Structural and Spectroscopic Studies of Valence-Delocalized Diiron(II,III) Complexes Supported by Carboxylate-Only Bridging Ligands

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The synthesis, molecular structures, and spectroscopic properties of a series of valence-delocalized diiron(II,III) complexes are described. One-electron oxidation of diiron(II) tetracarboxylate complexes afforded the compounds [Fe$_2$(µ$_2$-O$_2$-Cr$_{2}$s$_{2}$)$_2$]X, where L = 4′-BuC$_3$H$_7$N (1b), C$_3$H$_5$N (2b), and THF (3b); X = PF$_6$ (1b and 3b) and OTf$^-$ (2b). In 1b-3b, four µ-1,3 carboxylate ligands span relatively short Fe$^{2+}$-Fe distances of 2.663(11)−2.713(3) Å. Intense ($ε = 2700$−3200 M$^{-1}$ cm$^{-1}$) intervalence charge transfer bands were observed at 620−670 nm. EPR spectroscopy confirmed the $S = \frac{3}{2}$ ground spin state of 1b-3b, the valence-delocalized nature of which was probed by X-ray absorption spectroscopy. The electron delocalization between paramagnetic metal centers is described by double exchange, which, for the first time, is observed in diiron clusters having no single-atom bridging ligand(s).

Introduction

Metalloproteins having valence-delocalized Cu$_2$(I,II) or Fe$_2$(II,III) sites are important participants in biological electron transfer (ET) reactions. By delocalizing the charge over multiple nuclei, distortions associated with redox processes are significantly reduced, thus lowering Franck-Condon barriers for ET. Electron trafficking through such clusters is tightly regulated by a delicate interplay between geometric and electronic factors, the understanding of which has been greatly assisted by bioinorganic modeling studies. 1,2,3,5,6

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10 The Cu$_3$ centers in cytochrome c oxidase and nitrous oxide reductase use the Cu(I)Cu(I)/Cu(II) redox couple for intramembrane ET. By contrast, intraprotein ET has been reported in metalloenzymes that use the Cu(I)Cu(II)/Cu(II,III) redox couple. In the latter case, the short Cu−Cu distances (~2.4 Å) revealed by X-ray crystallography indicate direct Cu−Cu bonding, which is crucial for valence delocalization at low-symmetry protein sites. 10 Comparison with a model complex suggests that overlap between 3d$_{z^2}$ orbitals is

(7) Cu(II,III) denotes a valence-delocalized Cu(I)/Cu(II) center, which can be more appropriately described as Cu(1.5)Cu(1.5). In a similar way, Fe$_2$(II,III) represents a valence-delocalized Fe(II)/Fe(III) core.

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responsible for strong electronic coupling in Cu₄, although indirect superexchange via bridging cysteine thiolate ligands also occurs.12

Iron–sulfur clusters in electron transferases participate in many biological ET processes.5,10 The sulfido bridging ligands in [2Fe-2S] clusters mediate strong antiferromagnetic coupling and afford valence-trapped Fe(II)Fe(III) units upon reduction of the metal center.14,15 Similar vibronic trapping is responsible for the S = 1/2 ground spin state for oxo- or hydroxo-bridged Fe(II)Fe(III) centers.16–19 Valence-delocalized Fe₂(II,III)⁺ units with a ground spin state of S = 5/2, however, occur in two mutant forms of a [2Fe-2S] ferredoxin,20,21 and [2Fe-2S] subsites within mixed-valence [4Fe-4S] or [3Fe-4S] clusters.14 This interesting phenomenon, whereby valence localization shifts to delocalization upon formal dimerization of the {Fe₃S₄}⁺ units, has yet to be understood.22 The resonance energy associated with valence delocalization affects the cluster redox potential23,24 as well as the rate of ET.23

Studies of discrete valence-delocalized Fe₂(II,III) complexes can provide insights into the physical origin of parallel spin alignment observed in biological systems. Prior to this work, few synthetic diiron complexes, [Fe₂(µ-OH)]₃(Me₃TACN)₃Cl⁺ (A),26,27 [Fe₂(µ-OAc)]Cl⁺ (B),26,28 and [Fe₂(µ-OPr)₃(µ-O-CA₄Mε)(O₂CA₄Mε)₂]⁺ (C)26,29 were structurally characterized, having S = 5/2 ground spin states that arise from valence-delocalized Fe₂(II,III) cores (Figure 1). Various spectroscopic techniques were applied to understand the magnetic and electronic interactions between the metal centers in these compounds. Mössbauer spectroscopy provided the most compelling evidence for equivalent iron sites within the valence-delocalized Fe₂(II,III) cores.27b,28,29 In addition, Fe L-edge X-ray absorption spectroscopy (XAS) was employed to probe the electronic structure of valence-trapped and -delocalized Fe(II)Fe(III) complexes.26 Although Fe K-edge and preedge (1s → 3d region) XAS both can provide geometric and electronic structural information,2,21 this technique has not been used to address issues concerning electron delocalization in iron dimers.

Previously, we communicated the first example of valence-delocalized Fe₂(II,III) complexes having no single-atom bridging ligand(s).31 One-electron oxidation of tetracarboxylicative diiron(II) precursor compounds afforded a series of (µ-1,3-carboxylato)diiron(II,III) complexes, the S = 5/2 ground spin state of which was indicated by magnetic susceptibility measurements. Characteristic six–line patterns were observed in magnetic Mössbauer spectra recorded at 4.2 K, revealing that the extra electron in the S = 5/2 spin system is delocalized over two metal centers. The iron atoms are thus rendered equivalent on the Mössbauer time scale (~10⁻⁷ s). In this paper, we present a full description of the synthesis and

Figure 1. Solid-state structures of the cations in [(Me₃TACN)₂Fe₂(µ-OH)]ClO₄ (A),27d [L₃Fe₂(µ-OAc)]ClO₄ (B),28a and [Fe₂(µ-OPr)₃(µ-O-CA₄Mε)(O₂CA₄Mε)₂]⁺ (C)26,29 generated using the crystallographic coordinates, where N is blue, O is bright red, and Fe is dark red.

(26) Abbreviations used: Me₃TACN, 1,4,7-triethyl-1,4,7-triazacyclonane; L₁, [2 + 2] condensation product of propyleneimide and 2,6-diformyl-4-methylphenoxide; A⁺(µ-O-CA₄Mε)⁻; 2,6-dimesitylbenzotate; Ar⁺(µ-OPr)⁻; 2,6-dicyanobenzoate; RNR-R₂, the R₂ subunit of ribonucleotide reductase.
spectroscopic properties of the compounds [Fe₂(μ-O₂CArTol)₂(L₂)]X, where ArTolCO₂ = 2,6-di(p-tolyl)benzoate; L = 4'-BuC₃H₄N (1b), C₅H₅N (2b), and THF (3b); X = PF₆⁻ (1b and 3b) and OTf⁻ (2b). XAS studies disclosed the valence-delocalized nature of 1b—3b, further substantiating the previous assignment made by Mössbauer spectroscopy. Notably, the “extra” electron in the Fe₂(III) class remains delocalized even in the X-ray photoexcited states, demonstrating that XAS can be a useful probe for investigating this class of compounds.

**Experimental Section**

**General Considerations.** All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Dichloromethane was distilled over CaH₂ under nitrogen. Diethyl ether, pentanes, and THF were saturated with nitrogen and purified by passage through activated Al₂O₃ columns under nitrogen.32 The compounds [Fe₂(μ-O₂CArTol)₂(C₅H₅N)] (1a), [Fe₂(μ-O₂CArTol)₃(C₅H₅N)] (2a), and [Fe₂(μ-O₂CArTol)₂(O₂CArTol)₃] (3a) were prepared by a procedure analogous to that used to obtain 1b.17 Deep yellow CH₂Cl₂ solution (5 mL) of [Cp₂Fe](PF₆) (40 mg, 121 μmol) and AgOTf (22 mg, 88 μmol) was added dropwise to a CH₂Cl₂ (5 mL) suspension of [Cp₂Fe](PF₆) (30 mg, 91 μmol). The reaction mixture was dark emerald green following the addition. The solution was stirred for 1 h, and volatile fractions were removed under reduced pressure. The solid residue was washed with pentanes (10 mL) and filtered. Recrystallization from CH₂Cl₂/pentanes afforded 1b (86 mg, 50 μmol, 62%) as dark green microcrystalline material, which was analyzed by X-ray crystallography. FT-IR (KBr, cm⁻¹): 3024, 2962, 2923, 2870, 1618, 1583, 1514, 1497, 1440, 1405, 1386, 1306, 1272, 1232, 1211, 1187, 1153, 1110, 1069, 1030, 844, 792, 728, 704, 586, 557, 530, 488. UV–vis (CH₂Cl₂, λmax, nm (ε, M⁻¹ cm⁻¹)): 670 (3200), 450 (sh, 1600), 380 (sh, 3100). Anal. Calcd for C₁₀₂H₆₄N₂O₁₄Fe₂Fe₂P₂: C, 71.16; H, 5.47; N, 1.62. Found: C, 71.16; H, 5.85; N, 1.62.

[Fe₂(μ-O₂CArTol)₃(C₅H₅N)](OTf) (2b). To a rapidly stirred deep yellow CH₂Cl₂ solution (5 mL) of 1a (113 mg, 77 μmol) was added dropwise AgOTf (22 mg, 88 μmol) in CH₂Cl₂ (5 mL). The heterogeneous mixture was stirred for 1 h and filtered through Celite. The dark green filtrate was concentrated to ca. 5 mL. Vapor diffusion of pentanes into the resulting solution afforded dark brown crystals of 2b (90 mg, 55 μmol, 71%), which were suitable for X-ray crystallography. FT-IR (KBr, cm⁻¹): 3025, 2919, 1610, 1583, 1513, 1485, 1437, 1406, 1384, 1304, 1265, 1222, 1184, 1125, 1148, 1110, 1067, 1044, 1031, 1016, 845, 814, 790, 761, 727, 712, 704, 692, 636, 584, 528, 487, 416. UV–vis (CH₂Cl₂, λmax, nm (ε, M⁻¹ cm⁻¹)): 665 (2900), 455 (sh, 1800), 385 (sh, 1520), 340 (sh, 1382), 330 (sh, 1305), 320 (sh, 1270), 295, 260, 218, 197. Anal. Calcd for C₁₀₂H₆₄N₂O₁₄Fe₂Fe₂OTf: C, 71.16; H, 5.47; N, 1.62. Found: C, 71.62; H, 4.98; N, 1.64.

[Fe₂(μ-O₂CArTol)₃(C₅H₅N)]PF₆ (3b). This compound was prepared from 3a (154 mg, 105 μmol) and [Cp₂Fe](PF₆) (40 mg, 121 μmol) by a procedure analogous to that used to obtain 1b.18

(35) SMART v5.05; Bruker AXS Inc.; Madison, WI, 1998.
(37) Sheldrick, G. M. SADABS v2.03: Area-Detector Absorption Correction; University of Göttingen: Göttingen, Germany, 1999.
calibrated by a frequency counter and the magnetic field with a
NMR gaussmeter. The temperature of both instruments was
calibrated using devices from Lake Shore Cryotronics. For X- and
Q-band EPR, the magnetic field modulation was 100 kHz. All
experimental data were collected under non-saturation conditions.
For all measurements, ~2 mM frozen solutions were prepared in
a 1:2 mixture of dichloromethane and 2-chlorobutane, in which
the samples formed a nice glass.

**EPR Simulations.** Analysis of the EPR spectra utilized the
general spin Hamiltonian of the electronic system (eq 1). Simula-
tions of the EPR spectra were obtained from diagonalization of eq
1 with locally written software. The powder pattern was generated
for a uniform spherical distribution of the magnetic field vector B.
The transition intensities were calculated from the square of the
transition moment. The spectral line width was dominated by
D-strain, and simulations used distributions of the D and E/D values,
specified as $a_D$ and $a_{E/D}$, to give the correct line width. Least-squares
and deconvolution analyses of the spectra were combined to allow
relevant parameters to vary while maintaining a sum of multiple
species that best fit the experimental data. The simulations were
generated with careful consideration of all intensity factors, both
theoretical and instrumental. This approach allowed direct com-
parison of simulated spectra to the absolute intensity scale of the
experimental spectra having a known sample concentration. The
only unknown factor relating the spin concentration to signal
intensity is an instrumental one that depends on the microwave
detection system. This factor was determined by the spin standard
CuEDTA, however, for which the copper concentration was
accurately determined by plasma emission spectroscopy.

**X-ray Absorption Spectroscopy (XAS).** X-ray absorption
spectra were measured on unfocused wiggler beamline 7-3 at the
Stanford Synchrotron Radiation Laboratory (SSRL), with the ring
operating at 3 GeV and 70~100 mA. Solid samples of 1a, 1c, and
1b~3b were prepared by grinding ~30 mg of polycrystalline
powder with BN and pressing the mixture into a 1 mm thick
aluminum sample holder. Samples were maintained at 10 K inside
an Oxford Instrument CF-1208 liquid helium continuous flow
cryostat. A Si(220) double-crystal monochromator was used,
detuned 50% at 7987 eV in order to minimize contamination of the
radiation by higher harmonics. Vertical 1 mm monochromator
slits were used to define the beam size, minimizing beam
divergence and allowing for an energy resolution of ~1.4 eV at the
Fe K-edge. Spectra were measured in transmission mode using
dinitrogen-filled ionization chambers. The spectrum of Fe foil was
collected concomitantly, allowing for internal energy calibration
of the data. The first inflection point energy for the Fe foil spectrum
was set to 7111.2 eV. The reproducibility in the determination of edge
position was <0.2 eV. K-edge data were measured over the
energy range 7105~7150 eV. Multiple (4~5) scans over the
complete energy range were averaged for each sample. For each
spectrum, a smooth second-order polynomial was fit to the preedge
region, then extrapolated across the entire energy range, and
subtracted from the data.

**Results**

**Electrochemistry of [Fe$_2$(μ-O$_2$CAr$^{Tol}$)$_2$(4-BuC$_6$H$_4$N)$_2$]
(1a) and [Fe$_2$(μ-O$_2$CAr$^{Tol}$)$_2$(O$_2$CAr$^{Tol}$)$_2$(THF)$_2$] (3a).** Electro-
chemical properties of 1a and 3a were investigated by cyclic
cvatammetry, in order to select appropriate one-
electron chemical oxidants to accessed the Fe(II)/Fe(III) oxida-
tion states. Measurement was not made with 2a, due to its
limited solubility in CH$_2$Cl$_2$. Cyclic voltammograms of
a CH$_2$Cl$_2$ solution of 1a revealed a reversible oxidation at $E_{1/2}$ =
-216 mV vs Cp$_2$Fe$^+/Cp$Fe ($\Delta E_p$ = 89 mV) Figure 2).
A broad second oxidation wave occurs at ca. +1080 mV,
which does not display a corresponding reduction wave in the
return sweep. Under identical conditions, the compound
[Fe$_2$(μ-O$_2$C$^{Tol}$(4-BuC$_6$H$_4$N)$_2$](PF$_6$)$_2$ exhibited a similarly
reversible oxidation step at $E_{1/2}$ = -16 mV vs Cp$_2$Fe$^+/Cp$Fe-
Fe ($\Delta E_p$ = 97 mV) Figure S1, Supporting Information). A
positive shift ($\Delta E$ = +200 mV) in the oxidation potential is
consistent with the coordination of less electron-donating
fluoro-substituted ligands Ar$^Tol$CO$_2$F. A similar shift would
place the second oxidation peak of [Fe$_2$(μ-O$_2$C$^{Tol}$)$_2$-(4-BuC$_6$H$_4$N)$_2$] +
1280 mV, lying at the positive limit of the accessible potential window.
No second oxidation step was observed. Compound 3a
displayed a broad oxidation wave, beginning at ~150 mV and maximizing at +400 mV.
A significantly narrower reduction wave occurred at ~195
mV in the return sweep (Figure 3A). Similarly irreversible
redox behavior was observed even with increased scan rates
(50~500 mV/s) at a narrower potential sweep range from
-720 to +880 mV (Figure 3B).

**Synthesis and Structural Characterization of [Fe$_2$(μ-
O$_2$C$^{Tol}$)$_2$(4-BuC$_6$H$_4$N)$_2$](PF$_6$) (1b), [Fe$_2$(μ-O$_2$C$^{Tol}$)$_2$-(
C$_3$H$_6$N)$_2$](OTf) (2b), and [Fe$_2$(μ-O$_2$C$^{Tol}$)$_2$(THF)$_2$](PF$_6$)
(3b).** Reactions of 1a~3a with 1 equiv of [Cp$_2$Fe]PF$_6$ or
AgOTf in CH$_2$Cl$_2$ resulted in an instantaneous color change
from yellow to deep forest green. Dark brown-green blocks of
1b~3b were obtained in good yield (60~71%), following
recrystallization from CH$_2$Cl$_2$/pentanes. These compounds
are stable both in the solid state and in solution when prot-
ected from exposure to dioxygen or to coordinating solvents
such as THF, MeCN, or MeOH. Attempts to access a similar

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**Figure 2.** Cyclic voltammograms of [Fe$_2$(μ-O$_2$CAr$^{Tol}$)$_2$(4-BuC$_6$H$_4$N)$_2$] (1a)
in CH$_2$Cl$_2$ with 0.5 M (Bu$_4$N)PF$_6$ as supporting electrolyte and a scan rate
of 50 mV/s. The inset shows the reversible wave observed when the experiment was conducted at potentials below +300 mV vs Fe$^{3+}/Fe^{2+}$ (scan rate
= 25 mV/s).

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unit by oxidizing [Fe₂(μ-O₂C₅H₅N)₄]²⁺ with 1 equiv of [Cp₂Fe]PF₆ did not lead to any isolable product. The initial dark green reaction mixture gradually decomposed to an orange brown material. Steric shielding provided by the m-terphenyl units (Figure 4) apparently plays a crucial role in stabilizing the mixed valence diiron cores in 1b–3b.

The solid-state structures of 1b–3b were determined by X-ray crystallography. The molecular structures are shown in Figures 4 and 5; selected bond lengths and angles are listed in Table 1. Although severe disorder in the PF₆⁻ counterion and solvent molecules hampered detailed structural refinement of the model for 1b, its Fe⋯Fe distance of 2.713(3) Å, as well as the quadruply bridged core structure, is comparable to the corresponding properties of 2b and 3b. In 1b–3b, the Fe⋯Fe distances are 2.6633(11)–2.713(3) Å and four μ-1,3 carboxylate ligands bridge the Fe–Fe vector. This architectural feature is shared by a few structurally characterized paddle-wheel diiron(II) complexes.³³,⁴⁰,⁴¹

The two iron atoms are crystallographically inequivalent but display similar square-pyramidal coordination comprising four carboxylate oxygen atoms at the base and one N- or O-donor atom at the axial position. In order to minimize interligand steric repulsions, the benzoate rings in the ArTol CO₂⁻ ligands are twisted from the CO₂⁻ planes by 39.3°–45.7°. This conformation provides tetragonal pockets on either side of the Fe–Fe vector. The motion of the axial ligand confined within this pocket is significantly restricted. The dihedral angles between the two pyridine planes are 72.3° in 1b and 62.1° in 2b. Comparable Fe–O(carboxylate) distances were observed for each iron within the dimer (Table 1).

**Electronic Absorption Spectroscopy.** Compounds 1b–3b display intense visible absorption bands at λ_{max} =
Valence-Delocalized Diiron(II,III) Complexes

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2b and 3b

<table>
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<tr>
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<th>2b</th>
<th>3b</th>
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<tr>
<td>Fe1···Fe2</td>
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<tr>
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<td>123(5)</td>
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*Numbers in parentheses are estimated standard deviations of the last significant figures.

Figure 6. Electronic absorption spectra of 1b–3b in CH2Cl2 showing the IVCT transitions: (A) [Fe2(μ-O2C)2Ar4(4-tBuC5H4N)2](PF6) (1b) (•); (B) [Fe2(μ-O2C)Ar3J(4-tBuCH2N3)2](OTf) (2b) (○); (C) [Fe2(μ-O2C)Ar2J(THF)3](PF6) (3b) (– with circle).

620–670 nm (ε = 2700–3200 M⁻¹ cm⁻¹) and two shoulders at ~380 nm (ε = 3100–3400 M⁻¹ cm⁻¹) and ~450 nm (ε = 1600–1800 M⁻¹ cm⁻¹) in CH2Cl2 (Figure 6; Table 2). No other visible–NIR transitions occur up to 1650 nm (Figure S2, Supporting Information). Since both the pyridine and THF complexes behave similarly, the 620–670 nm bands are assigned as intervalence charge transfer (IVCT), rather than LMCT, transitions. The experimentally determined width at half-height (Δν/2) ranges between 3590 and 3970 cm⁻¹ for 1b–3b, values significantly lower than those predicted by Hush’s relationship for class II mixed valence centers (Δν/2 = [2310 νmax]¹/₂ = 5880–6120 cm⁻¹). This result strongly indicates that 1b–3b are valence-delocalized diiron(II,III) complexes. Similar IVCT bands are observed at 758–1060 nm (ε = 1250–2400 M⁻¹ cm⁻¹) for A–C (Figure 1; Table 2).²⁻²⁹

EPR Spectroscopy. Shown in Figure 7 are frozen solution EPR spectra of 1b–3b measured at X-band and Q-band. Compounds 3b and 1b exhibit similar signals at X-band (A and C) with resonances at g = 9.5 and 2.0. These resonances are near the expected values of g = 10 and 2 for the m_s = 1/2 doublet, based on the standard diagram of gobs vs EID for S = 1/2 complexes with EID ~ 0.³⁴ At Q-band (D and F), three resonances are observed at g = 8.9, 4.5, and 3.0, which are not the expected g values for EID ~ 0. For D ≪ hν, significant mixing of the doublets occurs, which invalidates the standard gobs vs EID diagram. We thus used simulations to determine the origin of the signals. Each simulation was generated with consideration of all intensity factors, both theoretical and experimental. The spin quantitations obtained by the spectra of Figure 7 were all within 15% of that expected from the diiron complex concentration. Table 3 summarizes the zero-field splitting (zfs) parameters for 1b–3b as determined from the simulations shown in Figure 7.

The X- and Q-band EPR spectra of 1b (Figure 7C,F) can be simulated using a unique set of parameters. From the simulations (dashed lines) overlaid on the data, we find D = 1.13 cm⁻¹ and EID = 0.007. The line widths are dominated by D strain, which is modeled with distributions in the parameters D and EID of Gaussian width σD and σEID. The spectral simulations determine both parameters independently, with values of σD = 0.02 cm⁻¹ and σEID = 0.004. The resonances at g = 8.9 and 3.0 are assigned to transitions within the m_s = 1/2 and ±1/2 doublets, respectively. The resonance at g = 4.5 arises from an interdoublet transition between the m_s = ±1/2 and −1/2 levels. For the Q-band simulations, a sharp feature at g = 9.5 in the simulations does not match the line width in the experimental data. We suspect that this feature is broadened in the experimental data by intermolecular magnetic dipole interactions owing to the formation of small molecular aggregates. This interpretation is supported by the fact that the signal line width strongly depends on the solvent used. Attempts to dissociate these aggregates by using lower sample concentration were not successful. The increased line width of 3b relative to 1b is due to a slightly increased rhombicity (EID = 0.011). Unlike 1b, the Q-band EPR spectrum of 3b (Figure 7D) lacks the interdoublet transition. This result can be attributed to an increase in D strain for 3b. Alternatively, given the differences in the axial donor ligands of 1b and 3b, the interdoublet transition expected for 3b at g = 4.5 could be shifted downfield by decreasing the value of D. Due to the mixing with the m_s = ±1/2 doublet, however, an increase in D would also shift the signal from the m_s = ±1/2 doublet at g = 3.0 downfield. We therefore conclude that the interdoublet transition of 3b is broadened away by D strain (σD = 0.08 cm⁻¹), not by shifts in the D value.

parameters listed in Table 3. A minimum line width of 0.3 mT was factored
Simulations (dashed lines) were calculated for each derivative using zfs
originates from an Fe(III) contaminant (<
features observed for 2b
2b
2b
2b
3b
A
B
C
Table 3. Summary of Pertinent Structural and Spectroscopic Data for 1b–3b and Related Mixed-Valence $S = \frac{9}{2}$ Fe$_2$(II,III) Systems

<table>
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<th></th>
<th>Fe····Fe (Å)</th>
<th>$\lambda_{max}$, nm (ε, M$^{-1}$ cm$^{-1}$)</th>
<th>$\Delta\nu_{1/2}$ (cm$^{-1}$)</th>
<th>$\mu_{eff}$/μB</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta\delta$ (mm/s)</th>
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<tbody>
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<td>1b</td>
<td>2.713(3)</td>
<td>670 (3200) 450 (1600)$^a$ 380 (3100)$^a$</td>
<td>5880 3590 11.0$^d$ 0.65 $\pm$ 0.63</td>
<td>31, this work</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2b</td>
<td>2.6982(13)</td>
<td>665 (2900) 455 (1800)$^a$ 385 (3400)$^a$</td>
<td>5900 3970 10.2$^c$</td>
<td>31, this work</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>3b</td>
<td>2.6633(11)</td>
<td>620 (2700) 450 (1600)$^a$ 385 (3200)$^a$</td>
<td>6120 3670 10.5$^c$</td>
<td>31, this work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>2.509(6)</td>
<td>758 (2400) 620 (2700) 450 (1600)$^a$ 385 (3200)$^a$</td>
<td>5500 3800 10.5$^d$</td>
<td>0.74 $\pm$ 2.14</td>
<td>27a–d</td>
<td></td>
<td></td>
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<tr>
<td>B</td>
<td>2.7414(8)</td>
<td>1060 (1250)</td>
<td>4670 3980 10.0$^c$</td>
<td>0.84 2.09</td>
<td>28a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2.6241(9)</td>
<td>780 (2000)</td>
<td>5880 3590 10.5$^c$</td>
<td>0.76 2.0</td>
<td>29</td>
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$^a$ $\Delta\nu_{1/2} = [2310 \nu_{max}]^{1/2}$ (refs 42, 43). $^a$ Shoulders determined from derivative spectra. $^c$ 300 K. $^d$ 30–300 K. $^e$ 70–300 K.

parameters and exist in approximately the same relative amounts. The EPR parameters of $D = 1.13$ cm$^{-1}$ and $E/D = 0.007$ obtained for species 1 (Figure 8B,E) are comparable to those of 1b and 2b (Table 3), whereas species 2 (Figure 8C,F) can be simulated with zfs parameters of $D = 1.13$ cm$^{-1}$ and $E/D = 0.03$. The ratio of the signal intensities of species 1 and 2 is not altered up to $\sim 200$ K, indicating that both have similarly large energy gaps between the ground ($S = \frac{9}{2}$) and the first excited ($S = \frac{7}{2}$) states originating from double exchange. The presence of multiple species of 2b having distinct $E/D$ values may be explained by invoking aggregation of the compound in the frozen solution samples. Such an aggregation may distort the local $D_{ab}$ symmetry of the metal center by perturbing the plane defined by the four carboxylate oxygen donor atoms. Deviation from the axial ($E/D = 0$) magnetic environment would result in the increased rhombicity of species 2 relative to species 1. Detailed information of the structural variations leading to the spectroscopically inequivalent species of 2b, however, is currently unavailable.

**X-ray Absorption Spectroscopy.** As shown in Figures 9 and 10, the Fe K-edge and preedge (1s $\rightarrow$ 3d transitions) spectra of 1b–3b are nearly identical and intermediate in energy between K-edges for structurally related diiron(II) complex 1a and diiron(III) complex 1c. Adding K-edge spectra for 1a and 1c at a weighted ratio of 50:50 yielded a spectrum comparable in rising edge energy to those of 1b–3b (Figure 10), consistent with the formal description of the oxidation states of the mixed-valence species as Fe(II)-Fe(III). K-edges or preedges for the mixed-valence complexes, however, are not a simple 50:50 superposition of the Fe(II)Fe(II) and Fe(III)Fe(III) spectra. The difference is clearly manifest by comparing the second derivatives of the
K-edge spectra (Figure S3, Supporting Information), or more specifically, the second derivatives of the preedge region (Figure 11), which highlight individual transitions obscured by the rising edge absorption. Each of the compounds 1b–3b has a pair of transitions in the preedge region, at energies that are almost exactly intermediate between those for 1a and 1c. This result suggests that the iron sites in each mixed-valence species are best described as delocalized Fe(2.5)Fe(2.5), rather than localized Fe(II)Fe(III). The spectrum for a localized complex should be the superposition of both Fe(II) and Fe(III) species.

**Discussion**

**Synthesis, Structures, and Spectroscopic Properties of Fe$_2$(II,III) Complexes.** Synthetic routes to 1b–3b are described in Scheme 1. Consistent with the oxidation poten-
tials determined for 1a and 3a, mixed-valence Fe\(^{2+}(II,III)\) complexes 1b–3b were readily accessed through one-electron oxidation by \([\text{Cp}_2\text{Fe}]^+\) (\(E^\circ^\prime = +460 \text{ mV vs SCE in CH}_2\text{Cl}_2\)) or Ag\(^+\) (\(E^\circ^\prime = +1110 \text{ mV vs SCE in CH}_2\text{Cl}_2\)). The redox behavior of 1a and 3a, as well as the structural outcome of their chemical oxidation, however, differs significantly.

Compound 1a undergoes minimal structural rearrangement following oxidation to 1b. Except for a slight but significant shortening of the Fe⋯Fe distance from 2.8229(9) Å to 2.713(3) Å, the coordination geometry afforded by the four \(\mu\)-1,3 bridging carboxylate and two N-donor ligands remains essentially identical. This behavior is consistent with the reversible interconversion between the Fe(II)Fe(II) and Fe(II)Fe(III) species observed by cyclic voltammetry of 1a in CH\(_2\)Cl\(_2\) (Figure 2). In contrast, significant core rearrangement accompanies oxidation of the metal centers in 2a and 3a. Double carboxylate shifts from terminal bidentate to \(\mu\)-1,3 bridging positions (Scheme 2) result in the significant shortening (\(\Delta\text{Fe⋯Fe} = 1.52\)–1.62 Å) of the Fe⋯Fe distances from 4.2189(13) Å to 2.6982(13) Å (2a \(\rightarrow\) 2b) and 4.2822(7) Å to 2.6633(11) Å (3a \(\rightarrow\) 3b). The irreversible electrochemical behavior of 3a in CH\(_2\)Cl\(_2\) (Figure 3) most likely results from such a core rearrangement concomitant with a change in oxidation state.

The broad oxidation wave of 3a initiates at \(-150 \text{ mV, shifted by } +180 \text{ mV relative to that of 1a. This shift is consistent with the coordination of less electron-donating (THF} < \text{4-tert-butylpyridine) ligands to the metal. Compared with the broad oxidation wave, however, the corresponding reduction peak of 3a is significantly narrower (Figure 3). This electrochemical behavior is nicely explained by the mechanism postulated in Scheme 2. In CH\(_2\)Cl\(_2\) at room temperature, 3a exists as an equilibrium mixture with its quadraply bridged isomer 3a’.

The X-band EPR spectra of 1b–3b are consistent with transitions originating within an \(S = \frac{3}{2}\) manifold of an axial system. In these compounds, a plane is established at each

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Valence-Delocalized Diiron(II,III) Complexes

metal center by the four oxygen atoms from the bridging carboxylate ligands. The \( z \)-axis of the \( D \) tensor is thus placed along the Fe–Fe vector. The \( D \) value in the \( S = \frac{1}{2} \) Fe(II)-Fe(III) system has contributions from the Fe(II) and Fe(III) sites, as well as from the intramolecular Fe–Fe magnetic dipole interaction. For a \( S_{tot} = \frac{1}{2} \) spin system arising from the coupling of a \( S = \frac{1}{2} \) and a \( S = 2 \) site, the system \( D \) value (\( D_{9/2} \)) is described by eq 2. The intrinsic \( D \) value for

\[
D_{9/2} = 0.167D_{\text{Fe(II)}} + 0.278D_{\text{Fe(III)}} + 0.278D_{\text{Fe–Fe}}
\]  

an Fe(III) site is usually \( \leq 0.5 \text{ cm}^{-1} \). We also have determined that the contribution from the dipolar interaction is \( \leq 0.5 \text{ cm}^{-1} \). Accordingly, if we ignore the small contribution from the last two terms, the \( D \) value for the Fe(II) site in \( 1b-3b \) is approximately \( 7 \text{ cm}^{-1} \). Similar EPR signals have been previously observed for \( A \) (Figure 1), which displays an axial X-band signal with \( g_z = 10.2 \) and \( g_\parallel = 2.3 \), fit using the zfs parameters \( D = 1.8 \text{ cm}^{-1} \) and \( E/D = 0.01 \). The X-band EPR spectra of the valence-trapped \( S = \frac{1}{2} \) Fe(II)Fe(III) core in the cryoreduced RNR-R2 \( 26 \) are described by the zfs parameters \( D = 1.5 \text{ cm}^{-1} \) and \( E/D = 0.05 \).

XAS: Valence-Delocalized Photoexcited States. Central to our analysis of the XAS data in this investigation is the ability to prepare three diiron complexes having different oxidation states but similar N/O ligand combinations and coordination geometry. The effective electron density at the metal can be influenced by changes in the oxidation states or ligand composition, which lead to a shift in the X-ray absorption edge, and/or change in the edge shape, respectively. By minimizing contributions from structural changes, the edge shift can be primarily correlated to the redox changes at the metal center.

The observed preedge XAS spectrum of \( 1b \) is fully consistent with a valence-delocalized Fe(2.5)Fe(2.5) description, since the simple linear combination of Fe(II) and Fe(III) sites cannot reproduce the observed spectral pattern. The electronic coupling responsible for the valence delocalization in the ground state may be equally well operative in the X-ray photoexcited state. Previous L-edge XAS studies similarly revealed differences between valence-localized and -delocalized dinuclear Fe(II)Fe(III) complexes. The multiplet structures of spectra for the valence-trapped complexes were well modeled by 50:50 superpositions of L-edge spectra for related Fe(II)Fe(II) and Fe(III)Fe(III) complexes. The spectrum for the valence-delocalized compound \( A \), in contrast, displays a broader and less well resolved multiplet structure. The corresponding Fe(II)Fe(II) or Fe(II)Fe(III) complexes, however, are not available for \( A \), and a direct spectral comparison could not be made. To the best of our knowledge, compounds \( 1b-3b \) represent the first examples of mixed-valence Fe(II,III) complexes, where the valence-delocalized nature is apparently retained in excited states produced by X-ray absorption. With such proper calibrations made possible by the existence of structurally related Fe(II)-Fe(II) and Fe(III)Fe(III) complexes, XAS should be able to probe the electronic structure of other mixed-valence Fe(II)-Fe(III) complexes.

Valence Delocalization. The parallel spin alignment of the Fe(II,III) cores in \( 1b-3b \) was confirmed by EPR studies and previous magnetic susceptibility measurements. Electron delocalization in this \( S = \frac{1}{2} \) spin system was indicated by the essentially identical geometric parameters obtained for the two iron atoms in the dimers in the solid state (Table 1). Although static disorder of valence-trapped Fe(II)Fe(III) cations or dynamic disordering due to rapid electron transfer between the metal centers \( 28 \) can equally well explain such structural results, Mössbauer \( 31 \) and XAS studies provide compelling evidence that the diiron(II,III) cores in \( 1b-1c \) remain valence-delocalized at \( < 10 \text{ K} \).

Such valence delocalization between paramagnetic centers is described by double exchange, \( 14,15,23,49 \) a mechanism by which delocalized electrons provide an additional coupling mechanism for the parallel alignment of the spins. Such resonance interaction between metal centers can be mediated either by direct metal–metal orbital overlap or by the bridging ligands. Notable structural features of the previously characterized valence-delocalized Fe(II,III) compounds \( A-C \) (Figure 1) include short metal–metal distances and the presence of single-atom bridging ligands. Oxygen atoms supplied by hydroxo, phenoxo, or alkoxo ligands promote the short Fe–Fe distances of \( 2.509(6)-2.7414(8) \text{ Å} \) in \( A-C \) and can mediate a strong metal–metal resonance interaction. Theoretical studies indicate that a direct \( \sigma \)-type overlap of the two \( d_\sigma \) orbitals is responsible for the valence delocalization in \( A \), \( 27d \) whereas both \( \sigma \)-type interaction between the Fe \( d_{\pi \gamma} \) orbitals and Fe–Ophenoxide bonding contribute to the similar phenomenon in \( B \). \( 3b \)

Although compounds \( 1b-3b \) feature short Fe–Fe distances comparable to those in \( A-C \) (Table 2), their quadruply bridged Fe(II,III) cores lack efficient coupling pathways afforded by single-atom bridging ligands. Double exchange observed in the \( \left[ \text{Fe}_2(\mu-O_2\text{C(CH}_3\text{)}_2\text{C}_6\text{H}_4)_2\right]^+ \) module is thus apparently mediated by the direct through-space interaction between the metal centers. Preliminary DFT calculations indicate that \( \pi \)-type overlap between \( d_\pi \) orbitals is responsible for the strong electron delocalization in \( 1b-3b \), the details of which are currently under investigation. \( 50 \)

Collectively, the synthesis and characterization of \( 1b-3b \) significantly expands the class of valence-delocalized diiron(II,III) clusters, affording a novel basis for correlating the geometric and electronic factors responsible for this novel phenomenon.

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Supporting Information Available: Cyclic voltammograms of $\left[\text{Fe}_2(\mu-\text{O}_2\text{Carb}=\text{Ph})_4(4'-\text{BuC}_6\text{H}_4\text{N})_2\right]$. NIR spectra of $1b$, and second derivatives of the K-edge spectra for $1a$, $1b$, and $1c$. This material is available free of charge via the Internet at http://pubs.acs.org.