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Article

Dinuclear Bis(1,2-diaryl-1,2-ethylenedithiolato)iron Complexes: $[Fe^{III}_2(L)_4]^n$ (n = 2–, 1–, 0, 1+)

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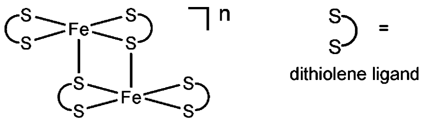
The electronic structures of four members of the electron-transfer series $[Fe_2(^1L)_4]^n$ (n = 2–, 1–, 0, 1+) have been elucidated in some detail by electronic absorption, IR, X-band electron paramagnetic resonance (EPR), and Mössbauer spectroscopies where $(^1L)^{2-}$ represents the ligand 1,2-bis(4-*tert*-butylphenyl)-1,2-ethylenedithiolate(2–) and $(^1L^{\bullet})^{-}$ is its π-radical monoanion. It is conclusively shown that all redox processes are ligand-centered and that high-valent iron(IV) is not accessible. The following complexes have been synthesized: $[Fe^{III}_2(^1L^{\bullet})_2(^1L)_2]^0$ (**1**), $[Fe^{III}_2(^2L^{\bullet})_2(^2L)_2]\cdot 2CH_2Cl_2$ (**1′**) where $(^2L)^{2-}$ is 1,2-bis(*p*-tolyl)-1,2-ethylenedithiolate(2–) and $(^2L^{\bullet})^{-}$ represents its π-radical monoanion, $[Cp_2Co][Fe^{III}_2(^1L^{\bullet})(^1L)_3]\cdot 4(toluene)\cdot 0.5Et_2O$ (**2**), and $[Cp_2Co]_2[Fe^{III}_2(^1L)_4]\cdot 2(toluene)$ (**3**). The crystal structures of **1′** and **2** have been determined by single-crystal X-ray crystallography at 100 K. The ground states of complexes have been determined by temperature-dependent magnetic susceptibility measurements and EPR spectroscopy: **1′** and **1** are diamagnetic ($S_t = 0$); **2** ($S_t = {}^1/_2$); **3** ($S_t = 0$); the monocation $[Fe^{III}_2(^1L^{\bullet})_3(^1L)]^+$ possesses an $S_t = {}^1/_2$ ground state (S_t = total spin ground state of dinuclear species). All species contain pairs of intermediate-spin ferric ions ($S_{Fe} = {}^3/_2$), which are strongly antiferromagnetically coupled ($H = -2JS_1\cdot S_2$, where $S_1 = S_2 = {}^3/_2$ and $J = \sim -250$ cm^{-1}).

Introduction

Bis(dithiolene)iron complexes,[1] $[FeL_2]^-$, are known to form dinuclear complexes of type A in solution and in the solid state.



A

n = 1+, 0, 1-, 2-

Each iron ion is in a square-pyramidal-based environment of five sulfur atoms, and one of the ligands of each $[FeL_2]^-$ subunit forms a single μ_2-sulfur bridge. It has been recognized by Balch, Holm, and co-workers[2] that these complexes form an extensive electron-transfer series; equation (1). For

$$2[FeL_2]^{2-} \underset{+2e}{\overset{-2e}{\rightleftharpoons}} [Fe_2L_4]^{2-} \underset{+e}{\overset{-e}{\rightleftharpoons}} [Fe_2L_4]^{1-} \underset{+e}{\overset{-e}{\rightleftharpoons}} [Fe_2L_4]^{0} \underset{+e}{\overset{-e}{\rightleftharpoons}} [Fe_2L_4]^{1+} \qquad (1)$$

$$E^0_{1/2} \qquad E^1_{1/2} \qquad E^2_{1/2} \qquad E^3_{1/2}$$

each such species, at least two differently charged ions have been found to be stable in solution depending on the nature of the dithiolene ligand (Scheme 1).

When the ligand is of the dithiolene type, only the dianion $[Fe_2(mnt)_4]^{2-}$ (mnt = maleonitrile-1,2-dithiolate) has been structurally characterized to date in many salts with differing cations.[3] If the ligand is a benzene-1,2-dithiolate (bdt) derivative, the corresponding dinuclear dianion $[Fe^{III}_2(bdt)_4]^{2-}$ and the monoanion $[Fe_2(L^{Bu})_4]^-$ have been structurally characterized by single-crystal X-ray crystallography,[4,5] where $(L^{Bu})^{2-}$ is 3,5-di-*tert*-butyl-1,2-benzenedithiolate. To the best of our knowledge, no neutral or cationic dinuclear species of this series has been fully characterized to date.

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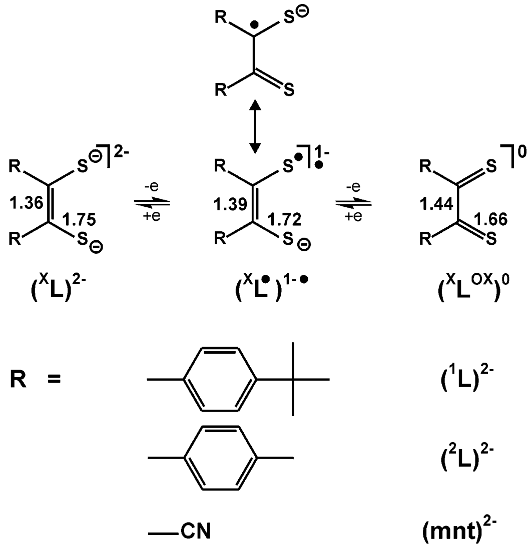
Scheme 1. Ligands and Abbreviations[a]



[a] Average C−C and C−S bond lengths are given in angstroms.

The electronic structures of the dinuclear dianions $[Fe_2(mnt)_2]^{2-}$ and $[Fe_2(L^{Bu})_4]^{2-}$ have been probed by magnetic susceptibility measurements,[3c,5] electronic absorption spectroscopy, and Mössbauer spectroscopy:[5,6] the ligands are all closed-shell dianions, mnt^{2-} or $(L^{Bu})^{2-}$, which renders the central metal ions trivalent Fe^{III} with an intrinsic spin $S_{Fe} = {}^3/_2$ (intermediate spin). Two of these are then strongly intramolecularly, antiferromagnetically coupled, yielding a diamagnetic ground state $S_t = 0$. The intrinsic intermediate spin ($S_{Fe} = {}^3/_2$) of the ferric ion has most clearly been established by Mössbauer spectroscopy (see the discussion in ref 5).

The picture is not so clear for the more oxidized monoanions,[2a,5] the neutral molecules, and the monocationic species. Their electronic structures have not been investigated to date. In fact, structural and definitive spectroscopic data [UV−vis, electron paramagnetic resonance (EPR), and Mössbauer] are lacking. Therefore, we have synthesized the dithiolene ligands $H_2(^1L)$ and $H_2(^2L)$ shown in Scheme 1 in situ[7] and prepared the dinuclear complexes shown in Chart 1. In nearly all known five-coordinate bis(dithiolene)iron complexes, the question of a possible redox noninnocence of the dithiolene ligand has not been explicitly addressed and, consequently, the d^n electron configuration of the central iron ion is not known. This situation was deplored by Kahn et al.[8] in 1999, after more than 35 years of research in this area.

Chart 1. Complexes Synthesized in This Study and Their Labels and Spin Ground States

Complexes

$[Fe^{III}_2(^1L^\bullet)_2(^1L)_2]$	(1)	$S_t = 0$
$[Fe^{III}_2(^2L^\bullet)_2(^2L)_2]\cdot 2\,CH_2Cl_2$	(1′)	$S_t = 0$
$[Cp_2Co][Fe^{III}_2(^1L^\bullet)(^1L)_3]\cdot 4\,toluene\cdot 0.5\,Et_2O$	(2)	$S_t = 1/2$
$[Cp_2Co]_2[Fe^{III}_2(^1L)_4]\cdot 2\,toluene$	(3)	$S_t = 0$

The present study has been designed to establish the spectroscopic and structural markers for the three possible oxidation levels of coordinated dithiolenes shown in Scheme 1. Ideally suited for this purpose are complexes that undergo a number of reversible one-electron-transfer steps as shown in eq 1. Structural and electronic structural investigations of each of these species should then provide a consistent description of the metal ion oxidation state and, concomitantly, the oxidation level of the ligands in the electron-transfer series. Here we present such a study on dinuclear iron complexes. In a forthcoming paper, we will then describe the same approach for mononuclear, five-coordinate adducts, $[FeL_2X]^n$ (L = dithiolene ligand).

Experimental Section

The two diaryl-based dithiolato ligands, namely, $(^1L)^{2-}$ and $(^2L)^{2-}$ (Scheme 1), were prepared in situ from their dithiophosphoric ester according to literature procedures[7−9] and were used for the synthesis of complexes without preceding isolation.

$[Fe^{III}_2(^1L^\bullet)_2(^1L)_2]$ (1). To a suspension of 4-*tert*-butylbenzoin (2.5 g, 7.56 mmol) in dry 1,4-dioxane (30 mL) was added P_4S_{10} (2.4 g, 5.4 mmol), and the resulting mixture was heated to reflux for 2 h. After cooling to 20 °C and filtration (removal of excess P_4S_{10}), an aqueous solution (6 mL of distilled H_2O) of $(NH_4)_2[Fe^{II}(SO_4)_2]\cdot 7H_2O$ (1.31 g, 3.34 mmol) was added to the light-yellow solution of the above in situ preparation of the ligand $(^1L)^{2-}$ and heated to reflux for 2 h in the presence of air. A dark-blue, microcrystalline precipitate formed, which was filtered off and washed with water (200 mL) and then acetone (20 mL). Slow methanol diffusion into a toluene solution of this material afforded hexagonal-shaped crystals that were found to be unsuitable for X-ray crystallography. Yield: 1.3 g (50%). MS (EI): *m/z* 1529 (calcd for $\{M\}^+$, 1528.9). Anal. Calcd for $C_{88}H_{104}S_8Fe_2$: C, 69.08; H, 6.85; S, 16.77; Fe, 7.30. Found: C, 68.8; H, 6.8; S, 16.3; Fe, 7.1.

$[Fe^{III}_2(^2L^\bullet)_2(^2L)_2]$ (1′). This complex was prepared as described for **1** by heating to reflux a mixture of 4,4′-dimethylbenzoin (5.0 g, 21 mmol) and P_4S_{10} (5.0 g, 11 mmol) in xylene (50 mL) and adding a water/methanol mixture (1:1, v/v; 30 mL) containing $(NH_4)_2[Fe^{II}(SO_4)_2]\cdot 7H_2O$ (5.0 g, 18 mmol). A black solid formed

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within 12 h at ambient temperature, which upon recrystallization in CH_2Cl_2 yielded crystals of $\mathbf{1'}\cdot 2CH_2Cl_2$ suitable for single-crystal X-ray crystallography. Anal. Calcd for $C_{64}H_{56}S_8Fe_2$: C, 64.41; H, 4.73; S, 21.49; Fe, 9.36. Found: C, 65.1; H, 5.0; S, 21.2; Fe, 9.1.

$[Cp_2Co][Fe^{III}_2(^1L^{\bullet})(^1L)_3]\cdot 4(toluene)\cdot 0.5Et_2O$ (2). To a vigorously stirred blue solution of **1** (0.2 g, 0.13 mmol) in dry toluene (10 mL) was added dropwise a toluene solution (2 mL) of cobaltocene ($[Cp_2Co]$; 0.025 g, 0.13 mmol) under strictly anaerobic conditions (argon-blanketing atmosphere). An immediate color change to bluish-green was observed. After this mixture was stirred for 4 h, degassed diethyl ether (10 mL) was carefully added, generating a layer. The mixture was allowed to stand at 4 °C for 12 h. Blocklike dark crystals formed that were suitable for X-ray crystallography. Yield: 0.15 g (53%). MS (ESI, negative ion mode, CH_2Cl_2): *m/z* 1528.8 (calcd for $\{M\}^-$, 1529). MS (ESI, positive ion mode): *m/z* 188 (calcd for $\{CoCp_2\}^+$, 188). Anal. Calcd for $C_{128}H_{151}S_8O_{0.5}Fe_2Co$: C, 72.36; H, 7.16; S, 12.07. Found: C, 72.3; H, 7.1; S, 12.0.

$[Cp_2Co]_2[Fe^{III}_2(^1L)_4]\cdot 2(toluene)$ (3). To a stirred, blue solution of **1** (0.2 g, 0.13 mmol) in toluene (10 mL) was added a toluene solution (2 mL) of $[Cp_2Co]$ (0.054 g, 0.28 mmol) under an argon atmosphere. An immediate color change to brown was observed, and a microcrystalline brown precipitate formed within 4 h, after which time the material was filtered off, washed with toluene (15 mL) and diethyl ether (10 mL), and dried. Yield: 0.12 g (48%). MS (ESI, negative ion mode, CH_2Cl_2): *m/z* 764 (calcd for $z = 2$, 764.4 $\{M\}^{2-}$). MS (ESI, positive ion mode): *m/z* 188 ($\{Cp_2Co\}^+$). Anal. Calcd for $C_{122}H_{104}S_8Fe_2Co_2$: C, 70.03; H, 6.74; S, 12.26. Found: C, 70.0; H, 6.7; S, 12.1.

Physical Measurements. The equipment used for IR, UV−vis, EPR, and Mössbauer spectroscopies has been described in refs 5 and 12a. The temperature-dependent magnetic susceptibilities of solid samples of complexes were measured by using a SQUID magnetometer (Quantum Design) at 1.0 T (4.2−300 K). Corrections for underlying diamagnetism were made by using tabulated Pascal's constants. Cyclic voltammograms (CVs) and coulometric experiments were performed with an EG&G potentiostat/galvanostat in CH_2Cl_2 solutions (0.10 M $[N(n\text{-}Bu)_4]PF_6$) at a glassy carbon working electrode. Ferrocene was used as an internal standard; all redox potentials are given versus the ferrocenium/ferrocene (Fc^+/Fc) couple.

X-ray Crystallographic Data Collection and Refinement of the Structures. A dark-red single crystal of $\mathbf{1'}\cdot 2CH_2Cl_2$ and a deep-blue specimen of $\mathbf{2}\cdot 4(toluene)\cdot 0.5Et_2O$ were coated with perfluoropolyether, were picked up with a glass fiber, and were immediately mounted in the nitrogen cold stream of the diffractometers to prevent loss of solvent. A Nonius Kappa CCD diffractometer equipped with a molybdenum-target rotating-anode X-ray source and a graphite monochromator (Mo Kα, $\lambda = 0.710\,73$ Å) was used for **2**, a sealed tube source in the case of **1′**. Final cell constants were obtained from least-squares fits of all measured reflections. Intensity data of **1′** were corrected for absorption with *SADABS*.[11a] The structures were readily solved by Patterson methods and subsequent difference Fourier techniques. The Siemens *ShelXTL*[10] software package was used for solution and artwork of the structure, and *ShelXL97*[11b] was used for refinement. All non-hydrogen atoms were refined anisotropically, except disordered parts in **2**. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic data of the compounds are listed in Table 1. Disorder of two toluene solvent molecules next to crystallographic inversion centers was found in **2**, and restrained split-atom models with occupation factors of 0.5 were refined. Two *tert*-butyl groups attached to C(12) and C(36) were detected to be disordered by rotation. Split positions were refined with occupation ratios of about 75:25 and 60:40, respectively. The geometries were restrained using SAME and SADI instructions of *ShelXL97*. A diethyl ether molecule was identified but was found to be poorly defined. The occupation factor was refined to about 0.5 and was therefore fixed to this value.

Table 1. Crystallographic Data for $\mathbf{1'}\cdot 2CH_2Cl_2$ and $\mathbf{2}\cdot 4(toluene)\cdot 0.5Et_2O$

	$\mathbf{1'}\cdot 2CH_2Cl_2$	$\mathbf{2}\cdot 4(toluene)\cdot 0.5Et_2O$
chemical formula	$C_{66}H_{60}Cl_4Fe_2S_8$	$C_{128}H_{151}CoFe_2O_{0.5}S_8$
fw	1363.2	2124.60
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	9.164(6)	12.5268(8)
b, Å	11.820(5)	13.5759(8)
c, Å	15.623(12)	38.237(3)
α, deg	97.05(4)	85.52(1)
β, deg	102.86(5)	88.85(1)
γ, deg	107.81(3)	65.67(1)
V, Å	1537.4(18)	5906.5(7)
Z	1	2
T, K	100(2)	100(2)
ρ_{calcd}, g cm^{-3}	1.472	1.195
reflns collected/$2\theta_{max}$	17 699/54.96	51 144/45.00
unique reflns [$I > 2\sigma(I)$]	7004	13 908/9442
no. of params/restraints	365/0	1213/57
λ, Å/μ(Mo Kα), cm^{-1}	0.710 73/9.59	0.710 73/5.70
R1[a]/GOF[b]	0.0594/1.036	0.0945/1.089
wR2[c] [$I > 2\sigma(I)$]	0.1264	0.2000
residual density, e Å^{-3}	+1.20/−0.78	+1.82/−0.55

[a] Observation criterion: $I > 2\sigma(I)$. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$ and $P = (F_o^2 + 2F_c^2)/3$.

Results

1. Synthesis and Characterization of Complexes. The reaction of the in situ generated[7] ligands $(^1L)^{2-}$ or $(^2L)^{2-}$ with an aqueous solution of $(NH_4)_2[Fe^{II}(SO_4)_2]\cdot 7H_2O$ (ratio 2:1) at elevated temperatures in the presence of air yielded deep-blue solutions from which dark-blue to black microcrystalline precipitates of neutral $[Fe_2(^1L)_4]$ (**1**) or $[Fe_2(^2L)_4]$ (**1′**) were obtained.

When a toluene solution of **1** reacted with cobaltocene, $[Cp_2Co]$, in a 1:1 ratio under strictly anaerobic conditions at ambient temperature, a dark-bluish-green solution was obtained. After this solution was layered with diethyl ether and cooled to 4 °C, dark-green crystals of **2** were obtained. The monoanion of **2** represents the one-electron-reduced form of **1**. Similarly, if the ratio cobaltocene to complex **1** is raised to 2:1 under otherwise the same reaction conditions described above for **2**, a brown microcrystalline precipitate of **3** was obtained.

The successful isolation of **1**−**3** implies the existence of an electron-transfer series as in eq 1. The CV of **1** in a CH_2Cl_2/toluene solution (1:1, v/v) containing 0.10 M $[N(n\text{-}Bu)_4]PF_6$ as the supporting electrolyte is shown in Figure 1. All potentials are referenced versus Fc^+/Fc. Three reversible one-electron-transfer waves are observed at $E^1_{1/2} = -0.81$ V, $E^2_{1/2} = -0.40$ V, and $E^3_{1/2} = +0.36$ V.

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(10) *ShelXTL*, version 5; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

(11) (a) *SADABS*; Bruker Analytical X-ray Systems Inc.: Madison, WI. (b) Sheldrick, G. M. *ShelXL97*; University of Göttingen: Göttingen, Germany, 1997.

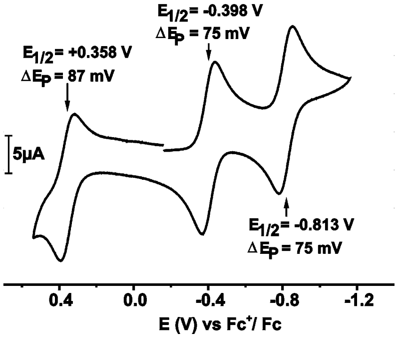

Figure 1. CV of **1** in a toluene/CH_2Cl_2 mixture (1:1, v/v) containing 0.10 M $[N(n\text{-}Bu)_4]PF_6$ as the supporting electrolyte at 25 °C at a glassy carbon working electrode at a scan rate of 100 mV s^{-1}.

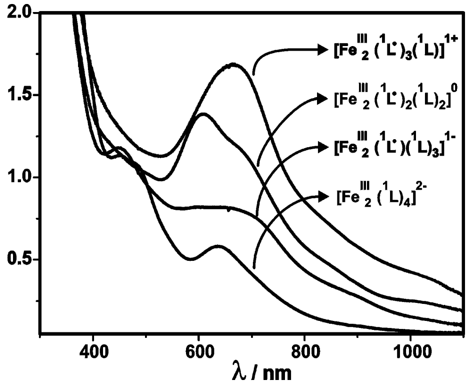

Figure 2. Electronic absorption spectra of **1** and of the coulometrically generated reduced forms $[Fe_2(^1L)_4]^-$ (**2**) and $[Fe_2(^1L)_4]^{2-}$ (**3**) and its coulometrically generated oxidized monocationic form in a toluene/CH_2Cl_2 mixture (1:1, v/v) containing 0.10 M $[N(n\text{-}Bu)_4]PF_6$ at 25 °C.

Coulometric experiments at appropriately fixed potentials show that the first two waves ($E^1_{1/2}$ and $E^2_{1/2}$) correspond to two successive one-electron reductions of neutral, dinuclear **1**. In contrast, the $E^3_{1/2}$ wave corresponds to a one-electron oxidation of neutral **1**, generating a dinuclear cation. Thus, $E^1_{1/2}$ corresponds to the 2−/1− couple, $E^2_{1/2}$ to the 1−/0 couple, and $E^3_{1/2}$ to the 0/1+ couple (eq 1). It is noteworthy that the benzene-1,2-dithiolato derivative $[Fe_2(L^{Bu})_4]^{2-}$ exhibits a very similar CV,[5] where the $E^1_{1/2}$, $E^2_{1/2}$, and $E^3_{1/2}$ values are at −0.63, −0.35, and +0.40 V (quasi-reversible), respectively. In addition, a reversible two-electron reduction at $E^0_{1/2} = -1.45$ V was observed that corresponds to the reversible generation of monomeric, square-planar $[Fe^{II}(L^{Bu})_2]^{2-}$ [12] (eq 1). This process has not been observed for **1**. Figure 2 displays the electronic spectra of **1** and its electrochemically generated monocation, monoanion, and dianion in a toluene/CH_2Cl_2 (1:1, v/v) solvent mixture (0.10 M $[N(n\text{-}Bu)_4]PF_6$). Table 2 summarizes the data.

Recently, we had shown[13] that the presence of S,S′-coordinated 3,5-di-*tert*-butyl-1,2-benzenedithiolate(1−) π radicals, $(L^{Bu\bullet})^-$, in coordination compounds is readily detected in the IR spectrum where the predominantly $C{=}S^\bullet$ stretching frequency is observed at ~1100 cm^{-1} as an intense band. In contrast, in complexes containing only S,S′-coordinated closed-shell dianions $(L^{Bu})^{2-}$, this band is not detected. A similar observation has been made in the IR spectra (KBr disks) of **1**−**3**, which are shown in Figure 3 in the range 800−1400 cm^{-1}. Interestingly, the spectra of both **1** and **2** display a $\nu(C{=}S^\bullet)$ frequency at 1164 cm^{-1}, which is absent in the spectrum of **3**. The IR spectrum of **1′** displays this stretching mode at 1184 cm^{-1}.

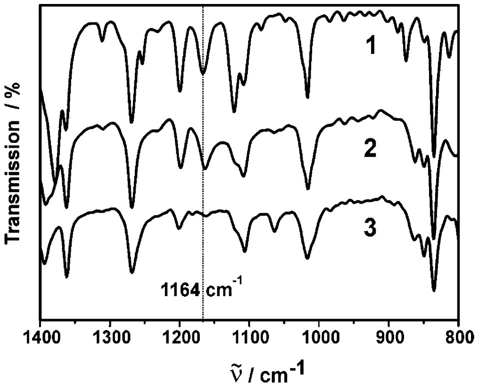

Figure 3. IR spectra of solid compounds **1**−**3** (KBr disks). The marked bands denote the $\nu(C{=}S^\bullet)$ stretching frequency in **1** and **2**, which is absent in **3**.

Table 2. Electronic Spectra of Complexes

complex	λ_{max}, nm (10^4 ε, M^{-1} cm^{-1})
1	605 (1.3), 685sh (1.2), 840sh, 1000sh (0.25)
1′	600 (1.0), 700sh (0.8), 840sh (0.4)
2	470 (1.2), 650b (0.8), 880sh
3	460 (1.2), 490 (1.1), 630 (0.6)
$[Fe^{III}_2(^1L^\bullet)_3(^1L)]^+$	680 (1.7), 820sh, ~1000sh (0.4)

We conclude that the dianion in **3** does not contain an $(^1L^\bullet)^-$ π-radical ligand but four closed-shell dianions $(^1L)^{2-}$ instead and that the charge distribution in **3** is to be described as $[Fe^{III}_2(^1L)_4]^{2-}$. From simple charge considerations, one would then imply the presence of two π radicals in neutral **1**, $[Fe^{III}_2(^1L^\bullet)_2(^1L)_2]$, and only one in the monoanion of **2**, $[Fe(^1L)_3(^1L^\bullet)]^-$, if the oxidation state of both iron ions in both compounds remains III+. In the analogous complex $[Fe^{III}_2(L^{Bu})_3(L^{Bu\bullet})]^-$, the $\nu(C{=}S^\bullet)$ mode[5] has been reported at 1107 cm^{-1}, which is again absent in $[Fe^{III}_2(L^{Bu})_4]^{2-}$.

Magnetic Properties. Solid samples of complexes **1**−**3** have been studied by measuring their molar magnetic properties in the temperature range 4.2−298 K and a 1 T external magnetic field by using a SQUID magnetometer.

Figure 4 shows the temperature dependence of the effective magnetic moments of **1** (top), **2** (middle), and **3** (bottom). The solid lines represent fits using the following model. The magnetism of $[Fe^{III}_2(mnt)_4]^{2-}$ has been successfully modeled for a number of different salts,[3b,c] assuming intramolecular antiferromagnetic coupling between two intermediate-spin ferric ions ($S_{Fe} = {}^3/_2$), yielding an $S_t = 0$ ground state by using the spin Hamiltonian $H = 2JS_1{\cdot}S_2$ ($S_1 = S_2 = {}^3/_2$) with $J \approx -250$ cm^{-1}. Similarly, the magnetism of $[Fe^{III}_2(L^{Bu})_4]^{2-}$ has been modeled with $J = -84$ cm^{-1}, affording also an $S_t = 0$ ground state;[5] for $[Fe^{III}_2(bdt)_4]^{2-}$, a coupling constant of −114 cm^{-1} has been reported,[5] where $(bdt)^{2-}$ represents

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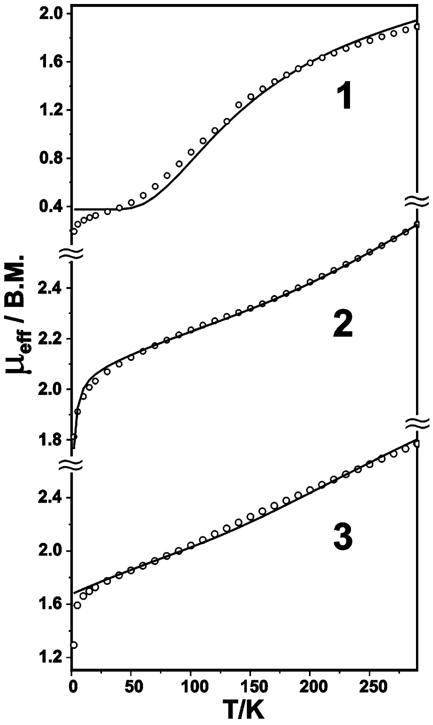

Figure 4. Temperature dependence of the magnetic moment of solid samples of **1** (top), **2** (middle), and **3** (bottom). The solid lines represent best fits; see the text for parameters.

the ligand benzene-1,2-dithiolate(2−). In the latter two cases, the intrinsic spin of the two ferric ions is $S_{Fe} = {}^3/_2$.

We found that the data of **3** can be readily fitted, using the same model involving two $S_{Fe} = {}^3/_2$ ferric ions, which are intramolecularly, antiferromagnetically coupled ($J = -250$ cm^{-1}; $S_t = 0$). Inclusion of a paramagnetic impurity of 8% ($S = {}^5/_2$) was necessary, and a large temperature-independent paramagnetism $\chi_{TIP} = 1500 \times 10^{-6}$ cm^3 mol^{-1}. The latter data are an indication that all samples of bis(dithiolene)iron complexes contain some degree of a colloidal $\{Fe^{III}(OH)O\}_x$ contaminant. Repeated recrystallizations did not improve matters.

The temperature dependence of the magnetic moments of **2** clearly established the $S_t = {}^1/_2$ ground state of the monoanion [μ_{eff}(4.2 K) = 1.8 μ_B]. The temperature dependence was successfully modeled assuming strong intramolecular antiferromagnetic coupling of two ferric ions ($S_{Fe} = {}^3/_2$; $J = -225$ cm^{-1}) and a slightly weaker antiferromagnetic coupling of a single π-radical anion ($S_{rad} = {}^1/_2$) to a ferric ion ($J = \sim -200$ cm^{-1}). Inclusion of a paramagnetic impurity of ~3.8% ($S = {}^5/_2$) and $\chi_{TIP} = 900 \times 10^{-6}$ cm^3 mol^{-1} and a Weiss constant $\theta = -1.28$ K was necessary in order to obtain a reasonable fit. The $S_t = {}^1/_2$ ground state of **2** has been confirmed by EPR spectroscopy (see below).

Complex **1** possesses an $S_t = 0$ ground state. In the temperature range 50−290 K (monotonic increase of μ_{eff} from 0.4 to 1.7 μ_B), the model of two antiferromagnetically coupled intermediate-spin ferric ions [$J_{FeFe} = -200$ cm^{-1} (fixed)] and two ligand π radicals ($J_{Fe(1)rad} = -140$ cm^{-1}) yields a satisfactory fit [PI = 0.8% ($S = {}^5/_2$); $\chi_{TIP} = 27 \times 10^{-6}$ cm^3 mol^{-1}].

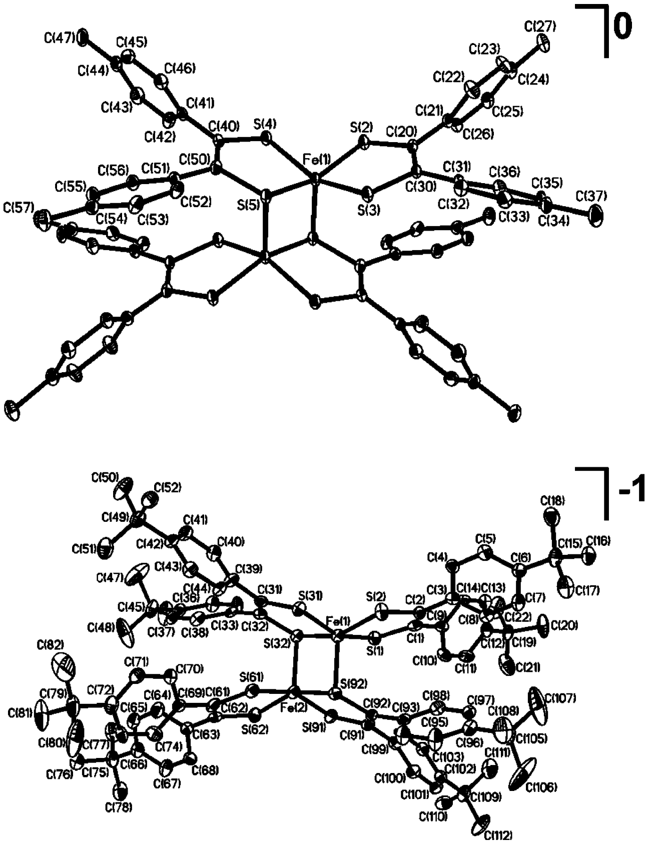

Figure 5. Structures of the neutral molecule in **1′** (top) and the corresponding monoanion in crystals of **2** (bottom). Non-hydrogen atoms are drawn at the 50% level.

Thus, the magnetism of **1**−**3** is in agreement with the description of the dinuclear species as $[Fe^{III}_2(^1L^•)_2(^1L)_2]^0$ for **1**, $[Fe^{III}_2(^1L^•)(^1L)_3]^-$ for **2**, and $[Fe^{III}_2(^1L)_4]^{2-}$ for **3**. This model implies that in the three species the oxidation state and the spin state of the central iron ion does not change; it is III+, and its intrinsic spin state is $S_{Fe} = {}^3/_2$ in all cases.

Crystal Structure Determinations. The structures of complexes **1′** and **2** have been determined by X-ray crystallography at 100(2) K. Figure 5 shows the structures of the dinuclear diferric neutral complex in **1′** (top) and that of the dinuclear monoanion in crystals of **2** (bottom). Table 3 summarizes important bond lengths.

Clearly, each iron ion in **1′** and **2** is S,S′-bound to two diaryldithiolene ligands as di- or monoanion (where aryl is a *p*-tolyl substituent in **1′** and a 4-*tert*-butylphenyl group in **2**). The metal ions possess a square-pyramidal-based coordination geometry, where the two 1,2-diaryldithiolenes occupy equatorial positions and where the iron ion is displaced by 0.47 Å in **1′** and 0.47 and 0.48 Å in **2** from the least-squares plane defined by the four sulfur atoms of the basal ligands. One dithiolene ligand of each FeL$_2$ fragment forms a sulfur bridge to another such fragment. The bridging sulfur atoms are in an apical position at one iron ion and in an equatorial position at the other. A similar structure has been reported for all dimeric (benzene-1,2-dithiolato)$_2$iron complexes.[2−5]

The neutral molecule in crystals of **1′** lie[5] on a crystallographic center of symmetry. This is not the case for the

Table 3. Selected Bond Distances in Angstroms in **1′** and **2**

		Complex **1′**			
Fe−S(2)	2.1850(15)	Fe−S(3)	2.1920(20)	Fe−S(5)	2.1948(14)
Fe−S(1)	2.2080(20)	Fe−S(5′)	2.3116(19)	Fe−Fe′	2.8215(18)
S(2)−C(20)	1.695(4)	S(3)−C(30)	1.713(4)	S(4)−C(40)	1.754(4)
S(5)−C(50)	1.760(4)	C(20)−C(30)	1.403	C(40)−C(50)	1.366(5)
		Complex **2**			
Fe(1)−S(1)	2.201(2)	Fe(1)−S(2)	2.203(3)	Fe(1)−S(32)	2.211(2)
Fe(1)−S(31)	2.216(2)	Fe(1)−S(92)	2.348(3)	Fe(1)−Fe(2)	2.804(2)
Fe(2)−S(62)	2.193(3)	Fe(2)−S(91)	2.207(2)	Fe(2)−S(61)	2.209(2)
Fe(2)−S(92)	2.216(2)	Fe(2)−S(32)	2.348(3)	S(1)−C(1)	1.730(9)
S(2)−C(2)	1.745(8)	C(1)−C(2)	1.379(11)	S(31)−C(31)	1.750(8)
S(32)−C(32)	1.773(8)	C(31)−C(32)	1.359(11)	S(61)−C(61)	1.721(9)
S(62)−C(62)	1.732(9)	C(61)−C(62)	1.408(12)	S(91)−C(91)	1.731(9)
S(92)−C(92)	1.760(8)	C(91)−C(92)	1.373(11)		

Table 4. Zero-Field Mössbauer Parameters of Complexes

	T, K	δ,[a] mm s^{-1}	Γ,[b] mm s^{-1}	ΔE_Q,[c] mm s^{-1}	S'_{Fe}[d]	S_t[e]	ref
1	80	0.25	0.28	1.93	$^3/_2$	0	this work
1′	80	0.26	0.30	2.18	$^3/_2$	0	this work
2	80	0.29	0.38	2.13	$^3/_2$	$^1/_2$	this work
3	80	0.36	0.24	2.26	$^3/_2$	0	this work
$[Fe^{III}_2(L)_4]^{2-}$	77	0.31		2.95	$^3/_2$	0	12
$[Fe^{III}_2(L^{Bu})_4]^{2-}$	80	0.36	0.44	2.87	$^3/_2$	0	5
$[Fe^{III}_2(L^{Bu})_3(L^{Bu\bullet})]^-$	80	0.28	0.46	2.70	$^3/_2$	$^1/_2$	5
$[Fe^{III}(L)_2(Bu\text{-}py)]^-$	80	0.33	0.31	3.03	$^3/_2$	$^3/_2$	5
$[Fe^{III}(L)(L^\bullet)(Bu\text{-}py)]^0$	80	0.29	0.29	3.02	$^3/_2$	1	5
$[N(n\text{-}Bu)_4]_2[Fe^{III}_2(mnt)_4]$	80	0.33		2.68	$^3/_2$	0	3[b−d]

[a] Isomer shift vs α-Fe at 298 K. [b] Width at half-height. [c] Quadrupole splitting. [d] Intrinsic spin state of iron ions. [e] Overall spin state. Ligand abbreviations: $(L)^{2-}$ = benzene-1,2-dithiolate(2−); $(L^\bullet)^-$ = benzene-1,2-dithiolate(1−) π radical; $(L^{Bu})^{2-}$ = 3,5-di-*tert*-butyl-1,2-benzenedithiolate(2−); $(L^{Bu\bullet})^-$ = 3,5-di-*tert*-butyl-1,2-dithiolate(1−) π radical; (Bu-py) = 4-*tert*-butylpyridine; $(mnt)^{2-}$ = maleonitrile-1,2-dithiolate(2−);$(mnt^\bullet)^-$ = maleonitrile-1,2-dithiolate(1−) π radical.

monoanionic dimer in crystals of **2**. Here, the dimer does not possess crystallographically imposed symmetry.

It is now quite revealing that the C−S bond lengths in the terminal ligands in **1′** at an average of 1.704(4) Å are significantly shorter than the corresponding bond distances of the bridging dithiolate at an average of 1.757(4) Å. Concomitantly, the “olefinic” C−C bond is *long* at 1.403(5) Å in the terminal but *shorter* at 1.366(5) Å in the bridging dithiolate. We interpret this observation as a clear manifestation that both ligands of each $[Fe(^2L)_2]^0$ fragment exist at different oxidation levels: the terminal, nonbridging ligand is best described as a $(^2L^\bullet)^-$ π-radical monoanion, whereas the bridging ligand is a closed-shell dianion $(^2L)^{2-}$. This ligand charge distribution renders the central iron ion trivalent (Fe^{III}); it is in a square-pyramidal-based S_5 environment and possesses an intrinsic intermediate-spin ground state ($S_{Fe} = {}^3/_2$).

Interestingly, the geometrical features in the dimeric monoanion in **2** are slightly different. First of all, the C−C and C−S distances of the two bridging dithiolene ligands are identical within experimental error in both crystallographically independent halves. The long C−S distance at an average of 1.754(8) Å, and the relatively shorter olefinic C−C bond at 1.366(10) Å in the bridging ligands apparently indicates again the presence of two $(^2L)^{2-}$ diamagnetic dianions. In contrast, the two terminal ligands are also nearly identical, but the average C−S distance at 1.732 Å is *longer* than the corresponding distance in **1′** and the average C−C bond length at 1.394 Å is slightly longer than what is expected for two $(^1L^\bullet)^-$ radicals. These distances would be in agreement with the presence of one $(^1L)^{2-}$ and another $(^1L^\bullet)^-$ ligand in the two terminal positions, affording a charge distribution as in $[Fe^{III}_2(^1L)_3(^1L^\bullet)]^-$, where the excess electron may be delocalized over both terminal positions (or not). A similar charge distribution has been proposed in the monoanion $[Fe^{III}_2(L)_3(L^\bullet)]^-$, where $(L)^{2-}$ represents the closed-shell dianion 1,2-benzenedithiolate and the monoanion is its one-electron-oxidized π-radical anion, $(L^\bullet)^-$. [5]

Dimeric dianions containing two ferric ions and four closed-shell dithiolato ligands have also been previously structurally characterized. It is noteworthy that the high-quality, low-temperature crystal structure determination of $[N(n\text{-}Bu)_4]_2[Fe^{III}_2(L)_4]$ exhibits clearly that both the terminal and bridging benzene-1,2-dithiolato ligands are of the closed-shell, dianionic type; the C−S bonds are all long at an average of 1.762 Å, and the phenyl rings do not display quinoid-type distortions.[5]

It is also quite remarkable that the average C−S bond length at 1.742 Å and the average olefinic C−C bond length at 1.352 Å in all structures containing $[Fe^{III}_2(mnt)_4]^{2-}$ dianions are identical within experimental error for the terminal and bridging mnt^{2-} dianions.[3] This is a clear indication that both ligands possess the same oxidation level, namely, closed-shell dianionic $(mnt)^{2-}$.

Mössbauer Spectroscopy. Zero-field Mössbauer spectra of solid samples of **1**−**3** have been recorded at 80 K; the results are summarized in Table 4. It is a remarkable observation that all dinuclear complexes with two sulfur-bridged, square-pyramidal-based FeS_5 entities display a *single* doublet with isomer shifts, δ, in the rather narrow range of

0.25−0.36 mm s^{-1} irrespective of the nature of the respective ligand, which can be a dithiolene(2− or 1−) or benzene-1,2-dithiolate(2− or 1−) anion; the quadrupole splitting $|\Delta E_Q|$ is large and in the range of 1.93−2.95 mm s^{-1}.

This is taken as an indication that the intrinsic oxidation state of all central iron ions is the same, namely, III+, for all complexes under consideration and that the intrinsic iron spin state is invariably $S_{Fe} = {}^3/_2$. This notion is nicely corroborated by the Mössbauer data reported previously[5] for the mononuclear monoanion $[Fe^{III}(L)_2(Bu\text{-}py)]^-$, which possesses a square-pyramidal-based FeS_4N geometry with the pyridine nitrogen in an apical position and an $S_{Fe} = {}^3/_2$ ground state: $\delta = 0.28$ mm s^{-1}; $|\Delta E_Q| = 2.70$ mm s^{-1}. Interestingly, its one-electron-oxidized, neutral $[Fe^{III}(L^\bullet)(L)(Bu\text{-}py)]^0$ form with a triplet ground state ($S_t = 1$) and a delocalized ligand π-radical anion displays very similar Mössbauer parameters ($\delta = 0.29$ mm s^{-1}; $|\Delta E_Q| = 3.02$ mm s^{-1}), indicating a ligand-centered rather than metal-centered oxidation of the monoanion to the neutral complex.[5]

As noted above, both iron ions possess an $S_{Fe} = {}^3/_2$ spin state in the monoanionic dinuclear species $[Fe^{III}_2(^1L)_3(^1L^\bullet)]^-$ in crystals of **2**. Only a *single* quadrupole doublet is observed despite the fact that the ligand distribution of three closed-shell $(^1L)^{2-}$ and one π-radical anion $(^1L^\bullet)^-$ per *two* iron ions is asymmetric. This rules out a metal-centered $Fe^{III}Fe^{IV}$ mixed valency and implies a ligand mixed valency of class II or III on the time scale of a Mössbauer experiment. Thus, the unpaired electron in the dianion is probably delocalized over at least two sites:

$$[(^1L^\bullet)Fe^{III}(\mu\text{-}^1L)_2Fe^{III}(^1L)]^- \leftrightarrow [(^1L)Fe^{III}(\mu\text{-}^1L)_2Fe^{III}(^1L^\bullet)]^-$$

Very similar behavior has been reported[5] for $[Fe^{III}_2(L^{Bu})_3(L^{Bu\bullet})]^-$.

X-Band EPR Spectra of $[Fe^{III}_2(^1L^\bullet)(^1L)_3]^-$ and $[Fe^{III}_2(^1L^\bullet)_3(^1L)]^+$. It has been shown above that **1** and **3** possess a diamagnetic ground state $S_t = 0$, respectively. Thus, intramolecular spin-exchange coupling between two ligand π radicals ($S_{rad} = {}^1/_2$) and two intermediate-spin ferric ions ($S_{Fe} = {}^3/_2$) in $[Fe^{III}_2(^1L^\bullet)_2(L)_2]^0$ yields an overall $S_t = 0$ ground state, as does the exchange coupling between two intermediate-spin ferric ions in $[Fe^{III}_2(^1L)_4]^{2-}$. The corresponding dimeric dianions $[Fe^{III}_2(L^{Bu})_4]^{2-}$ and $[Fe^{III}_2(mnt)_4]^{2-}$ also possess a diamagnetic ground state.[3,5]

Consequently, the corresponding monocationic complex $[Fe^{III}_2(^1L^\bullet)_3(^1L)]^+$ and its monoanionic analogue $[Fe^{III}_2(^1L^\bullet)(^1L)_3]^-$ must possess a paramagnetic ground state ($S_t = {}^1/_2$). This is confirmed by their EPR spectra shown in Figure 6.

Both species have been electrochemically generated from **1** in CH_2Cl_2/toluene (1:1, v/v) mixtures (0.1 M $[N(n\text{-}Bu)_4]PF_6$) by coulometry at appropriately fixed potentials. The spectra have been recorded in a frozen solution at 30 K. Both species display a remarkably similar rhombic signal with *g* values of 2.09, 2.04, and 2.01 for the monoanion and 2.08, 2.06, and 2.02 for the monocation.

Note that the analogous spectrum of the monoanion $[Fe^{III}_2(L^{Bu})_3(L^{Bu\bullet})]^-$ has also been reported with similar *g* values of 2.06, 2.06, and 2.01.[5] These spectra are quite typical for S-centered radical complexes; they are not in accord with a half-filled d orbital at one of the iron centers. Because the exchange coupling between the two intermediate-spin ferric ions is strong and the radical-to-iron ion coupling is weaker, the residual unpaired electron resides predominantly on the ligand π radical at a sulfur atom in the monocation and monoanion. Note that a similar rhombic signal has been reported for square-planar $[Au^{III}(L^{Bu})(L^{Bu\bullet})] \leftrightarrow [Au^{III}(L^{Bu\bullet})(L^{Bu})]$ with *g* values of 2.0690, 2.0320, and 1.911 (g_{iso} = 2.004), where the gold hyperfine splitting is small and not resolved.[14]

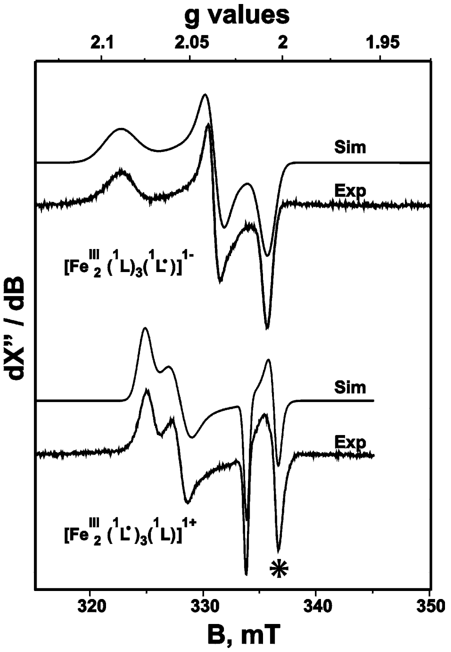

Figure 6. X-band EPR spectra of electrochemically generated monoanion $[Fe^{III}_2(^1L_3)(^1L^\bullet)]^-$ (top) and of the corresponding monocation $[Fe^{III}_2(^1L^\bullet)_3(^1L)]^+$ (bottom) in a frozen toluene/CH_2Cl_2 mixture (1:1, v/v) at 30 K (conditions: frequency, 9.43 GHz; modulation, 5.0 G; power, 10 μW). The asterisk denotes an organic impurity radical (6%) of unknown composition.

Discussion

The electronic structure of four dinuclear species of the electron-transfer series $[Fe_2(^1L)_4]^n$ (n = 2−, 1−, 0, 1+) has been elucidated by a combination of structure determinations and electronic, IR, electron spin resonance, and Mössbauer spectroscopies. The most salient feature of the series is the observation that each individual species displays only a single quadrupole doublet in their Mössbauer spectrum, indicating that both iron sites in this dinuclear complex are equivalent on the time scale of a Mössbauer experiment even if the ligand charge distribution is formally not equivalent as in **2**. The fact that the isomer shift and quadrupole splitting parameters vary only very slightly with an increase in the charge of the dinuclear species is quite indicative that the intrinsic spin state of the iron ions is the same in all complexes, namely, $S_{Fe} = {}^3/_2$.

Thus, the stepwise one-electron oxidations **3** → **2** → **1** are ligand-centered processes that involve the formation of

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π-radical monoanions $(^1L^\bullet)^-$ [or $(^2L^\bullet)^-$ in **1′**]. Structurally, it has been possible to show that the two terminal dithiolene ligands in **1′** possess an $(^2L^\bullet)^-$ oxidation level because the average C−S bond length is very *short* at 1.705(4) Å and the corresponding olefinic C−C bond is *long* at 1.403(5) Å. In contrast, two bridging dithiolene ligands are at the $(^2L)^{2-}$ oxidation level with an average C−S bond at 1.757(4) Å and an olefinic C−C bond length at 1.366(5) Å. Note that the neutral complex is centrosymmetric. Thus, a localized description of the neutral molecules in **1** and **1′** as $[(^1L^\bullet)Fe^{III}(\mu\text{-}^1L)_2Fe^{III}(^1L^\bullet)]^0$ and $[(^2L^\bullet)Fe^{III}(\mu\text{-}^2L)Fe(^2L^\bullet)]^0$ is appropriate. The diamagnetic ground states of **1** and **1′** are attained via strong intramolecular antiferromagnetic coupling of two intermediate-spin ferric ions and two terminal ligand π radicals.

Interestingly, the electronic spectra of **1** and **1′** display intense ($\epsilon > 10^4$ L mol^{-1} cm^{-1}) ligand-to-ligand charge-transfer bands at 605 and 685 nm, respectively. In the IR, a strong $\nu(C{=}S^\bullet)$ frequency at 1164 cm^{-1} is also typical for the presence of $(^1L^\bullet)^-$ radicals.

Two-electron reduction of **1** yields **3**, which contains the dianion $[Fe^{III}_2(^1L)_4]^{2-}$. The Mössbauer spectroscopic data prove the presence of two equivalent, intermediate-spin ferric ions, which couple antiferromagnetically, affording the observed diamagnetic ground state ($S_{Fe} = {}^3/_2$; $S_t = 0$). The coupling is strong with $J = \sim -250$ cm^{-1}. In the IR, no $\nu(C{=}S^\bullet)$ band is observed, indicating the absence of π-radical ligands. The same electronic structure has been elucidated[3] for $[Fe^{III}_2(mnt)_2]^{2-}$, although the intrinsic spin state at the iron ions has occasionally been described as $S_{Fe} = {}^1/_2$. This is clearly not in accord with the Mössbauer parameters shown in Table 4. Also, the complexes containing four $(bdt)^{2-}$-derived ligands, namely, $[Fe^{III}_2(L)_4]^{2-}$, $[Fe^{III}_2(L^{Bu})_4]^{2-}$,[5] and $[Fe^{III}_2(L^{CN})_4]^{2-}$,[15] where $(L)^{2-}$ is $(bdt)^{2-}$, $(L^{Bu})^{2-}$ is 3,5-di-*tert*-butyl-1,2-benzenedithiolate(2−), and $(L^{CN})^{2-}$ represents 4,5-dicyanobenzene-1,2-dithiolato, have been shown to contain two antiferromagnetically coupled, intermediate-spin ferric ions, yielding $S_t = 0$. In the structurally characterized cases, the C−S bonds are long (∼1.76 Å) and the C−C distances in the benzene rings are equidistant, indicating its aromatic character.

The electronic structure of the dinuclear monoanion in crystals of **2** is interesting because it is formally not possible to distribute three closed-shell dianions $(^1L)^{2-}$ and a single π-radical monoanion $(^1L^\bullet)^-$ equally (or symmetrically) over two ferric ions. Consequently, the monoanion $[Fe^{III}_2(^1L)_3(^1L^\bullet)]^-$ does not possess crystallographically imposed symmetry. The presence of at least one $(^1L^\bullet)^-$ π radical is established by the observation of a $\nu(C{=}S^\bullet)$ stretching mode at 1164 cm^{-1}. The structural data are in agreement with the notion that the two terminal ligand positions are occupied by one $(^1L^\bullet)^-$ and the other one by a $(^1L)^{2-}$. A degree of delocalization between these two may be present, although there is no real structural evidence outside the 3σ standard deviation available. On the other hand, the presence of strong intervalence charge-transfer bands at 650 and 889sh nm may indicate this class II or III behavior. The Mössbauer spectrum displaying a single quadrupole doublet does point to two equivalent ferric ions. The EPR spectrum and magnetism point to a model where the two ferric ions are strongly antiferromagnetically coupled, yielding a ligand radical $(^1L^\bullet)^-$ ($S_{rad} = {}^1/_2$) as the EPR-active species. Exactly the same behavior has been described previously[5] for the benzene-1,2-dithiolato(2−/1−)-containing species $[Fe^{III}_2(L^{Bu})_3(L^{Bu\bullet})]^-$.

The present CV and coulometric experiments on CH_2Cl_2 solutions containing **1** and 0.10 M $[N(n\text{-}Bu)_4]PF_6$ have shown that a dinuclear *monocationic* species is accessible and quite stable in solution. Its electronic and EPR spectra have been recorded. The data available on $[Fe^{III}_2(^1L^\bullet)_3(^1L)]^+$ are rather scarce, but its ground state $S_t = {}^1/_2$ has been established unequivocally. As noted above, the EPR spectrum resembles that of a sulfur-centered bis(aryl)dithiolate π-radical monoanion. We propose that the electronic structure of this monocation is best described by two antiferromagnetically coupled intermediate-spin ferric ions and also three antiferromagnetically coupled π radicals $(^1L^\bullet)^-$. The electronic spectrum of this species corroborates this assignment by the observation of three intense ligand-to-ligand charge-transfer bands >600 nm (Figure 2 and Table 2).

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Supporting Information Available: X-ray crystallographic files (CIF) for complexes **1′** and **2** and zero-field Mössbauer spectra of solid samples of compounds **1**−**3** at 80 K (Figures S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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