Conformational Tuning of Valence Delocalization in Carboxylate-Rich Diiron Complexes

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Mixed-valence metal clusters play important and diverse roles in the chemistry of transition elements in natural and synthetic systems.[1] An important goal of current research is to correlate structural properties with the extent and mechanism of valence delocalization in such clusters. These issues are of particular importance for understanding metalloprotein active sites such as iron−sulfur assemblies,[2a] the Cu_A sites in cytochrome *c* oxidase and nitrous oxide reductase,[2b] the Mn_4 cluster in the photosynthetic apparatus,[2c] and the carboxylate-rich non-heme diiron unit found in numerous enzymes.[2d] In diiron(II/III) enzymes and model complexes, antiferromagnetic coupling and vibronic trapping generally result in valence-localized systems with $S = 1/2$ ground states; parallel coupling of electronic spins, promoted by a "double exchange" mechanism and resulting in a valence delocalized $S = 9/2$ ground state, is exceedingly rare.[3−7] The only reported synthetic valence-delocalized molecules with $S = 9/2$ have very short Fe−Fe separations that are apparently responsible for the dominant double exchange; intermetal distances are 2.51 and 2.74 Å for $[(Me_3\text{-tacn})_2Fe_2(\mu\text{-OH})_3]^{2+}$[6] and $[(C_{24}H_{26}N_4O_2)Fe_2(\mu\text{-OAc})_2^+]$,[7] respectively. Here we report a new type of $S = 9/2$ complex, prepared using the bulky 2,6-dimesitylbenzoate ligand $(Mes_2ArCO_2^-)$. Interestingly, the complex exists in two structural

$= Mes_2ArCO_2$
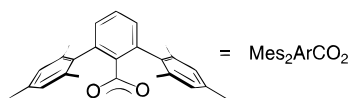
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(3) Blondin, G.; Girerd, J.-J. *Chem. Rev.* **1990**, *90*, 1359−1376.
(4) Only one [2Fe-2S] ferredoxin has been found with an $S = 9/2$ ground state. (a) Achim, C.; Bominaar, E. L.; Meyer, J.; Peterson, J.; Münck, E. *J. Am. Chem. Soc.* **1999**, *121*, 3704−3714. [2Fe-2S] fragments with $S = 9/2$ exist in [3Fe-4S] and [4Fe-4S] clusters, see: (b) Beinert, H.; Holm, R. H.; Münck, E. *Science* **1997**, *277*, 653−659.
(5) A mixed-valence form of ribonucleotide reductase-R2 with an $S = 9/2$ ground state has been characterized by EPR spectroscopy; whether this form is localized or delocalized is not known. See: (a) Hendrich, M. P.; Elgren, T. E.; Que, L., Jr. *Biochem. Biophys. Res. Commun.* **1991**, *176*, 705−710. (b) Davydov, R.; Sahlin, M.; Kuprin, S.; Gräslund, A.; Ehrenberg, A. *Biochemistry* **1996**, *35*, 5571−5576.
(6) $Me_3\text{-tacn} = $ 1,4,7-trimethyl-1,4,7-triazacyclononane. Gamelin, D. R.; Bominaar, E. L.; Kirk, M. L.; Wieghardt, K.; Solomon, E. I. *J. Am. Chem. Soc.* **1996**, *118*, 8085−8097.
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forms related by a simple conformational change that induces a switch from a completely valence-delocalized to a valence-trapped state. These findings provide a novel opportunity to examine the effect of intermetal distance on valence delocalization in diiron systems.

By using extremely sterically hindered carboxylate ligands, discrete, low-coordination-number iron complexes may be prepared without the use of chelating N-donors.[8] We recently reported[8a] the diiron(II) complex $(Mes_2ArCO_2)_4Fe_2(CH_3CN)_2$, which has a core structure closely related to those of the reduced forms of non-heme diiron enzymes.[9] This compound was found to react with dioxygen in noncoordinating solvents to form a purple species ($\lambda_{max} = 540$ nm), which we tentatively assigned as a diiron(III) peroxo species. Oxygenation of the diiron(II) complex at −30 °C in the presence of excess 2-propanol instead gave a blue solution, which upon purging with N_2 and cooling to −40 °C overnight afforded a solid.[10,11] Crystallization from Et_2O at −35 °C afforded blue plates that were suitable for X-ray diffraction studies. As shown in Figure 1a,b, the solid-state structure of $(Mes_2ArCO_2)_3Fe_2(OCHMe_2)_2 \cdot Et_2O$ (**1**) features a pair of five-coordinate irons bridged by two isopropoxide ligands and an additional bridging carboxylate. The isopropoxide groups adopt a configuration with the methyl−methyl axis perpendicular to the Fe−Fe vector. The mixed-valence $[Fe_2(\mu\text{-OCHMe}_2)_2]^{3+}$ core is puckered with acute O−Fe−O and Fe−O−Fe angles of 89.0° and 85.5° (av), respectively. The Fe−Fe distance of 2.6241(9) Å is significantly shorter than those of the related diiron(III) complexes $(Mes_2ArCO_2)_4Fe_2(\mu\text{-OCHMe}_2)_2$ (2.998(1) Å)[10] and $(Tol_2ArCO_2)_4Fe_2(\mu\text{-OH})_2$ (2.8843(9) Å).[8b] Both iron atoms display similar bond distances to their ligands at 173 K, consistent with valence delocalization.[12]

Altering the crystallization conditions $(Et_2O/(Me_3Si)_2O, 5 °C)$ afforded blue plates of the mixed-valence species (**2**) with a different unit cell. Unlike the structure of **1**, which was solvated with a molecule of Et_2O, that of **2** lacks cocrystallized solvent. The overall crystal structures are nearly identical, but there are some important differences.[13] Most noticeably, in **2** the bridging isopropoxide groups have rotated (ca. 90°) so that the methyl groups are coincident with the Fe−Fe vector (Figure 1c). Also, the Fe−Fe separation in **2** is 2.7485(5) Å, a 0.13 Å increase relative to **1** that apparently is due to the greater steric interactions between the bridging isopropyl groups and the mesityl units of the terminal carboxylates. Metal−ligand bond lengths are suggestive of valence localization at the collection temperature of 173 K.[12]

UV−visible spectroscopy of **1** or **2** dissolved in toluene revealed an absorption at $\lambda_{max} = 780$ nm ($\epsilon \approx 2000$ $M^{-1}cm^{-1}$). Since neither isopropoxide nor carboxylate should give rise to low-energy charge-transfer bands, this transition may be an intervalence transition similar to that found in $[(Me_3\text{-tacn})_2Fe_2$-

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(10) In the presence of excess oxygen, the blue solution decomposes to form a diiron(III) complex, $(Mes_2ArCO_2)_4Fe_2(\mu\text{-OCHMe}_2)_2$, which has been structurally characterized (Supporting Information).
(11) The blue complex can also be prepared from $(Mes_2ArCO_2)_4Fe_2(CH_3\text{-}CN)_2$ using 0.5 equiv of Me_3NO instead of dioxygen.
(12) For **1**, the average Fe−O bond lengths are 2.004 Å for Fe1 and 2.008 Å and Fe2 ($\Delta = 0.004$ Å). The analogous values for **2** are 2.039 and 1.998 Å ($\Delta = 0.041$ Å).
(13) Crystal structures of both conformational isomers were done twice using independently crystallized batches to ensure reproducibility.
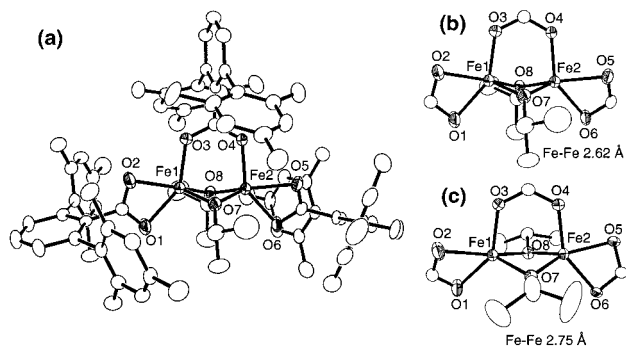
Figure 1. (a) ORTEP view of **1** drawn with 50% thermal ellipsoids. (b) Core atoms of **1**. Bond distances (Å): Fe1−Fe2, 2.6241(9); Fe1−O1, 2.104(3); Fe1−O2, 2.056(3); Fe1−O3, 2.001(3); Fe1−O7, 1.933(3); Fe1−O8, 1.926(3); Fe2−O4, 1.993(3); Fe2−O5, 2.101(3); Fe2−O6, 2.077-(3); Fe2−O7, 1.931(3); Fe2−O8, 1.942(3). (c) Core atoms of **2**. Bond distances (Å): Fe1−Fe2, 2.7485(5); Fe1−O1, 2.066(2); Fe1−O2, 2.129-(2); Fe1−O3, 2.017(2); Fe1−O7, 1.975(2); Fe1−O8, 2.008(2); Fe2−O4, 2.014(2); Fe2−O5$_{av}$, 2.06; Fe2−O6$_{av}$, 2.09; Fe2−O7, 1.911(2); Fe2−O8, 1.914(2).
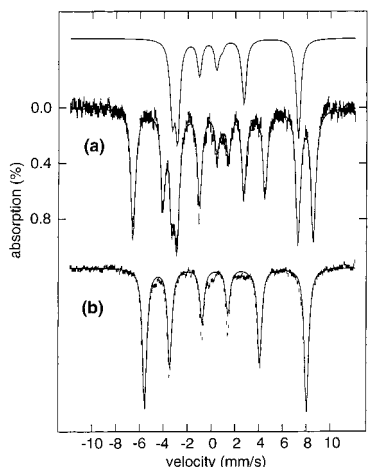

Figure 2. 4.2 K Mössbauer spectra of polycrystalline **2** (a) and **1** (b). The solid lines are spectral simulations yielding the parameters listed in Table 1. The solid line drawn above the spectrum of **2** indicates the contribution of the "ferrous" site. The spectra were simulated using a spin Hamiltonian for an $S = 9/2$ system with $D < 0$ and $E/D = 1/3$.

Table 1. 4.2 K Mössbauer Parameters for Delocalized **1** and Localized **2**

compound	δ (mm/s)	ΔE_Q (mm/s)	η	α (deg)	β (deg)	H_{int} (T)
1	0.76(2)	2.0(1)	0.7	0	38	41.0(10)
2 (site 1)	0.59(2)	1.6(1)	0.9	22	35	46.5(10)
2 (site 2)	0.94(2)	2.6(2)	0.5	0	5	31.5(10)

a ground Kramers doublet for which $g_z \gg g_x$, g_y; for $E/D = 1/3$, the ground doublet of an $S = 9/2$ system has $g_x \approx g_y \approx 0$ and $g_z \approx 17.8$. Such a doublet yields, for slow spin relaxation, a characteristic six-line Mössbauer spectrum for each iron site of an exchange coupled dimer. Spectra taken in weak applied magnetic fields depend on ΔE_Q, the asymmetry parameter η, the internal magnetic field H_{int}, and its direction (α,β) relative to the quadrupole tensor. The spectrum of **2**, shown in Figure 2a, contains two components of equal intensity, indicative of localized ferric and ferrous sites. Valence-trapped sites are also evident in the 200 K spectrum of **2** (not shown), which exhibits two doublets with $\Delta E_Q(1) = 1.57$ mm/s, $\delta(1) = 0.52$ mm/s and $\Delta E_Q (2) = 2.08$ mm/s, $\delta(2) = 0.87$ mm/s. In contrast, **1** is a delocalized system for which both Fe sites contribute identical spectra.[15] Thus, for **1**, *one* six-line pattern is observed at 4.2 K (Figure 2b) and one doublet at 200 K ($\Delta E_Q \approx 1.85$ mm/s, $\delta \approx 0.72$ mm/s). Note that the ΔE_Q, δ, and H_{int} values for **1** (Table 1) are nearly the arithmetic mean of the corresponding values of the two sites of **2**, as expected for a fully delocalized system (see eqs 3 and 4 of ref 4a). Additionally, preliminary Mössbauer spectra of frozen toluene solutions indicate a delocalized state similar to that of **1**.

For a mixed-valence Fe(II)Fe(III) dimer, the spin state and electron delocalization depend on an interplay of HDvV exchange, double exchange, and vibronic coupling. For sufficiently strong double exchange, the dimer has a valence-delocalized $S = 9/2$ ground state; an $S = 7/2$ state is also possible but much less likely (see Figure 2 of ref 16). The Mössbauer results (Table 1)[17,18] show that **1** is a class III[19] mixed-valence dimer for which a dominant double exchange interaction produces a delocalized ground state. If double exchange were absent in **2**, we would expect, at 4.2 K, δ values of ca. 0.45 and 1.2 mm/s for ferric and ferrous sites, respectively. The observation of $\delta(1) = 0.59$ mm/s and $\delta(2) = 0.94$ mm/s at 4.2 K suggests that double exchange, perhaps aided by ferromagnetic HDvV exchange ($H = JS_1 \cdot S_2$, $J < 0$), is sufficiently strong in **2** to produce the $S = 9/2$ ground state of **2**. Double exchange seems to be strong enough to produce some charge delocalization[20] but not strong enough to completely delocalize the system. Thus, it appears that **2** is a class II mixed-valence complex.

In conclusion, we have identified a correlation between metal−metal distance and degree of valence delocalization in topologically analogous $S = 9/2$ diiron complexes. The switching of ground-state electronic structure upon a conformational change (rotation of the C−O bond in the bridging isopropoxide accompanied by a change in Fe−Fe separation) is a unique feature of this system.

Supporting Information Available: Synthetic procedures, characterization and crystallographic data for all new compounds, and variable temperature magnetic susceptibility data for **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(μ-OH)$_3$]$^{2+}$.[6] Magnetic susceptibility measurements of **2** from 10 to 320 K suggest an $S = 9/2$ ground state. Thus, we observed at 30 K $\mu_{eff} = 10.3$ μ_B, which decreased to 9.6 μ_B at 320 K (see Supporting Information). Moreover, EPR spectra of solid **2** revealed between 2 and 16 K a broad isotropic signal at $g \approx 6.2$ that can be attributed to the middle Kramers doublet of an $S = 9/2$ multiplet with $E/D \approx 1/3$.[2a] Owing to rapid conversion of **1** to **2** upon grinding polycrystalline samples, we have so far been unable to obtain magnetic or EPR data on pure **1**.[14]

Figure 2 shows Mössbauer spectra of polycrystalline **1** and **2** at 4.2 K. The shapes of these spectra suggest that they result from

(14) Preliminary data of solid **1** contain a major feature at $g \approx 10$ that may result from the $\pm 3/2$ doublet of an $S = 9/2$ system with $E/D \approx 0.2$.

(15) The sample of **1**, shown in Figure 2b, contained a contaminant of **2** (22%) and a high-spin ferrous impurity (6%). We have removed their contributions from the data.

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(17) For six-line spectra, such as those of Figure 2, not all parameters are uniquely determined. Thus, there may exist an infinite manifold of {α,β,η} values that produce identical spectra. See ref 18.

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