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Inorganic Chemistry Article

Electronic Structure of Nitric Oxide Adducts of Bis(diaryl-1,2-dithiolene)iron Compounds: Four-Membered Electron-Transfer Series [Fe(NO)(L)$_2$]^z ($z = 1+, 0, 1–, 2–$)

Prasanta Ghosh,[†] Keira Stobie,[‡] Eckhard Bill,[†] Eberhard Bothe,[†] Thomas Weyhermüller,[†] Michael D. Ward,[§] Jon A. McCleverty,[‡] and Karl Wieghardt*,[†]

Max-Planck-Institut für Bioanorganische Chemie, Stiftstrasse 34-36, D-45470 Mülheim an der Ruhr, Germany, School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom, and Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom

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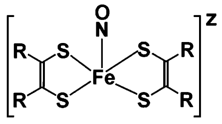
Four members of the electron-transfer series [Fe(NO)($S_2C_2R_2$)$_2$]^z ($z = 1+, 0, 1–, 2–$) have been isolated as solid materials (R = *p*-tolyl): [**1a**](BF$_4$), [**1a**]^0, [Co(Cp)$_2$][**1a**], and [Co(Cp)$_2$]$_2$[**1a**]. In addition, complexes [**2a**]^0 (R = 4,4-diphenyl), [**3a**]^0 (R = *p*-methoxyphenyl), [Et$_4$N][**4a**] (R = phenyl), and [PPh$_4$][**5a**] (R = –CN) have been synthesized and the members of each of their electron-transfer series electrochemically generated in CH_2Cl_2 solution. All species have been characterized electro- and magnetochemically. Their electronic, Mössbauer, and electron paramagnetic resonance spectra as well as their infrared spectra have been recorded in order to elucidate the electronic structure of each member of the electron-transfer series. It is shown that the monocationic, neutral, and monoanionic species possess an {FeNO}^{6} ($S = 0$) moiety where the redox chemistry is sulfur ligand-based, (L)$^{2-}$(L$^\bullet$)$^{1-}$: [Fe(NO)(L$^\bullet$)$_2$]$^+$ ($S = 0$), [Fe(NO)(L$^\bullet$)(L)]^0 $\leftrightarrow$ [Fe(NO)(L)(L$^\bullet$)]^0 ($S = 1/2$), [Fe(NO)(L)$_2$]$^-$ ($S = 0$). Further one-electron reduction generates a dianion with an {FeNO}^{7} ($S = 1/2$) unit and two fully reduced, diamagnetic dianions L^{2-}: [Fe(NO)(L)$_2$]$^{2-}$ ($S = 1/2$).

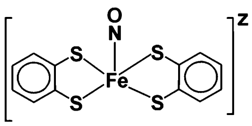
Introduction

McCleverty and co-workers established in a series of articles[1−3] that five-coordinate NO adducts of bis(dithiolene)iron complexes exist as a maximally five-membered electron-transfer series [Fe(NO)(dithiolene)$_2$]^z ($z = 1+, 0, 1-, 2-, 3-$).

In contrast, the corresponding 1,2-benzenedithiolate series, [Fe(NO)(bdt)$_2$]^z, consists only of two stable species, namely, the mono- and dianion ($z = 1-$ or $2-$) where salts of both anions have been structurally characterized by X-ray crystallography.[4] None of the above bis(dithiolene)iron complexes has been structurally characterized with the exception of [Et$_4$N][Fe(NO)(mnt)$_2$][5] and [Et$_4$N]$_2$[Fe(NO)(mnt)$_2$],[6] where the latter structure is of low quality (mnt^{2-} = maleonitrile-1,2-dithiolate).



z = 1+, 0, 1-, 2-, (3-)



z = 1-, 2-

Despite the fact that for a number of neutral or anionic species the Mössbauer,[7,8] EPR, and UV−vis spectra have been recorded and reported,[1−3] it is surprising that the electronic structures of these compounds have not yet been studied in detail. The problem is that all three components of these species can, in principle, be redox active: that is

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* To whom correspondence should be addressed. E-mail: wieghardt@mpi-muelheim.mpg.de.

[†] Max-Planck-Institut für Bioanorganische Chemie.

[‡] University of Bristol.

[§] University of Sheffield.

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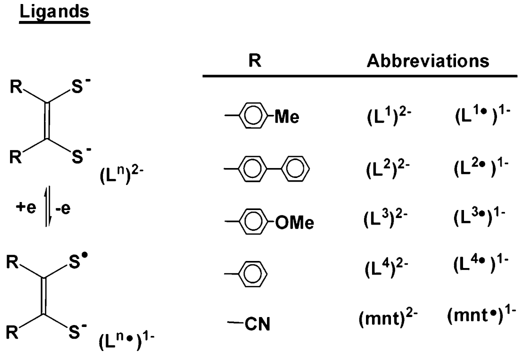
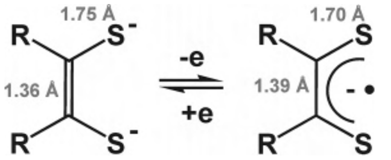
Chart 1



(a) the NO ligand is the archetypal noninnocent ligand which can be bound to an iron ion as NO$^+$ ($S = 0$), NO ($S = 1/2$), or NO$^-$ ($S = 0$ or 1), (b) the central iron ion can possess a d^6 ($S_{\mathrm{Fe}} = 0$, $S_{\mathrm{Fe}} = 1$, $S_{\mathrm{Fe}} = 2$) or d^5 ($S_{\mathrm{Fe}} = 1/2$, 3/2, 5/2) electron configuration, and (c) the dithiolene ligands may be coordinated as closed-shell dianion ($S_{\mathrm{L}} = 0$) or as π-radical monoanion ($S_{\mathrm{L}} = 1/2$).

In order to avoid the assignment of a formal oxidation state to the iron ion and a charge on the coordinated nitrosyl ligand Enemark and Feltham introduced the $\{\mathrm{FeNO}\}^n$ notation where n corresponds to the familiar number of d electrons on the metal when the nitrosyl ligand is formally (for the sake of electron bookkeeping) considered to be bound as NO$^+$.[9] In concert these three sources of redox activity will determine the overall electronic structure and spin ground state of each member of the electron-transfer series [Fe(NO)(dithiolene)$_2$]^z complexes (z = 1+/0/1−/2−).



In this study we used the ligands shown in Chart 1 which can exist either as closed-shell dianions (L^x)$^{2-}$ or in their one-electron oxidized forms as π radical monoanion (L$^{x\bullet}$)$^{1-}$. The two forms are known to possess distinctly different C−S and "olefinic" C−C bond lengths (see above). Therefore, it should be possible to determine the oxidation level of the dithiolene ligands in a given complex by high-quality X-ray crystallography.

We prepared and isolated four new members of the nitrosyl iron dithiolene electron-transfer series (Chart 2): [Fe(NO)(L$^{1\bullet}$)$_2$]$^+$ ($S = 0$), [**1a**]$^+$; [Fe(NO)(L$^{1\bullet}$)(L^1)]^0 ↔ [Fe(NO)(L^1)(L$^{1\bullet}$)]^0 ($S = 1/2$), [**1a**]^0; [Co(Cp)$_2$][Fe(NO)(L^1)$_2$] ($S = 0$), [**1a**]$^{1-}$; [Co(Cp)$_2$]$_2$[Fe(NO)(L^1)$_2$] ($S = 1/2$), [**1a**]$^{2-}$. Complexes [**2a**]^0, [**3a**]^0, [Et$_4$N][**4a**], and [PPh$_4$][**5a**] have been synthesized according to literature procedures (see Experimental Section).

It is the aim of this work to establish unequivocally the electronic structures of the monocations, the neutral complexes, and their mono- and dianions. This requires determination of n in the $\{\mathrm{FeNO}\}^n$ moieties and the oxidation level of the corresponding two dithiolene ligands. For this purpose the ν_{NO} stretching frequencies, the Mössbauer parameters of all complexes, and the EPR spectra of the paramagnetic neutral and dianionic forms have been measured.

Chart 2

Dinuclear Complexes

[Fe$^{\mathrm{III}}$(L$^{1\bullet}$)(L^1)]$_2$	**(1)**
[Fe$^{\mathrm{III}}$(L$^{2\bullet}$)(L^2)]$_2$	**(2)**
[Fe$^{\mathrm{III}}$(L$^{3\bullet}$)(L^3)]$_2$	**(3)**
[Fe$^{\mathrm{III}}$(L$^{4\bullet}$)(L^4)]$_2$	**(4)**
Na$_2$[Fe$^{\mathrm{III}}$(mnt)$_2$]$_2$	**(5)**

Mononuclear nitrosyl iron Complexes

[Fe(NO)(L$^{1\bullet}$)$_2$][BF$_4$]	**[1a][BF$_4$]**	**[1a]$^+$**
[Fe(NO)(L$^{1\bullet}$)(L^1)]	**[1a]**	**[1a]^0**
[Co(Cp)$_2$][Fe(NO)(L^1)$_2$]	**[Co(Cp)$_2$][1a]**	**[1a]$^{1-}$**
[Co(Cp)$_2$]$_2$[Fe(NO)(L^1)$_2$]	**[Co(Cp)$_2$]$_2$[1a]**	**[1a]$^{2-}$**
[Fe(NO)(L$^{2\bullet}$)(L^2)]	**[2a]**	**[2a]^0**
[Fe(NO)(L$^{3\bullet}$)(L^3)]	**[3a]**	**[3a]^0**
[Et$_4$N][Fe(NO)(L^4)$_2$]	**[Et$_4$N][4a]**	**[4a]$^{1-}$**
[PPh$_4$][Fe(NO)(mnt)$_2$]	**[PPh$_4$][5a]**	**[5a]$^{1-}$**

Experimental Section

Syntheses. The dinuclear complexes **1**,[10] **4**,[11] and **5**[12] and the mononuclear nitrosyl complexes [**3a**], [Et$_4$N][**4a**],[2] and [Et$_4$N] [**5a**][2] have been prepared according to literature procedures. We note that neutral [**1a**] has also been prepared previously.[3]

[Fe$^{\mathrm{III}}$(L$^{2\bullet}$)(L^2)]$_2$ (2). To a suspension of 4,4′-diphenylbenzoin (4.0 g; 10 mmol) in 1,4-dioxan (80 mL) solid P$_4$S$_{10}$ (4.0 g) was added and heated to reflux under argon for 2 h with stirring. The color of the solution turned orange. It was cooled to room temperature and filtered to remove excess P$_4$S$_{10}$. To the resulting orange solution was added an aqueous solution (10 mL) of FeCl$_2$·4H$_2$O (1.0 g; 5 mmol). After heating to reflux under argon for 2 h, the solution turned dark green and black microcrystals separated out which were filtered off and washed successively with methanol, water, and acetonitrile and dried in air. Yield: 1.6 g (40% with respect to iron). Anal. Calcd for C$_{104}$H$_{72}$S$_8$Fe$_2$: C, 73.91; H, 4.29; S, 15.18; Fe, 6.61. Found: C, 73.9; H, 4.5; S, 14.9; Fe, 7.1. UV−vis (CH$_2$Cl$_2$): $\lambda_{\max}(\epsilon)$ = 356 (19 300), 625 nm (5582 L mol^{-1} cm^{-1}).

[Fe$^{\mathrm{III}}$(L$^{3\bullet}$)(L^3)]$_2$ (3). A mixture of 4,4′-dimethoxybenzoin (4.00 g; 15 mmol) and P$_4$S$_{10}$ (4.00 g) in xylene (40 mL) was heated to reflux for 2 h, during which time the yellow mixture became deep

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Table 1. Crystallographic Data for [**1a**], [**2a**]·0.75 CH_2Cl_2, and [**Co**(**Cp**)$_2$][**1a**]

	[**1a**]	[**2a**]·0.75CH_2Cl_2	**[Co(Cp)$_2$][1a]**
formula	$C_{32}H_{28}FeNOS_4$	$C_{52.75}H_{37.50}Cl_{1.50}FeNOS_4$	$C_{42}H_{38}CoFeNOS_4$
fw	626.64	938.60	815.75
space group	*Pbcn*, No. 60	*C*2/*c* , No. 15	*P*2$_1$, No. 4
a, Å	17.0132(5)	18.7178(4)	8.7605(3)
b, Å	21.5449(6)	23.4237(6)	14.7549(5)
c, Å	16.2040(5)	21.2816(6)	15.0400(6)
β, deg	90	95.555(6)	91.709(4)
V, Å	5939.5(3)	9286.9(4)	1943.21(12)
Z	8	8	2
T, K	100(2)	100(2)	100(2)
ρ_{calcd}, g cm^{-3}	1.402	1.343	1.394
reflns collected/2Θ_{max}	44408/60.00	81627/60.00	32259/63.00
unique reflns/$I > 2\sigma(I)$	8646/7083	13473/12442	12751/12231
no. of params/restraints	359/0	569/7	455/1
λ, Å /μ(Kα), cm^{-1}	0.71073/8.16	0.71073/6.30	0.71073/10.48
R1^a/goodness of fit^b	0.0666/1.202	0.0504/1.052	0.0274/1.044
wR2^c ($I > 2\sigma(I)$)	0.1236	0.1374	0.0631
residual density, e Å^{-3}	+0.80/−0.51	+1.94/−1.49	+0.39/−0.31

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

red in color. After cooling to room temperature, a solution of iron(II) sulfate (4.00 g; 14 mmol) dissolved in water/methanol (1:1 v/v, 30 mL) was added gradually. During additional heating at reflux for 2 h, a black solution formed which was left overnight at 20 °C. The black solid formed was collected by filtration, washed with methanol and diethyl ether, and allowed to air dry.

[Fe(NO)(L$^{1\bullet}$)$_2$](BF$_4$) ([1a](BF$_4$)). To a stirred suspension of dinuclear [Fe$^{III}_2$(L$^{1\bullet}$)$_2$(L^1)$_2$] (**1**) (200 mg; 0.16 mmol) in CH_2Cl_2 (40 mL) was added [NO](BF$_4$) (38 mg; 0.33 mmol) under an Ar blanketing atmosphere. Within 3 h of stirring at 20 °C the color of the green solution turned brown. The solvent was removed by evaporation under reduced pressure, and the resulting brown material was washed with *n*-hexane (3×) and dried under Ar. Yield: 145 mg (60%). ESI mass spectrum (CH_2Cl_2) positive-ion mode: $m/z = 626.1$, calcd for {Fe(NO)(L^1)$_2$}$^+$ 626.6 and negative-ion mode $m/z = 87.2$ (BF$_4$)$^-$. Anal. Calcd for $C_{32}H_{28}NOBF_4S_4Fe$: C, 53.87; H, 3.96; N, 1.96; S, 17.97; Fe, 7.83. Found: C, 53.7; H, 4.1; N, 1.9; S, 17.8; Fe, 7.7.

[Fe(NO)(L$^{1\bullet}$)(L^1)] ([1a]^0). Argon was bubbled through a vigorously stirred suspension of **1** (200 mg; 0.16 mmol) in CH_2Cl_2 (40 mL) for 5 min. Then NO gas was bubbled through the solution for 80−90 s, after which time the flow of Ar was retained for 10 min. The color of the solution turned dark brown. Anhydrous methanol (10 mL) was added, and the reaction volume was reduced to one-half by slow evaporation of the solvent(s) in an Ar stream. After allowing this solution to stand for 3−4 days at 20 °C, black crystals precipitated which were filtered off and dried in air. Yield: 160 mg (77%). Anal. Calcd for $C_{32}H_{28}NOS_4Fe$: C, 61.33; H, 4.50; N, 2.23; S, 20.47; Fe, 8.91. Found: C, 61.6; H, 4.6; N, 2.2; S, 20.3; Fe, 8.8.

[Co(Cp)$_2$][Fe(NO)(L^1)$_2$], ([Co(Cp$_2$)][1a]). To a brown solution of [**1a**]^0 (100 mg; 0.16 mmol) in CH_2Cl_2 (30 mL) under an Ar atmosphere was added [Co(Cp)$_2$] (30 mg; 0.16 mmol) with stirring for 2 h. To the resulting light brown solution was added methanol (15 mL), which was allowed to slowly evaporate in a stream of Ar. Within 3−4 days black crystals separated out which were filtered off and dried under Ar. Yield: ~100 mg (77%). ESI mass spectrum (CH_2Cl_2 solution) negative-ion mode: $m/z = 596.3$, calcd for {Fe(NO)(L^1)$_2$-NO}$^-$ 596.6. Anal. Calcd for $C_{42}H_{38}NOS_4FeCo$: C, 61.84; H, 4.69; N, 1.72; S, 15.72; Fe, 6.85. Found: C, 61.3; H, 5.1; N, 1.6; S, 15.3; Fe, 7.0.

[Co(Cp)$_2$]$_2$[Fe(NO)(L^1)$_2$], ([Co(Cp$_2$)]$_2$[1a]). To a brown solution of [**1a**]^0 (100 mg; 0.16 mmol) in CH_2Cl_2 (30 mL) under an Ar atmosphere was added [Co(Cp)$_2$] (61 mg; 0.32 mmol) with stirring for 1.5 h. A microcrystalline light green solid separated out, which was collected by filtration, dried, and stored under Ar. Yield: 100 mg (62%). Anal. Calcd for $C_{52}H_{48}NOS_4FeCo_2$: C, 62.15; H, 4.81; N, 1.39; S, 12.76; Fe, 6.85. Found: C, 61.8; H, 5.2; N, 1.2; S, 12.5.

[Fe(NO)(L$^{2\bullet}$)(L^2)] ([2a]^0). Through a vigorously stirred suspension of dinuclear **2** (170 mg; 0.1 mmol) in CH_2Cl_2 (40 mL) under Ar was bubbled NO gas for ~90 s, after which time the Ar flow through the solution was continued for 1 h. The color of the solution changed to dark brown. After addition of dry methanol (10 mL) the reaction volume was reduced by one-half by evaporation of the solvent(s) in a stream of Ar. Within 2−3 days at 20 °C black crystals separated out which were collected by filtration and air dried. Yield: 150 mg (85%). ESI-mass spectrum (CH_2Cl_2): positive-ion mode, $m/z = 874.7$ and 844, calcd for the [Fe(NO)(L^2)$_2$]$^+$ ion is 874.9 and the [Fe(L^2)$_2$]$^+$ ion 844.9. Anal. Calcd for $C_{52}H_{36}NOS_4Fe$: C, 71.38; H, 4.15; N, 2.60; S, 14.66; Fe, 6.38. Found: C, 70.8; H, 4.4; N, 2.4; S, 15.1; Fe, 5.9.

X-ray Crystallographic Data Collection and Refinement of the Structures. Dark brown single crystals of [**1a**], [**2a**]·0.75 CH_2Cl_2, and [Co(Cp)$_2$][**1a**] were coated with perfluoropolyether, picked up with nylon loops, and immediately mounted in the nitrogen cold stream of the diffractometer to prevent loss of solvent. A Nonius Kappa-CCD diffractometer equipped with a Mo-target rotating-anode X-ray source and a graphite monochromator (Mo Kα, $\lambda = 0.71073$ Å) was used. Final cell constants were obtained from least-squares fits of all measured reflections. Intensity data of [**1a**] and [**2a**] were corrected for absorption using intensities of redundant reflections, but in the case of [Co(Cp)$_2$][**1a**] crystal faces were determined and a Gaussian absorption correction was performed.

The structures were readily solved by direct methods and subsequent difference Fourier techniques. The Siemens ShelXTL[13] software package was used for solution and artwork of the structure; ShelXL97[14] was used for refinement. All non-hydrogen atoms were refined anisotropically. 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.

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(13) *ShelXTL*, V.5; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1994.

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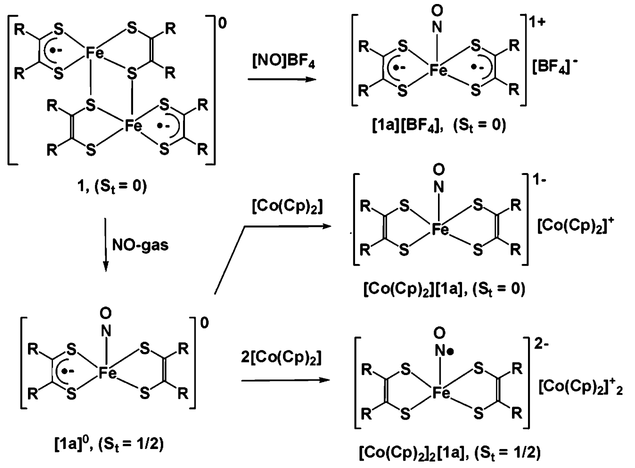
Scheme 1



Two dichloromethane solvent molecules in compound [**2a**] were found not to be fully occupied and to be disordered next to a crystallographic 2-fold axis. Split positions with occupation factors of 0.53 and 0.22 were refined to give a satisfactory disorder model. Thermal displacement parameters and C−Cl and Cl−Cl distances were restrained to be equal within errors using EADP and SADI instructions of ShelXL97.

Physical Measurements. X-band EPR spectra were recorded on a Bruker ELEXSYS E500 spectrometer equipped with a helium flow cryostat (Oxford Instruments ESR 910) and Hewlett-Packard frequency counter HP5253B. The spectra taken from frozen solutions were simulated by using a powder routine for spin $S = 1/2$ with anisotropic g values and Gaussian line widths.

Mössbauer data were recorded on an alternating constant-acceleration spectrometer. The minimum experimental line width was 0.24 mm s^{-1} (full width at half-height). The sample temperature was maintained constant in an Oxford Instruments VARIOX cryostat. Isomer shifts are quoted relative to iron metal at 300 K.

Magnetic susceptibilities of solid complexes were measured in the temperature range 1.5−300 K using a SQUID susceptometer (MPMS Quantum Design) with an external field of 1.0 T. Multiple-field variable-temperature measurements were done at three different fields for which the magnetization was equidistantly sampled on a $1/T$ temperature scale. Experimental data were corrected for underlying diamagnetism by use of tabulated Pascal's constants. The susceptibility and magnetization data were simulated with our own spin Hamiltonian routine for exchange-coupled systems.

Electrochemistry and Spectroelectrochemistry. In all experiments potential control was achieved using an EG&G Potentiostat/Galvanostat (model 273A) and M270 software, and solutions of the complexes in CH_2Cl_2 containing 0.2 M $[(n\text{-Bu})_4N]PF_6$ as supporting electrolyte were employed throughout. Cyclic voltammograms (CV) were recorded using a conventional three-electrode arrangement consisting of a glassy carbon working electrode (2 mm diameter), an Ag/Ag^+ (0.01 M $AgNO_3$) reference electrode, and a Pt wire counter electrode. Small amounts of ferrocene were added as an internal standard after completion of an experiment, and potentials are referenced versus the ferrocenium/ferrocene (Fc^+/Fc) couple.

Controlled potential electrolysis at appropriate fixed potentials was performed at −25 °C in a jacketed quartz cuvette with the same type of reference electrode, a Pt mesh working electrode, and a Pt brush counter electrode. The cuvette (optical path length 0.5 cm) was mounted directly in a spectrophotometer (Hewlett-Packard HP 8453) and allowed recording of UV−vis spectra in situ during electrolysis. After completion of electrolysis, samples of the electrolyzed solutions were taken and rapidly frozen for EPR analysis.

Table 2. ν(NO) Stretching Frequency of Complexes in the Infrared

complex	ν_{NO}, cm^{-1} [a] (KBr disk)
[**1a**](BF_4)	1833 (1760)
[**1a**]	1800,1783 (1725)
$[Co(Cp)_2]$[**1a**]	1758 (1693)
$[Co(Cp)_2]_2$[**1a**]	1575,1530(<1500)
$[N(n\text{-Bu})_4][FeNO(bdt)_2]$	1800
$[N(n\text{-Bu})_4][Co(Cp)_2][FeNO(bdt)_2]$	1600
[**2a**]	1791
[**3a**]	1764
$[Et_4N]$[**4a**]	1775
$[PPh_4]$[**5a**][b]	1814
$[PPh_4]_2$[**5a**][b]	1633

[a] Values in parentheses are for the corresponding $^{15}N^{18}O$ isotopomer. [b] Reference 2.

Infrared spectra of oxidized and reduced species were measured by performing electrolysis (at −25 °C) in a temperature-controlled optically transparent thin layer electrode (OTTLE; $d = 0.18$ mm) equipped with a platinum grid working electrode. The OTTLE was mounted in an FT infrared spectrophotometer (Perkin-Elmer, system 2000) monitoring the infrared spectral changes directly during electrolysis.

Results

Syntheses of Complexes. All mononuclear complexes of the present study have been prepared according to literature methods[2,3] as shown in Scheme 1 using the dinuclear complexes **1**− **4** as starting materials. Dinuclear species **1** has recently been described in detail by us.[10] By analogy with our studies of complex **1**, we suggest that the neutral species **2**−**4** also possess terminal radical monoanions $(L^\bullet)^{1-}$ and two bridging closed-shell dianions $(L)^{2-}$, where $(L)^{2-}$ and $(L^\bullet)^{1-}$ represent 1,2-diaryl-based ligands $[S_2C_2Ar_2]^{2-/1-}$ and its *cis*-1,2-dicyanoethene-1,2-dithiolate dianion $(mnt)^{2-}$ or the $(mnt^\bullet)^{1-}$ radical monoanion. The central ferric iron atoms possess an intrinsic intermediate spin state ($S = 3/2$). These two metal ions are intramolecularly antiferromagnetically coupled, yielding an overall diamagnetic ground state ($S_t = 0$).[10]

As shown in Scheme 1 oxidation of **1** with two equivalents of $[NO]BF_4$ in CH_2Cl_2 yields the monocation $[Fe(NO)(L^{1\bullet})_2]^+$, $[\mathbf{1a}]^+$, which has been isolated as a brown BF_4^- salt. The salt is diamagnetic ($S = 0$) and displays an intense ν_{NO} stretching frequency (Table 2) at 1833 cm^{-1} which is typical for an $\{FeNO\}^6$ moiety consisting of a low-spin ferrous ion (d^6, $S_{Fe} = 0$) and an NO^+ ligand coordinated linearly to the iron ion[15] which is bound to two radical monoanions $(L^{1\bullet})^{1-}$: $[Fe^{II}(NO^+)(L^{1\bullet})_2]^+$ ($S = 0$). This monocation represents the most oxidized member of the electron-transfer series (z = 1+, 0, 1−, 2−).

Interestingly, reaction of **1** with NO gas in CH_2Cl_2 solution produces black microcrystals of the neutral, paramagnetic complex $[Fe(NO)(L^\bullet)(L)]^0$ [**1a**] with $S = 1/2$. In the solid

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[15] (a) Hauser, C.; Glaser, T.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2000**, *122*, 4352. (b) Serres, R. C.; Grapperhaus, C. A.; Bothe, E.; Bill, E.; Weyhermüller, T.; Neese, F.; Wieghardt, K. *J. Am. Chem. Soc.* **2004**, *126*, 5138.

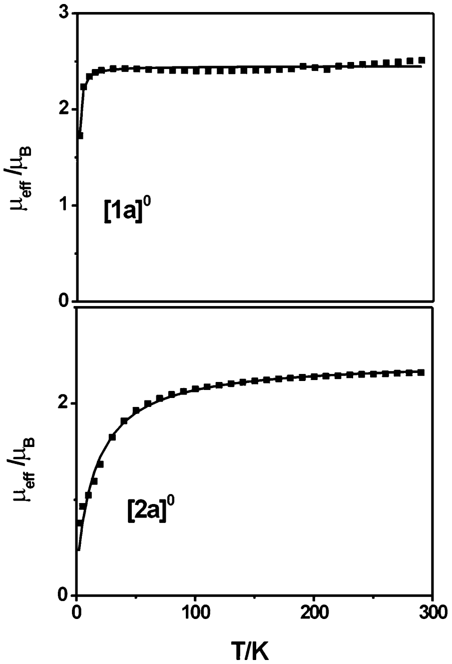

Figure 1. Temperature dependence of the magnetic moments of solid samples of $[\mathbf{1a}]^0$ (top) and $[\mathbf{2a}]^0$ (bottom). The solid lines represent best fits using a model of two interacting monomers with $S_1 = S_2 = 1/2$, $H = -2JS_1S_2$. Parameters are as follows: [**1a**] $J = -1.1$ cm^{-1}, $g_1 = g_2 = 2.0$ (fixed) and [**2a**] $J = -15$ cm^{-1} and a Weiss constant θ of -10 K, $g_1 = g_2 = 2.0$ (fixed).

state (KBr disk) it displays two ν_{NO} stretches at 1800 and 1783 cm^{-1}, indicating again the presence of an $\{FeNO\}^6$ moiety. Thus, one-electron reduction of $[\mathbf{1a}]^+$ is a ligand-based process $(L^{1\bullet})^{1-} + e \rightarrow (L^1)^{2-}$. The corresponding neutral complex [**2a**] has also been isolated as a solid. Both [**1a**] and [**2a**] are paramagnetic with an $S = 1/2$ ground state.

Figure 1 exhibits the temperature-dependent magnetic moments of solid samples of [**1a**] and [**2a**]. The solid lines represent best fits which were obtained using a model where the paramagnetic molecules are packed pairwise (see below) with an antiferromagnetic spin exchange coupling between two $S = 1/2$ molecules: for [**1a**] a very small antiferromagnetic coupling constant, J, of -1.1 cm^{-1} ($H = -2JS_1S_2$; $S_1 = S_2 = 1/2$; $g = 2.0$ (fixed)) has been obtained, whereas this coupling constant is -15 cm^{-1} for [**2a**] (an additional Weiss constant of $\theta = -10$ K had to be included for a good fit). We realize that this does not represent a physically correct model for the magnetism of [**2a**], but it does show a stronger antiferromagnetic coupling in [**2a**] than in [**1a**].

Reaction of neutral [**1a**] with one and two equivalents of cobaltocene, $[Co(Cp)_2]$, in CH_2Cl_2 under strictly anaerobic conditions produces the black salts $[Co(Cp)_2][Fe(NO)(L^1)_2]$ ($[Co(Cp)_2]$[**1a**]) and green $[Co(Cp)_2]_2[Fe(NO)(L^1)_2]$ ($[Co(Cp)_2]_2$[**1a**]), respectively. Interestingly, the ν_{NO} stretching frequencies of the mono- and dianion are observed at 1758 and 1575 cm^{-1}, respectively. This large difference of 183 cm^{-1} is a clear indication that the $\{FeNO\}^6$ moiety in the monoanion $[\mathbf{1a}]^{1-}$ is reduced to the $\{FeNO\}^7$ unit in the dianion $[\mathbf{1a}]^{2-}$.[2,3] Note that ν_{NO} varies from 1833 cm^{-1} in $[\mathbf{1a}]^{1+}$ to ~1800 cm^{-1} in $[\mathbf{1a}]^0$ and to 1758 cm^{-1} in $[\mathbf{1a}]^{1-}$, which represents ~35 cm^{-1} per one-electron reduction step, indicating that the $\{FeNO\}^6$ moiety is retained throughout the three species. $[Co(Cp)_2]_2$[**1a**] is paramagnetic with an $S = 1/2$ ground state (see below).

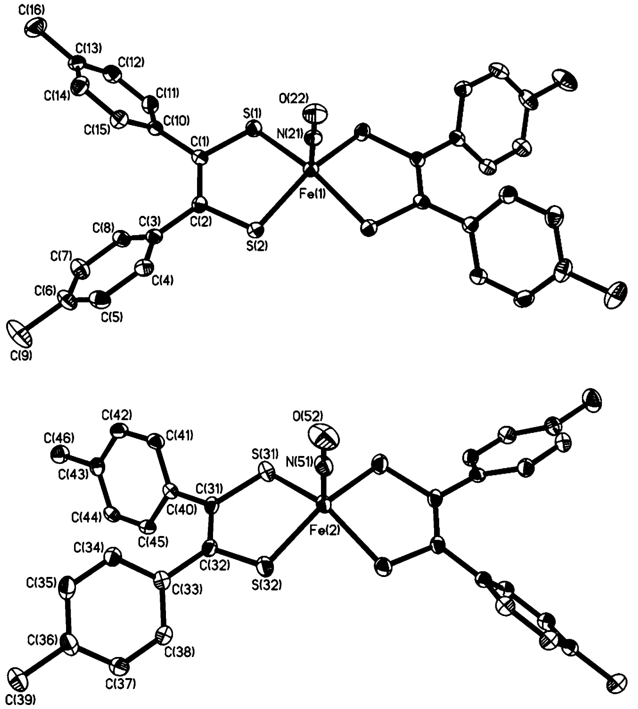

Figure 2. Structure of the two independent neutral molecules in crystals of $[\mathbf{1a}]^0$.

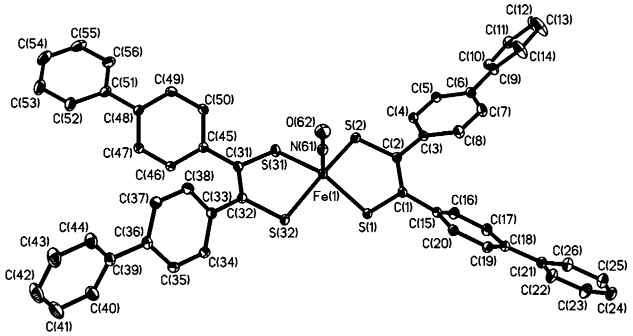

Figure 3. Structure of the neutral molecule in crystals of [**2a**].

Thus, it has been possible for the first time to isolate four members of a single five-coordinate iron nitrosyl dithiolene electron-transfer series $[Fe(NO)(L^1)_2]^z$ ($z = 1+, 0, 1-, 2-$).

The following complexes have been synthesized according to literature procedures: $[Fe(NO)(L^{3\bullet})(L^3)]$ ($[\mathbf{3a}]^0$),[3] $[Et_4N][FeNO)(L^4)_2]$ ($[Et_4N]$[**4a**]),[2] and $[NEt_4][Fe(NO)(mnt)_2]$ ($[NEt_4]$[**5a**]).[2] The neutral complex $[\mathbf{3a}]^0$ is again paramagnetic ($S = 1/2$), whereas complexes containing the monoanions $[\mathbf{4a}]^{1-}$ and $[\mathbf{5a}]^{1-}$ are both diamagnetic. Their NO stretching frequencies are given in Table 2. Notably, irrespective of the charge (neutral or monoanion), the similarity of their ν_{NO} stretching frequencies again indicates the presence of the same $\{FeNO\}^6$ moiety.

X-ray Structures. The structures of complexes $[\mathbf{1a}]^0$, $[\mathbf{2a}]^0 \cdot 0.75\ CH_2Cl_2$, and $[Co(Cp)_2]$[**1a**] have been determined by X-ray crystallography at 100(2) K. Figures 2 and 3 display the structures of the neutral molecules in crystals of [**1a**] and [**2a**], respectively, whereas that of the monoanion and

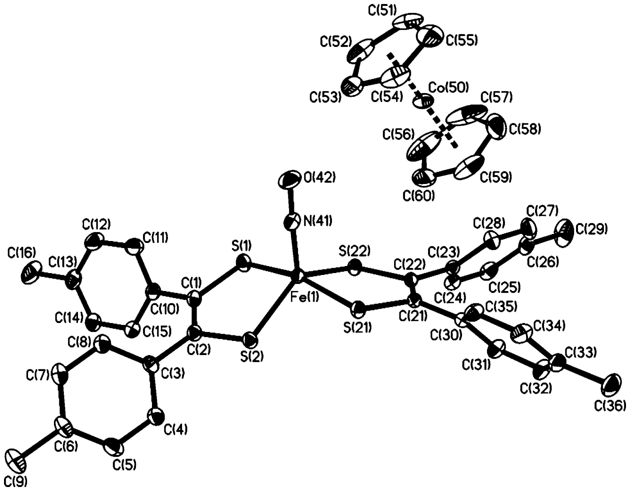

Figure 4. Structure of the monocation $[Co(Cp)_2]^+$ and monoanion $[\mathbf{1a}]^{1-}$ in crystals of $Co(Cp)_2$ [**1a**].

Table 3. Selected Bond Distances (Å)

	[**1a**][a]		
Fe1−N21	1.636(3)	S1−C1	1.703(3)
Fe1−S1	2.2118(7)	S2−C2	1.711(3)
Fe1−S2	2.2039(7)	C1−C2	1.387(4)
N21−O22	1.164(4)		
Fe2−N51	1.641(3)	S31−C31	1.705(3)
Fe2−S31	2.2090(8)	S32−C32	1.708(3)
Fe2−S32	2.2172(8)	C31−C32	1.390(4)
N51−O52	1.158(5)		
	[**2a**]		
Fe1−N61	1.6430(2)	S1−C1	1.714(2)
Fe1−S1	2.1902(5)	S2−C2	1.712(2)
Fe1−S2	2.2068(5)	C1−C2	1.397(3)
Fe1−S31	2.2099(5)	S31−C31	1.715(2)
Fe1−S32	2.2549(5)	S32−C32	1.718(2)
N61−O62	1.163(2)	C31−C32	1.401(3)
	$[Co(Cp)_2]$[**1a**]		
Fe1−N41	1.624(1)	N41−O42	1.176(2)
Fe1−S1	2.2335(4)	S1−C2	1.734(2)
Fe1−S2	2.2186(4)	S2−C2	1.743(2)
Fe1−S21	2.2504(4)	C1−C2	1.374(2)
Fe1−S22	2.2148(4)	S21−C21	1.752(2)
S22−C22	1.755(2)	C21−C22	1.361(3)

[a] Data for both crystallographically independent molecules are given.

cation in crystals of $[Co(Cp)_2]$[**1a**] are shown in Figure 4. Table 3 summarizes important bond distances.

Complex $[\mathbf{2a}]^0$ crystallizes in an orthorhombic space group containing two crystallographic independent molecules in the unit cell. The conformations of the four *p*-tolyl groups differ slightly in both molecules, but the geometrical features of both $Fe(NO)(S_2C_2)_2$ parts are within experimental error identical.

Crystals of $[\mathbf{1a}]^0$ and $[\mathbf{2a}]^0$ consist of mononuclear, neutral five-coordinate nitrosyliron species, $[Fe(NO)(S_2C_2R_2)_2]$, where R = *p*-tolyl in [**1a**] and 4,4-diphenyl in [**2a**]. The nitrosyl group is coordinated in the apical position of a square-based pyramidal FeS_4N coordination polyhedron; the two bidentate dithiolate ligands occupy the four basal sites. The Fe−NO groups are linear in both cases (180° for both conformers in [**1a**] and 178.7(2)° in [**2a**]). The central iron ion lies ~0.50 Å above the best plane of the four sulfur donor atoms.

As shown in Figure 5, two neutral molecules are packed in the solid state in [**1a**] in such a way that the two basal S_4 planes roughly face each other, giving rise to four weak S···S interactions. These S···S distances are for S2···S32A and S2A···S32 at 3.728 Å and for S1···S31 and S1A···S31A at 3.705 Å. These interactions may provide a pathway for the observed very weak antiferromagnetic spin exchange coupling ($J = -1.1$ cm^{-1}) in solid [**1a**].

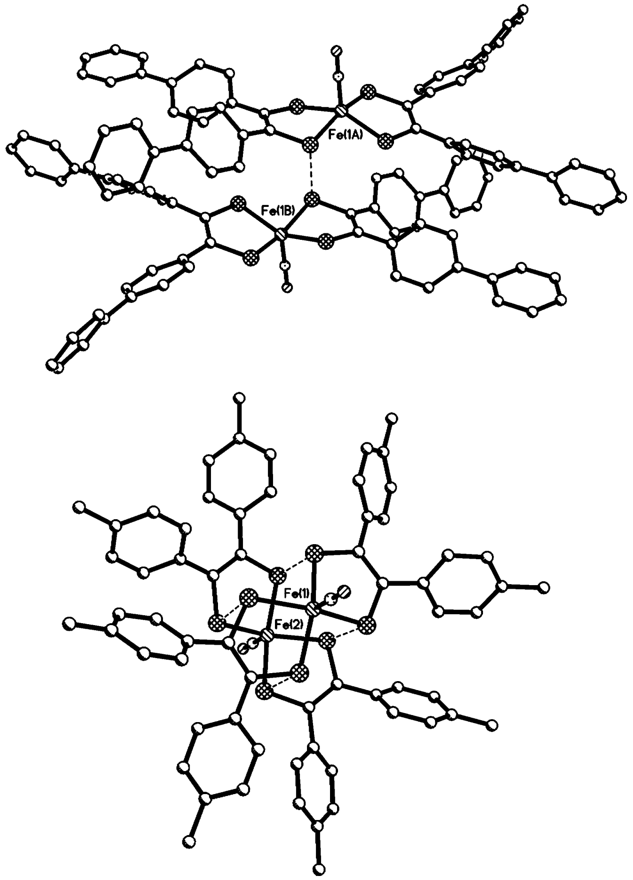

Figure 5. Schematic packing diagram of two neutral molecules in [**2a**] (top) and [**1a**] (bottom). The dotted lines indicate the shortest S···S contacts (see text).

Interestingly, in solid [**2a**] the neutral molecules also pack pairwise (Figure 5) but in a slightly different fashion. Only one shorter S···S distance at 3.619 Å is observed between S32A and S32B of two different molecules. No other S···S interactions are present. This relatively shorter interaction may account for the observed stronger intermolecular antiferromagnetic coupling in [**2a**].

The geometrical features of the Fe(NO) moiety in [**1a**] and [**2a**] are very similar to those reported for many five- or six-coordinate nitrosyliron complexes containing an $\{FeNO\}^6$ moiety.[18] The $\{FeNO\}^6$ unit is diamagnetic and has been described from DFT calculations[15b,16,19] as consisting of a

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(16) Li, M.; Bonnet, D.; Bill, E.; Neese, F.; Weyhermüller, T.; Blum, N.; Sellmann, D.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 3444.

(17) Sellmann, D.; Blum, N.; Heinemann, F.; Hess, B. A. *Chem. Eur. J.* **2000**, *7*, 1874.

(18) López, J. P.; Heinemann, F. W.; Prakash, R.; Hess, B. A.; Horner, O.; Jeandey, C.; Oddou, J.-L.; Latour, J.-M.; Grohmann, A. *Chem. Eur. J.* **2002**, *8*, 5709.

(19) (a) Gonzales, M. C.; Scherlis, D. A.; Esiú, G. L.; Olabe, J. A.; Estrin, D. A. *Inorg. Chem.* **2001**, *40*, 4127. (b) Wanner, M.; Scheiring, T.; Kaim, W.; Slep, L. D.; Baraldo, L. M.; Olabe, J. A.; Zalis, S.; Baerends, E. J. *Inorg. Chem.* **2001**, *40*, 5704.

low-spin ferrous ion ($S_{Fe} = 0$, d^6) and an NO^+ ligand. Thus, the $\{FeNO\}^6$ unit carries a 3+ charge which requires the two dithiolene ligands to adopt two different oxidation levels: one closed-shell dianion, $[S_2C_2R_2]^{2-}$, and a π-radical monoanion, $[S_2C_2R_2]^{1-\bullet}$. The average C−S distances in [**1a**] and [**2a**] are short at 1.71 Å, and concomitantly, the average "olefinic" C−C is long at 1.39 Å. These parameters are in agreement with the presence of one radical and one closed-shell ligand in $[\mathbf{1a}]^0$ and $[\mathbf{2a}]^0$, respectively.[20,21] The bond lengths are not in agreement with the presence of two closed-shell dianons.[21] In principle, the following three formal electron distributions may be considered for the neutral species $[Fe(NO)(S_2C_2R_2)]_2]^0$: $[\{FeNO\}^7(L^\bullet)_2]$, $[\{FeNO\}^6(L^\bullet)(L)]$, and $[\{FeNO\}^5(L)_2]$.

It is conceivable that the proposed chelating ligand mixed valency in the $\{FeNO\}^6$ case is of class III (delocalized), giving thus rise to two equivalent ligands as observed in $[\mathbf{1a}]^0$ and $[\mathbf{2a}]^0$. Since an $\{FeNO\}^5$ species has to the best of our knowledge not been characterized to date, the crystallography suggests an electronic structure for the neutral complexes $[\mathbf{1a}]^0$ and $[\mathbf{2a}]^0$ as $[Fe^{II}(NO^+)(L^\bullet)(L)]^0 \leftrightarrow [Fe^{II}(NO^+)(L)(L^\bullet)]^0$.

Reduction of [**1a**] produces the monoanion $[Fe(NO)(L^1)_2]^-$, the structure of which is shown in Figure 4 together with its $[Co(Cp)_2]^+$ cation in crystals of $[Co(Cp)_2]$ [**1a**]. Overall the structure of this anion is very similar to that of its neutral counterpart [**1a**]. The geometric details of the Fe−NO moiety in [**1a**] and $[\mathbf{1a}]^-$ are within experimental error identical, but the average C−S bond length at 1.75 Å and the av. "olefinic" C−C bond at 1.36 Å in $[\mathbf{1a}]^-$ have increased and decreased, respectively, in comparison with the same bonds in neutral [**1a**]. This is a clear indication that reduction of [**1a**] involves only the dithiolene ligands in $[\mathbf{1a}]^-$. Thus, the metrical details in $[\mathbf{1a}]^-$ suggest an electronic structure as in $[Fe^{II}(NO^+)(L^1)_2]^-$.

Electro- and Spectroelectrochemistry. It was shown in 1967 by electrochemistry that the present nitrosyliron complexes exist within a five-membered electron-transfer chain,[1−3] corresponding to $[Fe(NO)(S_2C_2R_2)_2]^z$, where z can be −3, −2, −1, 0, 1+. No single system permitted detection and/or isolation of all five species. It was shown that the $(mnt)^{n-}$ and perfluoromethyl ligands ($S_2C_2R_2$; R = CN or CF_3) stabilize the more reduced species, giving access to the trianions but not to the monocations, whereas the diaryl-based ligands, (L^{1-4}), facilitate formation of the more highly oxidized species, giving access to monocations but not trianions.[2,3]

We studied complexes [**1a**]−[**5a**] by cyclic and square-wave voltammetry in CH_2Cl_2 solutions containing 0.10 M $[N(n\text{-}Bu)_4]PF_6$ as supporting electrolyte at 20 °C at a glassy carbon working electrode. All potentials are referenced vs the ferrocenium/ferrocene (Fc^+/Fc) couple (internal standard).

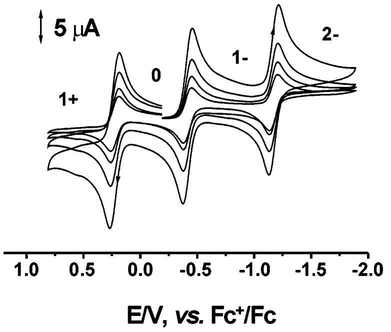

Figure 6. Cyclic voltammogram of [**2a**] in CH_2Cl_2 at 20 °C (0.20 M $[N(n\text{-}Bu)_4]PF_6$) supporting electrolyte; glassy carbon working electrode; scan rates 50, 100, 200, and 400 mV s^{-1}).

Table 4. Redox Potentials of Complexes[a)] Determined by Cyclic and Square Wave Voltammetry at 20 °C

complex	$E^1_{1/2}$, V/(1+/0)[b]	$E^2_{1/2}$, V (0/1−)	$E^3_{1/2}$, V (1−/2−)	$E^4_{1/2}$, V (2−/3−)
[**1a**]	0.17	−0.44	−1.22	n.o.
[**2a**]	0.22	−0.41	−1.17	n.o.
[**3a**]	0.17	−0.46	−1.21	n.o.
[**4a**]	0.26	−0.42	−1.21	n.o.
[**5a**]	n.o.	+0.65	−0.38	−1.83 (q.r.)

[a] Conditions: CH_2Cl_2 solution (0.20 M $[N(n\text{-}Bu)_4]PF_6$) at 20 °C, scan rate 200 mV s^{-1}, glassy carbon working electrode. [b] All redox potentials are referenced vs the ferrocenium/ferrocene couple (Fc^+/Fc); n.o. = not observed to −2.0 V vs Fc^+/Fc; q.r. = quasi reversible.

Figure 6 shows the cyclic voltammogram of [**2a**]; Table 4 summarizes the redox potentials.

In each case three reversible one-electron-transfer waves are observed. From coulometric measurements at appropriately fixed potentials it was established that the neutral complexes [**1a**]−[**4a**] undergo a reversible one-electron oxidation generating a monocation and two successive one-electron reductions with successive formation of a mono- and a dianion as shown in eq 1

$$[\mathbf{1a}]^{+} \underset{E^{1}_{1/2}}{\underset{+e}{\overset{-e}{\rightleftharpoons}}} [\mathbf{1a}] \underset{E^{2}_{1/2}}{\underset{+e}{\overset{-e}{\rightleftharpoons}}} [\mathbf{1a}]^{1-} \underset{E^{3}_{1/2}}{\underset{+e}{\overset{-e}{\rightleftharpoons}}} [\mathbf{1a}]^{2-} \qquad (1)$$

For $[Fe(NO)(mnt)_2]^-$ ($[\mathbf{5a}]^-$) it was shown that a di- and trianion are accessible via two successive one-electron reduction steps and a neutral species via a one-electron oxidation, eq 2, but no monocation could be detected

$$[\mathbf{5a}]^{0} \underset{+e}{\overset{-e}{\rightleftharpoons}} [\mathbf{5a}]^{1-} \underset{+e}{\overset{-e}{\rightleftharpoons}} [\mathbf{5a}]^{2-} \underset{+e}{\overset{-e}{\rightleftharpoons}} [\mathbf{5a}]^{3-} \qquad (2)$$

Since all four diaryl-based species of each electron-transfer series are stable in solution, their solution infrared spectra have been recorded in the range 1500−1900 cm^{-1} where the NO stretching band is generally observed. The $^{15}N^{18}O$ isotopomers have also been prepared, and their IR solution spectra have also been recorded. The results are shown in Figure 7 for the series $[\mathbf{1a}]^z$ (z = 1+, 0, 1−, 2−).

Table 2 gives the NO stretching frequencies of all isolated complexes (KBr disks). Interestingly, ν_{NO} decreases from 1838 cm^{-1} for the monocation $[\mathbf{1a}]^+$, to 1800 cm^{-1} in the neutral complex $[\mathbf{1a}]^0$, and then to 1765 cm^{-1} in the

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[20] Patra, A.; Bill, E.; Bothe, E.; Chlopek, K.; Neese, F.; Weyhermüller, T.; Stobie, K.; Ward, M. D.; McCleverty, J. A.; Wieghardt, K. *Inorg. Chem.* **2006**, *45*, 7877.

[21] The av. C−S and C−C bond lengths in $[Au^{III}(L)_2]^-$ are 1.77 and 1.36 Å, respectively, where $(L)^{2-}$ is 1,2-di(4-*tert*-butylphenyl)ethylene-1,2-dithiolate(2−), see: Kokatam, S.; Ray, K.; Pap, J.; Bill, E.; Geiger, W. E.; LeSuer, R. J.; Rieger, P. H.; Weyhermüller, T.; Neese, F.; Wieghardt, K. *Inorg. Chem.*, in press.

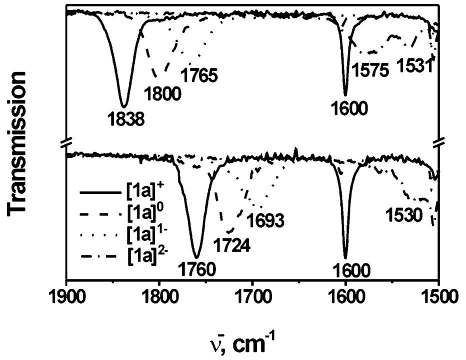

Figure 7. Observed infrared spectra changes during the electrochemical oxidation of $[\mathbf{1a}]^0$ to $[\mathbf{1a}]^+$ and reductions of $[\mathbf{1a}]$ to $[\mathbf{1a}]^{1-}$ and $[\mathbf{1a}]^{2-}$ at −25 °C in CH_2Cl_2 (0.10 M $[N(n\text{-}Bu)_4]PF_6$) (top) and its corresponding $^{15}N^{18}O$-labeled isotopomers (bottom).

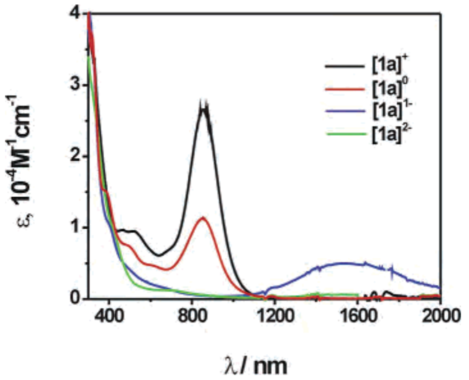

Figure 8. Spectroelectrochemistry of $[\mathbf{1a}]^0$ showing the electronic spectra of electrochemically generated $[\mathbf{1a}]^+$, $[\mathbf{1a}]^{1-}$, and $[\mathbf{1a}]^{2-}$ and of $[\mathbf{1a}]^0$ in CH_2Cl_2 solution (0.20 M $[N(n\text{-}Bu)_4]PF_6$) at −25 °C.

monoanion $[\mathbf{1a}]^{1-}$, i.e., a decrease of only ~35 cm^{-1} per one-electron reduction. In stark contrast, further reduction of the monoanion $[\mathbf{1a}]^{1-}$ to the corresponding dianion $[\mathbf{1a}]^{2-}$ induces a shift of ~190 cm^{-1} (from 1765 cm^{-1} in $[\mathbf{1a}]^{1-}$ to 1575 cm^{-1} in $[\mathbf{1a}]^{2-}$). It is noteworthy that the observed bands at 1600 cm^{-1} in the monocation and at 1531 cm^{-1} in the dianion do not involve the Fe−NO moiety since no shift of the bands is observed in the corresponding $^{15}N^{18}O$ isotopomers. Typically, ν_{NO} is shifted by ~75 cm^{-1} to lower energy in the $^{15}N^{18}O$ isotopomers. These results indicate that a $\{Fe{-}NO\}^6$ moiety prevails in the diamagnetic monocation, paramagnetic neutral species, and monoanion. Only in the dianion does an $\{FeNO\}^7$ moiety appear to be present. In the trianion $[Fe(NO)(mnt)_2]^{3-}$ an $\{FeNO\}^8$ moiety may be present. However, we have no data at present to support this notion, but in $[Fe(NO)(cyclam\text{-}ac)]^0$ which contains an $\{FeNO)\}^8$ moiety ν_{NO} has been observed at 1271 cm^{-1}.[15b]

We also recorded the electronic spectra of $[\mathbf{1a}]^0$ and the electrochemically generated species $[\mathbf{1a}]^+$, $[\mathbf{1a}]^{1-}$, and $[\mathbf{1a}]^{2-}$ in the range 250−2000 nm, and these are displayed in Figure 8. Table 5 summarizes the spectra of the other complexes.

Table 5. Electronic Spectra of Electrochemically Generated Complexes in CH_2Cl_2 Solution (0.10 M $[N(n\text{-}Bu)_4]PF_6$) at 25 °C

complex	z	λ_{max}, nm ($10^4\,\epsilon$, $M^{-1}\,cm^{-1}$)
$[\mathbf{1a}]^z$	2−	316(sh,3.0), 420(1.0), 710(0.12)
	1−	310(3.7), 410(sh,1.0), 678(0.12), 1560(0.6)
	0	384(1.5), 490(0.7), 607(0.5), 855(1.1)
	1+	460(1.0), 523(1.0), 858(2.7)
$[\mathbf{2a}]^z$	2−	421(sh,2.0), 500(sh,1.0), 709(0.17)
	1−	406(sh,1.8), 675(0.2), 1560(0.6)
	0	402(1.7), 507(0.9), 630(0.5), 873(1.4)
	1+	376(sh,3.0), 486(1.0), 596(1.2), 903(3.0)
$[\mathbf{3a}]^z$	2−	275(6.4)
	1−	383(sh), 1005(0.2)
	0	386(sh), 671(sh), 926(0.6)
	1+	382(sh), 465(sh), 593(0.6), 954(1.7)
$[\mathbf{4a}]^z$	2−	325(sh), 418(2.2)
	1−	309(6.6), 389(sh), 638(sh), 1510(0.7)
	0	306(6.8), 375(sh), 490(sh), 590(sh), 822(1.8)
	1+	486(sh), 806(3.4)
$[\mathbf{5a}]^z$	3−	383(1.2), 533(0.1)
	2−	319(2.2), 418(0.1)
	1−	435(sh), 1363(0.4)
	0	295(2.6), 456(0.4), 752(0.2)

It is remarkable that the spectra of the monocations, $[\mathbf{1a}]^+$−$[\mathbf{4a}]^+$, are so very similar. In each case a very intense absorption maximum at ~850 nm ($\epsilon \approx 2.5 \times 10^4$ $M^{-1}\,cm^{-1}$) is observed which we assign to a ligand-to-ligand charge-transfer band (LLCT) of a nearly planar $(L^\bullet)Fe^{II}(L^\bullet)$ unit. Such LLCT bands have been observed in the spectra of planar $[M^{II}(L^\bullet)_2]^0$ (M = Ni, Pd, Pt) complexes[22] and $[Fe^{II}(CN)(L^\bullet)_2]$;$^{1-}$[20] $(L^{6\bullet})^{1-}$ representing the 1,2-di(4-*tert*-butylbutylphenyl)-1,2-ethylenedithiolate(1−) radical and $(L^\bullet)^{1-}$ any dithiolato radical anion. Since the latter complexes do not contain a M−NO moiety, the presence of this transition is an excellent marker for the $Fe^{II}(L^{1\bullet})_2$ unit. Thus, the infrared and electronic spectra of the monocations indicate that the electronic structure is probably best described as $[Fe^{II}(NO^+)(L^\bullet)_2]^{1+}$.

The electronic spectra of the neutral species $[\mathbf{1a}]$−$[\mathbf{5a}]$ are also very similar: an intense absorption maximum in the range 750−930 nm ($\epsilon \approx 10^4$ M^{-1} cm^{-1}) is again observed, although it is noted that its intensity is approximately only one-half of that observed for the similar CT band of the monocations. This transition is likely to be an intervalence charge-transfer band (IVCT) of a planar $M(L)(L^\bullet)$ unit which has also been reported for all planar $[M^{II}(L)(L^\bullet)]^{1-}$ (M = Ni, Pd, Pt) species.[22] Thus, we propose an electronic structure $[Fe^{II}(NO^+)(L^\bullet)(L)]^0 \leftrightarrow [Fe^{II}(NO^+)(L)(L^\bullet)]^0$ ($S = 1/2$) for the neutral complexes. The ligand mixed valency may be of class III type (delocalized).

The monoanionic complexes display a weak charge-transfer band at >1200 nm ($\epsilon \approx 5000$ M^{-1} cm^{-1}) but no LLCT or IVCT band in the range 750−950 nm. Therefore, it is concluded that reduction of the neutral species to the corresponding monoanions is ligand-based involving reduction of the radical $(L^\bullet)^{1-}$ monoanion to the closed-shell dianion $(L)^{2-}$: $[Fe^{II}(NO^+)(L)_2]^{1-}$ ($S = 0$).

Finally, reduction of the mono- to dianions involves the process $\{FeNO\}^6 \rightarrow \{FeNO\}^7$ which is NO based.[16−19] This implies that the coordinated cation (NO^+) ($S = 0$) is reduced to a coordinated neutral $(NO)^\bullet$ ($S = 1/2$). This process is accompanied by a dramatic decrease in the NO stretching frequency (Table 2) but does not bring about a dramatic change in the electronic spectrum with the exception that the CT band in the near-infrared at ~1200 nm is no longer

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(22) Ray, K.; Weyhermüller, T.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2005**, *44*, 5345.

Table 6. X-Band EPR Spectra of Complexes in Frozen CH_2Cl_2 Solutions at 30 K

complex	g_x	g_y	g_z	A_{xx}, (^{14}N)[a]	A_{yy}, (^{14}N)[a]	A_{zz}, (^{14}N)[a]
[**1a**]^0	2.0224	2.0127	1.999	n.o.	n.o.	n.o.
[**2a**]^0	2.0230	2.0130	2.000	n.o.	n.o.	n.o.
[**3a**]^0	2.019	2.010	1.997	n.o.	n.o.	n.o.
[**4a**]^0	2.020	2.010	1.997	n.o.	n.o.	n.o.
[**1a**]$^{2-}$	2.0496	2.0297	2.0097	0.0	14.4	15.6
[**2a**]$^{2-}$	2.0512	2.0296	2.0102	0.0	14.2	14.7
[**5a**]$^{2-}$ [b]	2.060	2.028	2.005	13.9	15.4	15.8

[a] Nitrogen hyperfine coupling constants ($\times 10^4$ cm^{-1}). [b] Reference 24; n.o. = not observed.

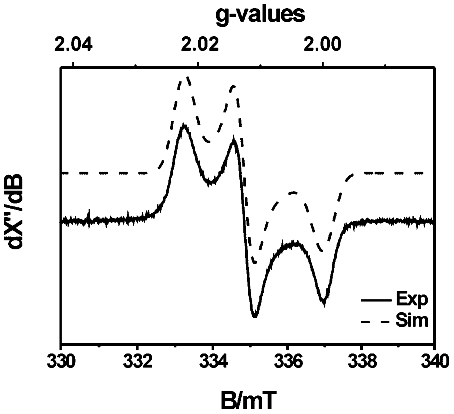

Figure 9. X-Band EPR spectrum of [**1a**]^0 in frozen CH_2Cl_2 at 20 K. Conditions: $\nu = 9.43$ GHz; power 1.0×10^{-5} mW, modulation 3.0 G. g values are given in Table 6.

present. We propose the following electronic structure for the dianions: $[Fe^{II}(NO^{\bullet})(L)_2]^{2-}$ ($S = 1/2$).

X-band EPR Spectroscopy. Two members, namely, the neutral and dianionic complexes, of the present electron-transfer series are paramagnetic, both possessing an $S = 1/2$ ground state. The X-band EPR spectra have been recorded in frozen CH_2Cl_2 solutions (0.10 M $[N(n\text{-}Bu)_4]PF_6$) at 30 K, and the results are summarized in Table 6.

EPR spectra of the neutral complexes [**1a**]−[**4a**] are very similar, consisting of a rhombic signal with small g anisotropy ($g = 2.02-1.999$), and ^{14}N hyperfine splitting has not been observed. The spectrum of [**1a**] is shown in Figure 9. These spectra are typical of an S-centered radical which is consistent with the presence of a π-radical monoanionic ligand $(L^{1-4\bullet})^{1-}$. This simple EPR signal is representative of a nearly planar $(L^{\bullet})Fe^{II}(L) \leftrightarrow (L)Fe^{II}(L^{\bullet})$ unit and has also been observed in $[Au^{III}(L)(L^{\bullet})]^0 \leftrightarrow [Au^{III}(L^{\bullet})(L)]^0$ complexes.[23] These spectra are in accord with an electronic structure description of the neutral species as $[Fe(NO)(L^{\bullet})(L)]^0 \leftrightarrow [Fe(NO)(L)(L^{\bullet})]^0$ where the diamagnetic $\{FeNO\}^6$ unit consists of a low-spin Fe(II) ($S_{Fe} = 0$; d^6) and a coordinated, diamagnetic NO^+ ligand.

Interestingly, the EPR spectra of the dianions [**1a**]$^{2-}$, [**2a**]$^{2-}$, and [**5a**]$^{2-}$ are quite different as shown in Figure 10 for [**2a**]$^{2-}$. These spectra display a first-order hyperfine interaction with the nitrogen nucleus (^{14}N, $I = 1$) of the NO group. The spectra closely resemble those reported for other five- and six-coordinated $\{FeNO\}^7$ ($S = 1/2$) species.[15,16] From DFT calculations[16] it has been concluded that these complexes should be described as low-spin Fe(II) coordinated to a neutral $NO^{\bullet}$ radical. The spectrum of [**5a**]$^{2-}$ has been reported and interpreted previously.[24]

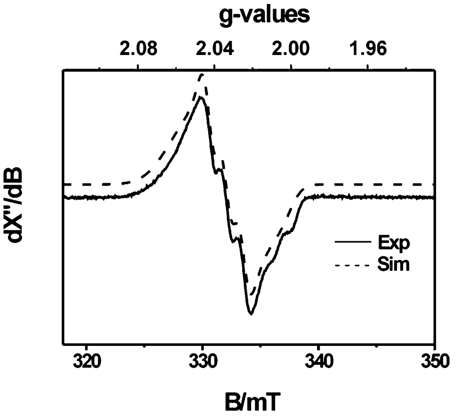

Figure 10. X-Band EPR spectrum of [**2a**]$^{2-}$ in frozen CH_2Cl_2 at 30 K. Conditions: $\nu = 9.43$ GHz, power 1.0×10^{-5} mW; modulation 7.0 G. For simulation parameters, see Table 6.

Table 7. Zero-Field Mössbauer Parameters of Complexes at 80 K

complex	δ, mm s^{-1} [b]	ΔE_Q, mm s^{-1} [c]
[**1a**](BF_4)	0.07	1.40
[**1a**]	0.06	1.70
$[Co(Cp)_2]$[**1a**]	0.04	1.88
$[Co(Cp)_2]_2$[**1a**]	0.20	1.16
[**2a**]	0.07	1.68
$[(n\text{-}Bu)_4N][FeNO(bdt)_2]$[a]	0.01	2.48
$[Co(Cp)_2][N(n\text{-}Bu)_4]\text{-}[FeNO(bdt)_2]$[a]	0.27	1.12
[**3a**]	0.08	1.59
[**4a**]	0.06	1.65
$[NEt_4]$[**4a**]	0.01	1.98[d]
$[PPh_4]$[**5a**]	0.03	1.70
$[Et_4N]_2$[**5a**]	0.33	0.79

[a] $(bdt)^{2-}$ = benzene-1,2-dithiolate(2−), ref 4. [b] Isomer shifts vs α-Fe at 298 K. [c] Quadrupole splitting. [d] Reference 8.

Mössbauer Spectroscopy. Table 7 summarizes the zero-field Mössbauer parameters for solid samples of complexes at 80 K. In each case a single quadrupole doublet has been observed.

It is significant that values for the isomer shift, δ, and quadrupole splitting ΔE_Q, for the monocations, the neutral complexes, *and* the corresponding monoanions are all observed in the narrow range $\delta = 0.08-0.01$ mm s^{-1} and $\Delta E_Q = 1.4-2.0$ mm s^{-1}. This is a clear indication that the $\{FeNO\}^6$ moiety is retained in the complexes irrespective of their charge or dithiolene oxidation level. This conclusion has also been reached by the infrared (Table 2) and UV−vis spectral studies reported above.

In contrast, one-electron reduction of the monoanion generating the corresponding dianion brings about a significant change in the Mössbauer parameters. Now the isomer shift is observed in the range $\delta = 0.20-0.33$ mm s^{-1} and $\Delta E_Q = 0.80-1.2$ mm s^{-1}. In agreement with previous reports,[8] we think that these complexes contain the $\{FeNO\}^7$ moiety.

We also measured the zero-field Mössbauer spectra of structurally characterized[7] $[N(n\text{-}Bu)_4][Fe(NO)(bdt)_2]$ and [Co-

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(23) Ray, K.; Weyhermüller, T.; Goossens, A.; Crajé, M. W. J.; Wieghardt, K. *Inorg. Chem.* **2003**, *42*, 4082.

(24) Teschmit, G.; Kirmse, R. *Inorg. Chem. Commun.* **1999**, *2*, 465.

Table 8. Comparison of Zero-Field Mössbauer Parameters at 80 K of Five- and Six-Coordinate $\{Fe(NO)\}^n$ ($n = 6-8$) Complexes

complex	δ, mm s$^{-1\,a}$	×e7ΔE_Q×e7, mm s$^{-1\,b}$	$\{FeNO\}^n$, n	ref
$[Fe(NO)(cyclam\text{-}ac)]^{2+}$	0.01	1.76	6	15b
$[Fe(NO)(cyclam\text{-}ac)]^{1+}$	0.26	0.74	7	15b
$[Fe(NO)(cyclam\text{-}ac)]^{0}$	0.41	1.69	8	15b
$[Fe(NO)(pyS_4)]^{+}$	0.04	1.63	6	16
$[Fe(NO)(pyS_4)]^{0}$	0.33	0.40	7	16
$[Fe(NO)(pyN_4)]^{3+}$	0.04	1.84	6	18
$[Fe(NO)(pyN_4)]^{2+}$	0.31	0.84	7	18
$[Et_4N][Fe(NO)(mnt)_2]$	0.05	1.68	6	8a
$[PPh_4]_2[Fe(NO)(mnt)_2]$	0.21	0.97	7	8a

[a] Isomer shift vs α-Fe at 298 K. [b] Quadrupole splitting, [c] 4.2 K.

$(Cp)_2][N(n\text{-}Bu)_4][Fe(NO)(bdt)_2]$, where again the data indicate the presence of an $\{FeNO\}^6$ and $\{FeNO\}^7$ moiety, respectively.

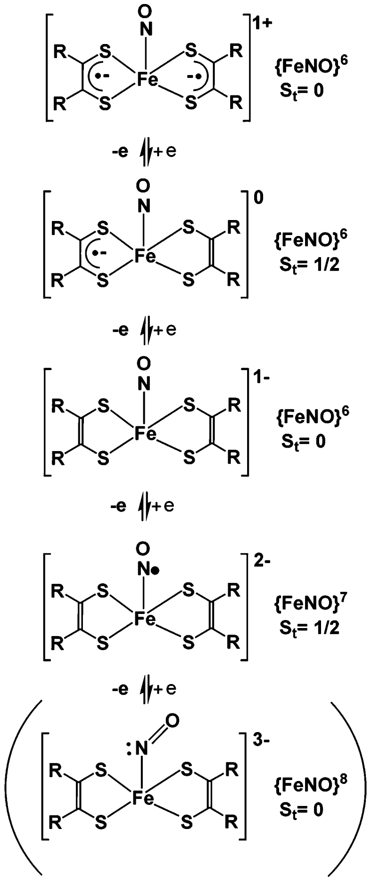
Discussion

In order to delineate the factors determining the electronic structures of the various nitrosyl iron complexes $[Fe(NO)(dithiolene)_2]^n$ ($n = 1+, 0, 1-, 2-, 3-$), it is instructive to compare their spectroscopic properties with those of other five- and six-coordinate nitrosyl iron complexes containing $\{FeNO\}^{6-8}$ cores and redox-innocent, four- or five-coordinate auxiliary ligands. Table 8 summarizes the Mössbauer parameters of six-coordinate species with an $\{FeNO\}^6$ and/or $\{FeNO\}^7$ core. It is evident that the isomer shift, δ, increases from ~0.03 mm s^{-1} for $\{FeNO\}^6$ to ~0.26 mm s^{-1} for $\{FeNO\}^7$ complexes. Concomitantly, the quadrupole splitting, ΔE_Q, decreases from ~1.7 to ~0.8 mm s^{-1}. Recent DFT calculations coupled to spectroscopic studies have established[15b,16,19] a consensual description of the electronic structure of these complexes: the $\{FeNO\}^6$ species consist of a low-spin Fe(II) ($S_{Fe} = 0$; d^6) coordinated by a diamagnetic NO$^+$ cation, and the $\{FeNO\}^7$ species with an $S = 1/2$ ground state are best described as low-spin Fe(II) ($S_{Fe} = 0$; d^6) coordinated by a NO$^\bullet$ radical ($S = 1/2$). Interestingly, the Mössbauer parameters do not vary greatly with the coordination number (5 or 6) or the nature of the donor atoms of the auxiliary ligand (4S + 1N or 5N).

It is therefore informative that the pair $[Fe(NO)(bdt)_2]^{1-/2-}$ (Table 7) and $[Fe(NO)(mnt)_2]^{1-/2-}$ (Table 8) display the same characteristic Mössbauer and EPR parameters as discussed above. This is taken as evidence for the presence of $\{FeNO\}^6$ and $\{FeNO\}^7$ moieties, respectively, and closed-shell $(bdt)^{2-}$ and $(mnt)^{2-}$ ligands in both cases. It is also revealing that the electronic spectra of the dianions with an $\{FeNO\}^7$ ($S = 1/2$) moiety do not display absorption maxima >500 nm with molar extinction coefficients $> 5 \times 10^3$ M^{-1} cm^{-1}. In contrast, the monoanions display a relatively weak maximum ($\sim 4 \times 10^3$ M^{-1} cm^{-1}) in the near-infrared (NIR) at 1304 nm[7] for $[Fe(NO)(bdt)_2]^{1-}$ and 1363 nm (4×10^3 M^{-1} cm^{-1}) for $[Fe(NO)(mnt)_2]^{1-}$. The exact nature of this transition, which is also present in [**1a**]$^{1-}$, [**2a**]$^{1-}$, [**3a**]$^{1-}$, and [**4a**]$^{-}$ (Table 5), is at present unclear.

A further significant spectroscopic observation is the fact that on going from $\{FeNO\}^6$ to $\{FeNO\}^7$ species ν_{NO} decreases by ~200 cm^{-1} (for example, from 1800 to 1600 cm^{-1} in $[Fe(NO)(bdt)_2]^{1-/2-}$ and from 1814 to 1633 cm^{-1} for $[Fe(NO)(mnt)_2]^{1-/2-}$ (see ref 2)). This is again nicely in accord with the notion that an NO$^+$ ligand in a given $\{FeNO\}^6$ complex is reduced to an $\{FeNO\}^7$ species with a coordinated NO$^\bullet$ molecule. Taken together, the spectroscopic evidence clearly establishes that in all mono- and dianions of this study ([**1a**]$^{1-/2-}$−[**5a**]$^{1-/2-}$) the dithiolene ligands are closed-shell dianions $(L^x)^{2-}$ ($x = 1-5$).

Scheme 2



Structurally, a few pairs of mono- and dianions have been characterized by X-ray crystallography including $[Fe(NO)(mnt)_2]^{1-/2-}$ [5,6] and $[Fe(NO)(bdt)_2]^{1-/2-}$.[7] A linear Fe−NO group is present in the $\{FeNO\}^6$ species, as expected, whereas in the $\{FeNO\}^7$ complexes it is bent (150−170°). Significantly, the C−S bond lengths in the mono- and dianions are long and nearly identical which indicates the presence of closed-shell dianions $(mnt)^{2-}$ and $(bdt)^{2-}$, thereby ruling out the presence of coordinated π-radical monoanions $(mnt^\bullet)^{1-}$ or $(bdt^\bullet)^{1-}$.

It is also a reliable spectroscopic feature of $\{FeNO\}^7$ ($S = 1/2$) complexes that their EPR spectra (including all dianions of the present study as summarized in Table 6) exhibit ^{14}N hyperfine splitting. This has been discussed for $[Fe(NO)(mnt)_2]^{2-}$ by Kirmse and Teschmit[24] and for $[Fe(NO)(S_2CN(CH_3)_2)_2]$[25] and $[Fe(NO)(S_2CNEt_2)_2]$.[26] Note that the latter two complexes contain two redox-innocent

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(25) Feltham, R. D.; Crain, H. *Inorg. Chim. Acta* **1980**, *40*, 37.

(26) Goodman, B. A.; Raynar, J. B.; Symons, M. C. R. *J. Chem. Soc. (A)* **1969**, *2572*.

dithiocarbamato(1−) ligands. A similar EPR spectrum has been reported for $[Fe(NO)(i\text{-}mnt)_2]^{2-}$, where $(i\text{-}mnt)^{2-}$ is 1,1-dicyanoethene-2,2-dithiolate(2−).[27]

In summary, all spectroscopic evidence and DFT calculations for the present mono- and dianions are in excellent agreement with the electronic structures: (a) $[Fe^{II}(NO^+)(L^n)_2]^{1-}$ ($S_{Fe} = 0$; d^6; $S_t = 0$) containing two closed-shell dianions $(L^n)^{2-}$ and (b) $[Fe^{II}(NO^\bullet)(L^n)_2]^{2-}$ ($S_{Fe} = 0$; d^6; $S_t = 1/2$) containing again two dianions $(L^n)^{2-}$.

As pointed out above it is quite remarkable that the Mössbauer parameters for the monoanion, neutral complex, and monocation are within a very narrow range identical, indicating the presence of the same $\{FeNO\}^6$ moiety (low-spin Fe(II) with an NO^+ ligand) irrespective of the overall charge or spin state of the complex (the monocations and monoanion possess an $S = 0$ ground state, whereas the neutral species is paramagnetic ($S = 1/2$)). This result clearly points to sulfur-ligand-based redox processes when oxidation of the monoanion to the neutral and then to the corresponding monocation occurs. The NO stretching frequency depends somewhat on the overall charge of the complex, which is normal: it is observed at the highest frequency in the monocation and decreases by only ~35 cm^{-1} per one-electron reduction, a smaller decrease than frequently observed, further indicating that reduction processes in this series of complexes are not primarily associated with the NO ligand.

Simple charge considerations require that the monoanionic forms $[\mathbf{1a}]^{1-}$−$[\mathbf{5a}]^{1-}$ contain each two closed-shell dianionic ligands $(L^x)^{2-}$, but the neutral complexes $[\mathbf{1a}]^0$−$[\mathbf{5a}]^0$ must have three negative charges per two dithiolene ligands (one dianion $(L^x)^{2-}$ and one radical monoanion $(L^\bullet)^{1-}$), and, finally, the monocations $[\mathbf{1a}]^{1+}$−$[\mathbf{4a}]^+$ must contain two negative charges per two dithiolene ligands (two π-radical anions $(Lx^\bullet)^{1-}$).

The $\{FeNO\}^6$ moiety in the monocations, neutral complexes, and monoanions is best described as containing a low-spin Fe(II) ($S_{Fe} = 0$; d^6) coordinated by an NO^+ ligand. In a previous report[20] we have shown that the monoanion $[Fe^{II}(L^\bullet)_2(CN)]^{1-}$ and the neutral complex $[Fe^{II}(L^\bullet)_2\{P(OPh)_3\}]$ also contain an $Fe^{II}(L^\bullet)_2$ chromophore with a low-spin Fe(II) center where $(L^\bullet)^{1-}$ represents the π-radical monoanion of di-(4-*tert*-butylphenyl)-1,2-ethylenedithiolate. The Mössbauer parameters of these two low-spin Fe(II) complexes are remarkably similar to those of the present (nitrosyl)iron species, namely, $\delta = 0.11$ and 0.08 mm s^{-1} and $\Delta E_Q = 2.55$ and 2.55 mm s^{-1}, respectively.

In addition, the electronic spectra of these two non-nitrosyl species also display an intense (1.1×10^4 and 1.8×10^4 M^{-1} cm^{-1}) absorption maximum at 723 and 687 nm, respectively. From DFT calculations on $[Fe^{II}(L^\bullet)_2(CN)]^-$ it was shown that an electronic configuration containing low-spin Fe(II) and two π-radical monoanions prevails. The above intense absorption maximum is assigned as a ligand-to-ligand CT band which is characteristic of all planar $M(L^\bullet)_2^z$ chromophores[22] (M = Ni^{II}, Pd^{II}, Pt^{II}, Au^{III}). This absorption maximum is present in all of the monocations $[\mathbf{1a}]^{1+}$−$[\mathbf{4a}]^{1+}$ for which therefore an electronic structure as in $[Fe^{II}(NO^+)(L^\bullet)_2]^{1+}$ is deduced from the above spectroscopic data.

Similarly, planar $[M(L)(L^\bullet)]^z \leftrightarrow [M(L^\bullet)(L)]^z$ chromophores (M = Ni^{II}, Pd^{II}, Pt^{II}, Au^{III}; $z = 1-$ or 0)[22] have been shown to display intervalence charge-transfer bands (IVCT) in the NIR with approximately one-half of the intensity of the LLCT band in the $[M(L^\bullet)_2]^z$ species. The same holds true for the neutral (nitrosyl)iron complexes $[\mathbf{1a}]^0$−$[\mathbf{4a}]^0$ (Table 5). Furthermore, the EPR spectra of the neutral $S = 1/2$ species display rhombic signals with small g anisotropy and no ^{14}N hyperfine splitting. These spectra are characteristic of sulfur-centered radicals. Therefore, from all spectroscopic data we can safely deduce the following electronic structure of these neutral complexes: $[Fe^{II}(NO^+)(L^\bullet)(L)]^0 \leftrightarrow [Fe^{II}(NO^+)(L)(L^\bullet)]^0$.

Finally, a summary of all elucidated electronic structures of the series $[Fe(NO)(L)_2]^z$ ($z = 1+, 0, 1-, 2-$) is given in Scheme 2.

We note that the trianion $[Fe(NO)(mnt)_2]^{3-}$ has been deduced to exist from electrochemical experiments only.[1−3] No spectroscopic data are available, and therefore, the proposed structure in Scheme 2 is tentative. We also note that the photoelectron spectra of $[M(mnt)_2]^{2-/1-}$ species (M = Fe, Co, Ni, Cu) have recently been reported.[28]

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support and the EPSRC (U.K.) for a studentship (K.S.).

Supporting Information Available: Crystallographic details on positional and displacement parameters; bond lengths and angles for compounds [**1a**], [**2a**], and $[Co(Cp)_2]$[**1a**] in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[28] Waters, T.; Wang, X.-B.; Woo, H.-K.; Wang, L.-S. *Inorg. Chem.* **2006**, *45*, 5841.