *O*-hydroxycinnamate and hydroxylated bibenzyls as intermediates. These compounds have been detected as natural products in a few mosses.[5,6]

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Supplementary Material Available: Details of the X-ray study including space group, experimental conditions, tables of atomic coordinates, thermal parameters, interatomic distances, and interatomic angles for **1**, and spectral data (UV, IR, MS, ^{13}C NMR, and ^{1}H NMR) for **1** and **2** (6 pages). Ordering information is given on any current masthead page.

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A Binuclear Mixed-Valence Ferromagnetic Iron System with an $S = 9/2$ Ground State and Valence Trapped and Detrapped States

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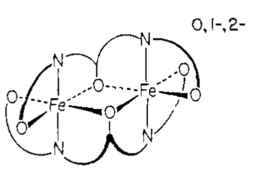
We have recently described the synthesis and certain physicochemical properties of a series of binuclear iron complexes $[Fe_2(salmp)_2]^{0,1-,2-}$ (**1–3**), derived from trianionic binucleating ligand salmp (**4**).[1,2] These complexes are part of a set whose members contain the bridge unit $Fe_2(\mu\text{-}OR)_2$ and, in turn, are members of a much larger set including some ten types of oxygen-bridged binuclear complexes.[1] There is substantial interest in binuclear Fe complexes because of the presence of binuclear, magnetically coupled units in proteins.[3] Subset **1–3** is unique because each oxidation level has been structurally defined and each, from magnetic susceptibility behavior, is *ferromagnetic*.[1] The current EPR and Mössbauer studies confirm this property and provide data elucidating the temperature dependence of the electron distribution in mixed-valence complex **2**.



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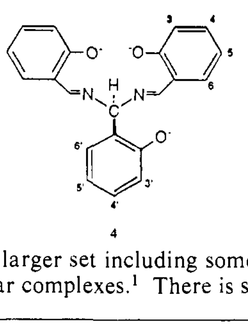

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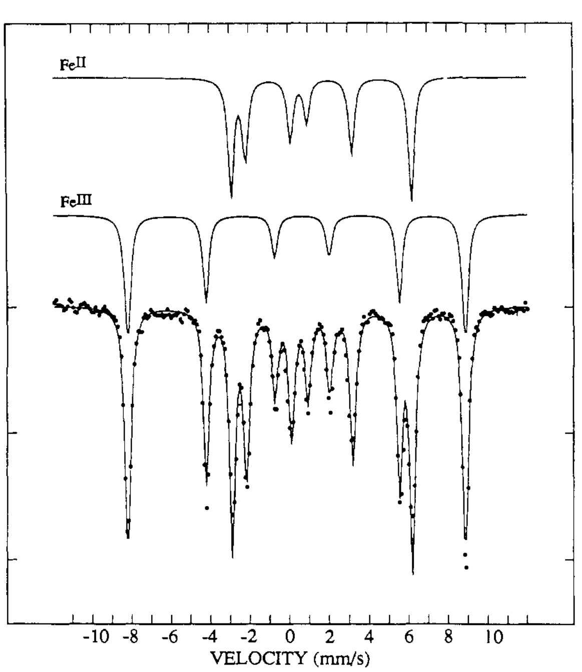

Figure 1. Mössbauer spectrum of polycrystalline $(Et_4N)[Fe_2(salmp)_2]$ at 1.5 K. Solid lines are simulations using an $S = 9/2$ spin Hamiltonian with the parameters quoted in the text. For the electronic system at hand, the values of the asymmetry parameter η and the angle β are not unique.[5] We used $\eta = +2$, $\beta = 30°$ for the Fe^{II} site and $\eta = -2$ and $\beta = 25°$ for the Fe^{III} site. Spectral decompositions into these two sites are shown above the data.

The X-band EPR spectrum of **2** (not shown) exhibits broad resonances centered at $\mathbf{g} \approx 6.4$ and 11. From variable-temperature studies, we tentatively conclude that these resonances originate from the first ($\mathbf{g}_y \approx 11$) and second excited Kramers doublet of an $S = 9/2$ system with $D \cong 1.5$ cm^{-1} and $E/D \approx 0.15$–0.33, where D and E are zero-field splitting parameters. For this range of E/D, an $S = 9/2$ system has a ground-state doublet with uniaxial magnetic properties ($\mathbf{g}_x \approx \mathbf{g}_z \approx 0$, $\mathbf{g}_y \approx 17.5$). Such doublets produce Mössbauer spectra that exhibit a six-line pattern for each Fe site. The exceptionally well-resolved spectrum of **2** in Figure 1 is consistent with this expectation.[6] Spectral simulations confirm the $S = 9/2$ spin state and yield the following information. (i) The two Fe sites occur in a 1:1 occupation ratio; there is no evidence for additional Fe species. (ii) The quadrupole splitting $\Delta E_Q = -0.92$ mm/s, the isomer shift[7] $\delta = 0.55$ mm/s, and the magnetic hyperfine coupling constant $\mathbf{a} = 29.0$ MHz are typical of high-spin Fe(III), whereas the parameters of the other site ($\Delta E_Q = +2.35$ mm/s, $\delta = 1.12$ mm/s, $a_y = 18.1$ MHz) are characteristic of high-spin Fe(II).[8-10] The value $\mathbf{a} = 29.0$ MHz

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(2) Abbreviations: bpmp, 2,6-[bis(2-pyridylmethyl)aminomethyl]-4-methylphenolate(1−); DMA, *N*,*N*-dimethylacetamide; hxta, *N*,*N*′-(2-hydroxy-5-methyl-1,3-xylylene)bis(*N*-carboxymethyl)glycinate(5−); Me_3tacn, 1,4,7-trimethyl-1,4,7-triazacyclononane; salmp, bis(salicylideneamino)-2-methylphenolate(3−).

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(6) The low-temperature Mössbauer spectra of **2** are essentially the same for the Et_4N^+ salt[1] as a polycrystalline sample and in acetonitrile or DMA solution.

(7) Isomer shifts are referenced to Fe metal at 300 K.

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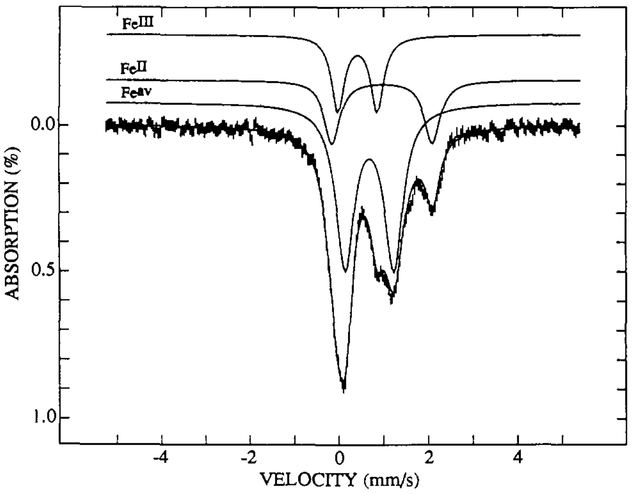

Figure 2. Mössbauer spectrum of polycrystalline $(Et_4N)[Fe_2(salmp)_2]$ at 297 K. The solid line through the data is the result of a least-squares fit to three doublets using the parameters in Table I. Curves shown above the data outline the individual quadrupole doublets.

Table I. Mössbauer Spectroscopic Parameters of Polycrystalline $(Et_4N)[Fe_2(salmp)_2]$ at 297 K

site	ΔE_Q, mm/s	δ, mm/s	Γ_l,[a] mm/s	Γ_h,[a] mm/s	%[b]
$\mathrm{Fe^{II}}$	2.24	0.99	0.44	0.39	20
$\mathrm{Fe^{III}}$	0.88	0.44	0.35	0.35	20
$\mathrm{Fe^{av}}$	1.08	0.71	0.44	0.55	60

[a] Full width of low- and high-energy doublet lines. [b] Percent of total absorption. Because the recoilless fractions of the three components may differ at 297 K, the percentages do not necessarily correspond to the fraction[5] of molecules in the designated states.

is typical for octahedral Fe(III) sites with O/N coordination.[11] (iii) The z-axes of both electric field gradient tensors are tilted by $\beta \cong 30°$ relative to the z-axis of the common zero-field splitting tensor.

At 100 K the electronic relaxation is fast, and the Mössbauer spectrum consists of two doublets characteristic of localized Fe(III) and Fe(II) sites. At somewhat higher temperatures, a new doublet ($\mathrm{Fe^{av}}$) appears; its intensity increases gradually as the temperature is raised. The spectrum of polycrystalline **2** in Figure 2 has been analyzed as follows. The high-energy features of all three doublets are well resolved. Assuming that the temperature dependencies of the δ values of the $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ sites are determined solely by the second-order Doppler shift ($\delta_{4.2K} - \delta_{300K} = 0.12$ mm/s), the two positions of the low-energy lines in the unresolved feature at ca. 0 mm/s can be fixed. With this information, the position of the low-energy line of the $\mathrm{Fe^{av}}$ doublet can then be calculated. For the final least-squares fit, the $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ doublets were constrained to have the same absorption area. The Mössbauer parameters listed in Table I convey an unusual result, viz., that the isomer shift of the $\mathrm{Fe^{av}}$ doublet is exactly the average of the shifts of the $\mathrm{Fe^{III}}$ and $\mathrm{Fe^{II}}$ sites.

From the preceding results, we draw the following conclusions concerning the electronic structure of mixed-valence **2**. (1) The complex is ferromagnetically coupled to afford an $S = 9/2$ ground state, which is well isolated from other states of the spin ladder. (2) Below 100 K, the complex is valence-trapped (class II[12]) in the polycrystalline state and in acetonitrile and DMA solutions. (3) Above 100 K, the complex exists as an apparent equilibrium mixture of valence-trapped (ca. 40% at 297 K) and "valence-detrapped" forms. Collective properties 1–3 are unique to this subset of oxygen-bridged iron dimers. All other synthetic iron dimers with various oxygen bridge modes,[1] including those in the $Fe_2(\mu\text{-}OR)_2$ set, are antiferromagnetically coupled, as are binuclear units in proteins.[3,13] The oxygen-bridged dimers $[Fe_2(hxta)(OAc)_2]^{2-}$ [9] and $[Fe_2(bpmp)(EtCO_2)_2]^{2+}$,[10] with the bridges $Fe_2(\mu\text{-}OR)(\mu\text{-}\eta_2\text{-}RCO_2)_2$, are valence-trapped (at least up to $T \approx 55$ K) but are antiferromagnetic. $[Fe_2(Me_3tacn)_2(OH)_3]^{2+}$ has an $S = 9/2$ ground state but is valence-delocalized (an example of double exchange[14]) very possibly because, unlike **2** (Fe–Fe = 2.79, 2.83 Å[1]), it is triply bridged with a short Fe–Fe distance (2.50 Å).[15] No other binuclear Fe complex displays property (3). Additional experiments are aimed at determining whether the doublet $\mathrm{Fe^{av}}$ reflects valence-detrapping (transitions between $\mathrm{Fe^{III}}$ and $\mathrm{Fe^{II}}$ that are fast on the Mössbauer time scale but slow on the vibrational time scale) or actual valence delocalization.[16] The results summarized here and elsewhere[1,3] emphasize the diversity of electronic properties of oxygen-bridged Fe complexes and the dependency of these properties on the details of the bridging interactions. Ferromagnetic binuclear Fe units now are a possibility that must be considered in analyzing the electronic structures of proteins.[13,17]

Acknowledgment. This research was supported at the University of Minnesota by NSF Grant DMB 86-05050 and at Harvard University by NIH Grant GM 28856.

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(11) This comparison cannot be made for the Fe(II) site because its **a**-tensor is expected to be quite anisotropic. Owing to the uniaxial nature of the ground Kramers doublet, only the components of the magnetic hyperfine tensor along the y-axis are determined at 1.5 K. We can, however, assume that $\mathbf{a}_x \approx \mathbf{a}_y \approx \mathbf{a}_z$ for high-spin Fe(III). The observed magnetic hyperfine tensors **A** of the coupled $S = 9/2$ state are related to the intrinsic **a**-tensors of each site by $\mathbf{A}(\mathrm{Fe^{II}}) = (4/9)\mathbf{a}(\mathrm{Fe^{II}})$ and $\mathbf{A}(\mathrm{Fe^{III}}) = (5/9)\mathbf{a}(\mathrm{Fe^{III}})$.

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(16) At 1.5 K and 100 K the Mössbauer spectra of **2** as a polycrystalline sample and in DMA solution are essentially the same. Poor signal-to-noise in DMA (mp −20 °C) at 210 K did not allow us to resolve the question whether the appearance of $\mathrm{Fe^{av}}$ is a solid-state effect or an intrinsic electronic phenomenon; samples enriched in ^{57}Fe are in preparation.

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Reductive Elimination of Methane from a Cationic Rhenium Methyl Hydride. Evidence for an Intermediate Methane Complex

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Although intramolecular "agostic" interactions between transition-metal centers and pendant C–H bonds are well-characterized,[1] there is less evidence for the coordination of free hydrocarbon C–H bonds to transition-metal moieties.[2] Such σ complexes of alkanes are of great importance due to the intense current interest in homogeneous alkane activation reactions.[3] As part of our studies of the reactivity of rhenium alkyls of the type

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