

Valence-Delocalized Diiron(II,III) Cores Supported by Carboxylate-Only Bridging Ligands

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In the present communication we disclose the synthesis and characterization of a series of valence-delocalized diiron(II,III) complexes supported only by bridging carboxylate ligands. The existence of this class of compounds first emerged during an investigation of the dioxygen reactivity of tetra(carboxylate)-diiron(II) complexes as models for dioxygen-activating centers in non-heme diiron enzymes.^{1,2} An intriguing green $S = 9/2$ paramagnetic component was detected in the metastable mixture formed in the reaction of a diiron(II) complex with dioxygen, preliminary Mössbauer studies of which indicated it to be a valence-delocalized diiron(II,III) cluster.² An independent synthesis of this green species and related complexes has now been achieved, spin-coupling in which apparently is dominated by a double exchange mechanism.^{3,4} These findings provide the first observation of this phenomenon in diiron clusters having no single-atom bridging ligand(s), and suggest that a direct metal–metal interaction promoted by the short intermetal distance may help achieve the spin delocalization.

The diiron(II) precursor compound $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_4(4\text{-}^t\text{BuC}_5\text{H}_4\text{N})_2]$ (**1**)² undergoes a reversible one-electron oxidation ($E_{1/2} = -216$ mV vs $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$; $\Delta E_p = 89$ mV, scan rate = 25 mV/s) as revealed by cyclic voltammetry in CH_2Cl_2 solution (Figure S1). Compound **1** can be oxidized chemically, either by $[\text{Cp}_2\text{Fe}](\text{PF}_6)$ or by AgOTf , in CH_2Cl_2 (Scheme 1) to generate dark emerald green solutions of $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_4(4\text{-}^t\text{BuC}_5\text{H}_4\text{N})_2]\text{X}$ ($\text{X} = \text{PF}_6^-$ or OTf^-) (**4**). Compound **4** is thermally stable but decolorizes upon exposure to dioxygen or addition of coordinating solvents (THF, MeCN, or MeOH). The analogous green mixed-valence diiron compounds $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_4(\text{py})_2](\text{OTf})$ (**5**) and $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_4(\text{THF})_2](\text{PF}_6)$ (**6**) were prepared from the corresponding diiron(II) precursors, $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_2(\text{O}_2\text{CAR}^{\text{Tot}})_2(\text{py})_2]$ (**2**) and $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_2(\text{O}_2\text{CAR}^{\text{Tot}})_2(\text{THF})_2]$ (**3**),¹ by the same route (Scheme 1). The structure of **4** (Figure S2), as determined by X-ray crystallography,⁵ reveals a shortening by ~ 0.11 Å of the $\text{Fe}\cdots\text{Fe}$ separation (2.713(3) Å) compared with that in the precursor compound **1** (2.823(1) Å).² Each iron center in **4** retains square-pyramidal coordination with negligible geometric changes upon 1-electron oxidation of the diiron(II) complex, consistent with the reversible nature of the redox process

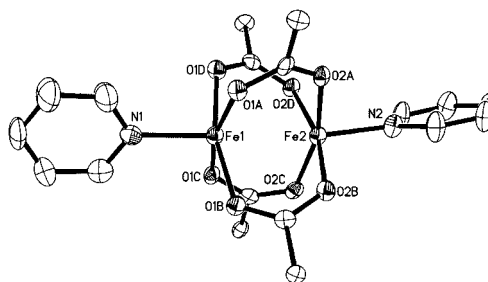
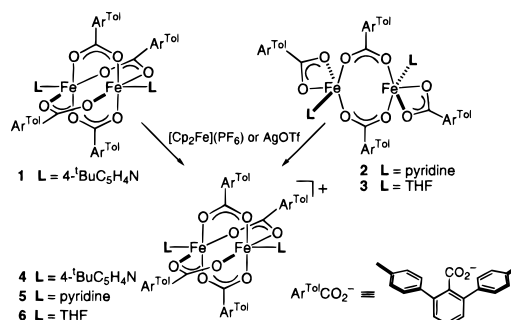


Figure 1. ORTEP diagram of the $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_4(\text{py})_2](\text{OTf})$ (**5**) cation showing 50% probability thermal ellipsoids for non-hydrogen atoms. For clarity, all atoms of the 2,6-di(*p*-tolyl)benzoate ligands, except for the carboxylate groups and the α -carbon atoms, were omitted. Selected interatomic distances (Å): $\text{Fe1}\cdots\text{Fe2}$, 2.6982(13); $\text{Fe1}-\text{O1A}$, 2.011(3); $\text{Fe1}-\text{O1B}$, 2.008(3); $\text{Fe1}-\text{O1C}$, 2.013(4); $\text{Fe1}-\text{O1D}$, 2.012(4); $\text{Fe1}-\text{N1}$, 2.104(4); $\text{Fe2}-\text{O2A}$, 2.015(3); $\text{Fe2}-\text{O2B}$, 1.989(3); $\text{Fe2}-\text{O2C}$, 2.000(3); $\text{Fe2}-\text{O2D}$, 2.005(3); $\text{Fe2}-\text{N2}$, 2.085(4).

Scheme 1



as observed by cyclic voltammetry. In contrast, the pyridine (**2**) and THF (**3**) derivatives undergo significant structural reorganization upon 1-electron oxidation. In both cases, the two carboxylate ligands in the precursor complex shift from terminal chelating to bidentate bridging (Scheme 1), with concomitant shortening of the $\text{Fe}\cdots\text{Fe}$ separations from 4.2189(13) Å to 2.6982(13) Å (**5**) and from 4.2822(7) Å to 2.6633(11) Å (**6**) (Figures S3 and S4). As illustrated in Figure 1, the $\text{Fe}-\text{N}/\text{Fe}-\text{O}$ distances are similar for both iron centers in **5** at 188 K (average $\text{Fe1}-\text{O}$, 2.011(7) Å; $\text{Fe2}-\text{O}$, 2.002(6) Å), consistent with the valence-delocalized nature of the diiron cluster.

The electronic spectrum of **4** in CH_2Cl_2 (Figure S5) displays a broad intervalence charge-transfer band at 670 nm ($\epsilon \approx 3200$ $\text{M}^{-1} \text{cm}^{-1}$). Similar broad visible absorptions were observed for **5** and **6**. The values of $\Delta\nu_{1/2}$ calculated by Hush's relationship^{6,7} for class II mixed-valence compound are much larger than those measured for **4–6** (Table S1), indicating the valence-delocalized nature of these centers. The $S = 9/2$ ground-state resulting from the high-spin iron(II)iron(III) unit is characterized by a broad $g = 10$ signal in the EPR spectrum displayed by a frozen $\text{CH}_2\text{-Cl}_2$ solution of **4**.⁸ Consistent with this result, the μ_{eff} value of 11.0 μ_B (300 K) obtained from the magnetic susceptibility data (Figure S6) on a powder sample of **4** is close to the spin-only value of 9.9 μ_B ($g = 2.00$) for the $S = 9/2$ total spin system. Similar values were obtained for **5** and **6** (Table S1).⁹

The electronic structure of **4** was further probed by Mössbauer studies. At 4.2 K and in a weak applied magnetic field (50 mT),

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(8) This signal is identical with that recorded for the $S = 9/2$ component in the paramagnetic species generated from the reaction of **1** with dioxygen at low temperature, detailed parameters of which were reported previously.²

(9) Detailed analysis of the magnetic susceptibility data is currently in progress.

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(5) Crystal data: triclinic, $P1$, $a = 16.472(5)$ Å, $b = 16.706(5)$ Å, $c = 17.888(5)$ Å, $\alpha = 108.243(5)^\circ$, $\beta = 90.614(5)^\circ$, $\gamma = 90.587(5)^\circ$, $Z = 2$, $T = -85$ °C, $R = 0.104$. This structure was not fully refined due to severe disorder in the lattice solvent molecules and the PF_6^- counterion.

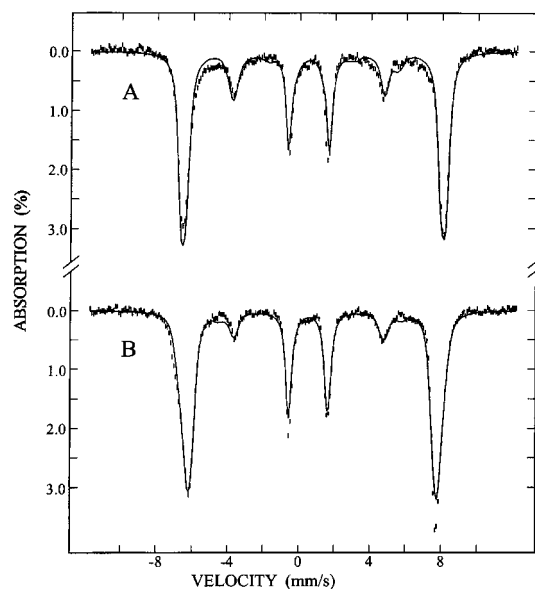


Figure 2. Mössbauer spectra of the solid powder sample of **4** recorded at 4.2 K with a magnetic field of 4 (A) and 8 (B) T parallel to the γ -rays. The solid lines are theoretical simulations using the parameters listed in the text.

the spectrum of a solid powder sample of **4** is broad and featureless, indicative of intermediate electronic relaxation (data not shown). In a strong applied field (>3 T), however, the effects of electronic relaxation diminish and well-resolved spectra are obtained. Figure 2 shows Mössbauer spectra of **4** recorded at 4.2 K with a magnetic field of 4 (spectrum A) and 8 (spectrum B) T applied parallel to the γ -rays. A distinct six-line pattern is observed under these experimental conditions, indicating that the two iron sites contribute identically to the spectra. This observation demonstrates unambiguously that **4** is valence-delocalized. Analysis of the data yields the following parameters: $D = 1.7 \text{ cm}^{-1}$, $E/D = 0.013$, $\Delta E_Q = -0.55 \text{ mm/s}$, $\delta = 0.65 \text{ mm/s}$, $\mathbf{A}/g_n\beta_n = -(11.1, 11.6, 16.0) \text{ T}$.¹⁰ The isomer shift of 0.65 mm/s lies between that of high-spin ferric and high-spin ferrous ions having N/O ligands. Although this value is comparable to those (0.67–0.84 mm/s) observed for other valence-delocalized $S = 1/2$ diiron(II,III) complexes,^{11–13} it falls near the lower end of the observed range, consistent with the formally five-coordinate geometry of the iron centers. The $|\Delta E_Q|$ value is unusually small for delocalized diiron(II,III) compounds, however, for which it is typically $\sim 2 \text{ mm/s}$.^{11–13} The low $|\Delta E_Q|$ value of **4** suggests a quantum admixture of the d_z^2 with other 3d orbitals, most probably d_{xy} , since d_z^2 and d_{xy} generate opposite electric field gradients.¹⁴ The precise nature of this quantum admixture, however, is presently uncertain.

(10) In the Mössbauer analysis, the E/D parameter ratio was fixed at the value of 0.013 determined from the EPR measurement.² The magnetic hyperfine tensor \mathbf{A} was assumed to be collinear with the electronic zero-field splitting tensor \mathbf{D} . Allowing the \mathbf{A} tensor to rotate through an Euler angle $\beta = 23^\circ$ would reduce the A_z value to -14 T , which is more in line with that observed for another $S = 1/2$ valence-delocalized iron(II,III) complex.¹¹

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In conclusion, we have synthesized valence-delocalized diiron(II,III) complexes supported solely by carboxylate-bridging ligands. Encapsulation of the dimetallic core in a sterically hindered, nonrigid framework^{1,2,13,15} may facilitate the efficient conversion of the diiron(II) precursor to the corresponding mixed-valence complexes. Mixed-valence clusters mediate electron transfer and multielectron redox processes in living systems. Our understanding of the spin-coupling mechanisms in such clusters has been advanced by comparison with well-defined synthetic model complexes having comparable spectral and magnetic properties.^{16–18} In most high-spin iron(II)iron(III) clusters,^{19–26} antiferromagnetic Heisenberg–Dirac–van Vleck (HDvV) exchange dominates to afford an $S = 1/2$ ground state. Several examples of valence-delocalized diiron(II,III) cores with $S = 1/2$ ground states have also been characterized, however. Included are two mutant forms of a [2Fe-2S] ferredoxin,^{17,27} and four synthetic diiron(II,III) complexes,^{11–13,28} all of which have single-atom bridging ligands, either hydroxo, phenoxo, or alkoxo.²⁹ In all cases, double exchange was attributed to parallel alignment of the electron spins and delocalization over the two metal centers. Clearly, the factors that govern the different valence-delocalization mechanisms in biological or synthetic systems have yet to be delineated fully. In the compounds described here, direct metal–metal interactions may play an important role in spin delocalization by double exchange, the details of which are currently under investigation.

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Supporting Information Available: Details of the synthetic procedures, X-ray crystallographic tables, and physical characterization of **4–6** (PDF) and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) Antiferromagnetically coupled (μ -oxo)diiron(II,III) centers are observed in both synthetic and biological systems.^{20–22} Recently, we reinvestigated the low-temperature dioxygen reaction of a (μ -hydroxo)bis(μ -carboxylato)-diiron(II) complex.²³ The metastable green intermediate thus generated, which previously was assigned as the (μ -peroxo)diiron(III) species,²⁴ proved to be a mixture containing a significant quantity (18–25%) of $S = 1/2$ mixed-valence iron(II)iron(III) component. This species may arise from outer-sphere one-electron oxidation of the diiron(II) precursor complex, as reported for related compounds.^{25,26}

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