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Article

N,N-Coordinated π Radical Anions of *S*-Methyl-1-phenyl-isothiosemicarbazide in Two Five-Coordinate Ferric Complexes $[Fe^{III}(L^{Me\bullet})_2X]$ ($X = CH_3S^-, Cl^-$)

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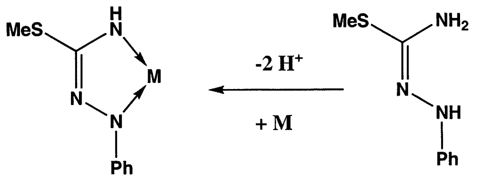
The reaction between $[Fe^{III}(dmf)_6](ClO_4)_3$ and the ligand *S*-methyl-1-phenyl-isothiosemicarbazide, $H_2[L^{Me}]$, and triethylamine (1:3:6) in methanol under an argon blanketing atmosphere at elevated temperatures (reflux) yields a purple solution from which upon cooling to 20 °C dark green crystals of $[Fe^{III}(L^{Me\bullet})_2(SCH_3)]$ (**1**) were obtained in 15% yield. From a similar reaction mixture using $FeCl_3$ as starting material in the solvent acetone under anaerobic conditions at –80 °C, dark green crystals of $[Fe^{III}(L^{Me\bullet})_2Cl]$ (**2**) were obtained in 21% yield. The structures of complexes **1** and **2** have been determined by single-crystal X-ray crystallography at 100 K. Both complexes are five-coordinate square base pyramidal ferric species containing two N,N-coordinated, monoanionic π radicals, $(L^{Me\bullet})^{1-}$, of the parent *S*-methyl-1-phenyl-isothiosemicarbazide(2–) dianion in the basal positions whereas the axial position is occupied by methylthiolate in **1** and chloride in **2**, respectively. The electronic structure of both species has been elucidated by their electronic spectra, magnetic properties, and X-band EPR and Mössbauer spectra. Both possess an $S_t = {}^1/_2$ ground state which is attained via an antiferromagnetic coupling between the spins of an intermediate spin ferric ion ($S_{Fe} = {}^3/_2$) and two ligand π radical anions ($S_{rad} = {}^1/_2$).

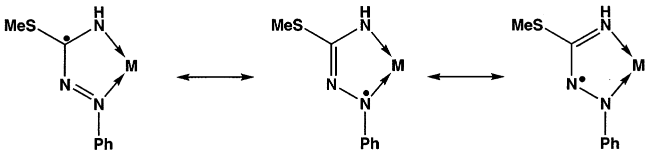
Introduction

The doubly deprotonated form, $(L^{Me})^{2-}$, of the neutral molecule *S*-methyl-1-phenyl-isothiosemicarbazide, $H_2[L^{Me}]$, yields, in principle, a dianion which could function as a bidentate ligand in coordination compounds as shown below.



$(L^{Me})^{2-}$ $H_2[L^{Me}]$

To the best of our knowledge such a compound has not been structurally characterized to date. Revenco et al.[1−4] have in a series of papers shown that in the presence of an oxidant such as air the one electron oxidized form, namely, the monoanionic radical $(L^{Me\bullet})^{1-}$, can bind in an N,N-fashion to nickel(II)[1,2] or cobalt(III) ions.[3]



$(L^{Me\bullet})^{1-}$

Thus, the diamagnetic complexes $[Ni^{II}(L^{Me\bullet})_2]$ (square planar) and $[Co^{III}I(L^{Me\bullet})_2]$ (square base pyramidal) have been structurally characterized.[1,3] The same authors have also shown[2]

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(1) Revenco, M. D.; Simonov, Yu. A.; Vyrtosu, N. I.; Gerbeleu, N. V.; Bourosh, P. N.; Belski, B. K.; Indrichian, K. M. *Zh. Neorg. Khim.* **1988**, *33*, 2049; *Russ. J. Inorg. Chem.* **1988**, *33*, 1168.

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(3) Revenco, M. D.; Gerbeleu, N. V.; Simonov, Yu. A.; Bourosh, P. N.; Vyrtosu, N. I.; Sobolev, A. N.; Malinovskii, T. I. *Dokl. Akad. Nauk SSR* **1988**, *300*, 127.

(4) Taraszewska, J.; Revenco, M. D.; Timco, L. *Pol. J. Chem.* **1997**, *71*, 253.

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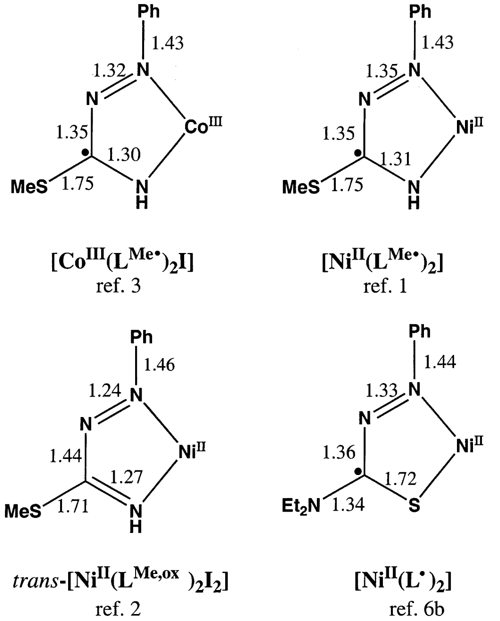


$[Co^{III}(L^{Me\bullet})_2I]$ ref. 3

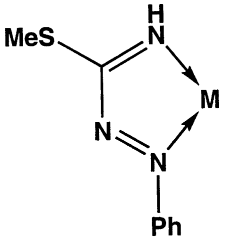
$[Ni^{II}(L^{Me\bullet})_2]$ ref. 1

trans-$[Ni^{II}(L^{Me,ox})_2I_2]$ ref. 2

$[Ni^{II}(L^{\bullet})_2]$ ref. 6b

Figure 1. Metrical details of the five-membered chelate rings in $[Ni^{II}(L^{Me\bullet})_2]$, $[Co^{III}(L^{Me\bullet})_2I]$, and $[Ni^{II}(L^{Me,ox})_2I_2]$ from refs 1, 2, and 3. The average error of a given bond distance is ~±0.01 Å (≡3σ).

that the π radical monoanion can be further one-electron oxidized yielding the neutral ligand, $(L^{Me,ox})^0$.The octahedral, paramagnetic complex *trans*-$[Ni^{II}(L^{Me,ox})_2I_2]$ ($S_t = 1$) has been structurally characterized.[2]



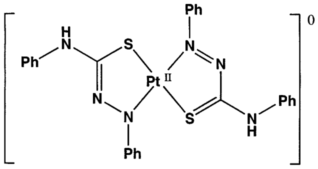
$(L^{Me,ox})^0$

It was convincingly demonstrated that high-quality X-ray crystallography allows the unambiguous assignment of the ligand oxidation level as $(L^{Me\bullet})^{1-}$ or $(L^{Me,ox})^0$ because the two C−N and the N−N bond distances in the five-membered chelate ring of a given N,N-coordinated ligand differ in a characteristic manner as shown in Figure 1. The N−N bond length in complexes containing N,N-coordinated $(L^{Me\bullet})^{1-}$ π radical anions is 1.34 ± 0.01 Å but much shorter at 1.24 ± 0.01 Å in species with $(L^{Me,ox})^0$ ligands. Similarly, the two C−N bond distances in $(L^{Me\bullet})^{1-}$ complexes are 1.31 ± 0.01 and 1.35 ± 0.01 Å whereas in species containing $(L^{Me,ox})^0$ ligands these distances are found at 1.27 ± 0.01 and 1.44 ± 0.01 Å. The first C−N bond length given involves the imide nitrogen whereas the second involves the diimine (or hydrazine) nitrogen of the chelate ring.

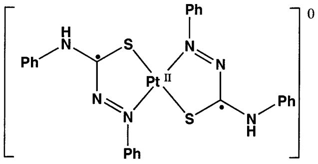
On the basis of the resonance structures given above we predict that in a complex containing an N,N-coordinated dianion $(L^{Me})^{2-}$ the $C-N_{imine}$ and $C-N_{diimine}$ bond lengths are at ~1.40 and ~1.28 Å, respectively, and that the N−N distance is long at ~1.42 Å.

Here we report the synthesis and the structural and spectroscopic characterization of two ferric complexes, namely, $[Fe^{III}(L^{Me\bullet})_2(SCH_3)]$ (**1**) and $[Fe^{III}(L^{Me\bullet})_2Cl]$ (**2**), both of which possess an $S_t = {}^1/_2$ ground state. The electronic structure of both species is shown to be adequately described as containing two π radical anions $(L^{Me\bullet})^{1-}$ ($S_{rad} = {}^1/_2$) and an intermediate spin ferric ion ($S_{Fe} = {}^3/_2$) which are strongly antiferromagnetically coupled yielding the observed $S_t = {}^1/_2$ ground state.

It is noted that similar complexes of Pt^{II}, Ni^{II}, and Zn^{II} containing S-dealkylated thiosemicarbazone derivatives have been described.[5,6] Holm et al.[5] have proposed two valence bond structures as in **A** consisting of a diamagnetic ligand dianion and its two-electron oxidized neutral form. We note that it is also possible to describe this complex as singlet diradical as in structure **B**.



A



B, S_t=0

The crystal structure of this Pt^{II} species has not been reported, but the structure of $[Ni^{II}(L^{\bullet})_2]$ where $(L^{\bullet})^{1-}$ represents the *N*,*N*-diethylphenylazothioformamide(1−) monoanionic π radical has been published.[6b] Details are shown in Figure 1. The corresponding $[Zn(L^{\bullet})_2]$ complex has a triplet ground state ($S_t = 1$) demonstrating the presence of two ligand radicals.[6a]

Experimental Section

Air-sensitive materials were manipulated under argon according to standard Schlenk line procedures or under nitrogen in a glovebox. CH_3OH was distilled under argon and dried over 4 Å molecular sieves prior to use. Acetone was predried over Na_2SO_4, then distilled over 4 Å molecular sieves, and stored under argon over sieves. Phenylhydrazine hydrochloride, ammonium thiocyanate, methyl iodide, silver perchlorate, and silver trifluoromethanesulfonate were purchased from Aldrich. Anhydrous iron(III) chloride was purchased from Merck. All chemicals were used without further purification. Hexa(dimethylformamide)iron(III) tris(perchlorate), $[Fe^{III}(dmf)_6](ClO_4)_3$ was synthesized according to a published procedure.[7]

***S*-Methyl-1-phenyl-isothiosemicarbazide, $H_2[L^{Me}]$.** The starting material 1-phenylthiosemicarbazide was synthesized according to Fischer's procedure.[8] Phenylhydrazine hydrochloride (14.5 g, 10

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(5) Forbes, C. E.; Gold, A.; Holm, R. H. *Inorg. Chem.* **1971**, *10*, 2479.

(6) (a) Jensen, K. A.; Bechgaard, K.; Pedersen, C. Th. *Acta Chem. Scand.* **1972**, *26*, 2913. (b) Hazell, R. G. *Acta Chem. Scand.* **1976**, *A30*, 322.

(7) Hodgkinson, J.; Jordan, R. B. *J. Am. Chem. Soc.* **1973**, *95*, 763.

(8) Fischer, K. E. *Liebigs Ann.* **1882**, *212*, 325.

mmol) and ammonium thiocyanate (7.6 g, 10 mmol) were suspended into 50 mL of absolute ethanol. The mixture is heated to reflux for 12 h and then left to cool to 20 °C overnight. A white precipitate was filtered off, washed with water (3 × 40 mL), and dried over KOH under reduced pressure to yield 10.59 g of 1-phenylthiosemicarbazide (yield: 68%). ^{1}H NMR (d_6-DMSO, 400 MHz, 300 K): δ (ppm) = 6.66 (d, J = 7.6 Hz, 2H, *o*-ArH), 6.76 (t, J = 7.6 Hz, 1H, *p*-ArH), 7.172 (t, J = 7.6 Hz, 2H, *m*-ArH), 7.43 (s, 1H, NC(=S)NH2), 7.74 (s, 1H, NC(=S)NH2), 7.87 (s, 1H, ArNH), 9.24 (s, 1H, ArNHNHC). ^{13}C NMR (d_6-DMSO, 400 MHz, 300 K): δ (ppm) = 113 (CH, *o*-Ar), 147.5 (CH, *p*-Ar), 128 (CH, *m*-Ar), 147.5 (Cq, Ar), 182 (Cq, NC(=S)N). 1-Phenylthiosemicarbazide (3.4 g, 2 mmol) was suspended in 30 mL of absolute ethanol. Methyl iodide (1.34 mL, 3.08 g, 2.2 mmol) was added, and the mixture was heated to reflux for 2 h. The solvent ethanol was then removed by evaporation, and the yellow oil was dissolved in 15 mL of dichloromethane. Upon standing in the freezer overnight, a pale yellow precipitate was obtained. It was filtered off, washed with dichloromethane (2 × 3 mL), and dried under vacuum. Yield: 5.42 g (80%). ESI-MS (CH_2Cl_2, positive ion): m/z = 182 for $C_8H_{12}N_3S$ $\{H_3[L^{Me}]\}^+$. Coalescence processes, observed around 340 K while recording a temperature-dependent ^{1}H NMR spectrum (d_6-DMSO, 400 MHz, 300 K − 350 K) of this compound, led us to the conclusion that two tautomers exist in equilibrium in a 1:5 ratio at 298 K. ^{1}H NMR (d_6-DMSO, 400 MHz, 300 K, m = minor tautomer only, M = major tautomer only): δ (ppm) = 2.48 (s, 0.5H, SMe(m)), 2.70 (s, 2.5H, SMe(M)), 6.79 (d, 2H, J = 3.6 Hz, *o*-ArH), 6.90 (t, 1H, J = 3.6 Hz, *p*-ArH), 7.27 (t, 2H, J = 3.6 Hz, *m*-ArH), 8.43 (s, 0.83 H, NH(M)), 8.55 (s, 0.17 H, NH(M)), 9.51 (s(br), 1.7 H, NH_2(M)), 11.17 (s, 0.83 H, NH(M)). ^{13}C NMR (d_6-DMSO, 400 MHz, 300 K): δ (ppm) = 12.6 (SCH_3(m)), 13.2 (SCH_3(M)), 113.0 (CH, *o*-Ar(m)), 113.3 (CH, *o*-Ar(M)), 121.0 (CH, *p*-Ar), 129.2 (CH, *m*-Ar), 146 (Cq, Ar), 170.6 (Cq, CSMe(M)), 176.8 (Cq, CSMe(m)).

Exchange of the iodide by addition of 1 equiv of silver triflate in ethanol quantitatively led, upon filtration and removal of the solvent, to the trifluoromethanesulfonate salt of this ligand $[H_3(L^{Me})]CF_3SO_3$. ESI-MS (positive ion): m/z = 182 for $C_8H_{12}N_3S$ $\{H_3[L^{Me}]\}^+$. ESI-MS (negative ion): m/z = 149 ($CF_3SO_3^-$). No changes in the ^{1}H NMR spectrum in d_6-DMSO as compared to that of the hydroiodide salt were observed.

$[Fe^{III}(L^{Me\bullet})_2(SCH_3)]$ (1). In a Schlenk flask under argon the ligand $[H_3(L^{Me})]I$ (942 mg, 3 mmol) was dissolved in 20 mL of dry CH_3OH. Upon addition of $AgClO_4$ (621 mg, 3 mmol) to the orange solution, yellow AgI precipitated, which was removed by filtration through Celite; then $[Fe(dmf)_6](ClO_4)_3$ (793 mg, 1 mmol) was added. Dropwise addition of 1 equiv of Et_3N (415 μL, 303 mg, 3 mmol) induces a darkening of the solution. After 30 min of stirring at room temperature, a second equivalent of Et_3N (415 μL, 303 mg, 3 mmol) was added. The dark solution was heated to reflux for 3 h. The purple solution was filtered hot, and it was then slowly cooled to 20 °C. Filtration of the cold solution under argon yielded 100 mg (15%) of dark green needles of X-ray quality. EI-MS: Anal. Calcd for $C_{17}H_{21}FeN_6S_3^+$: m/z = 461. Found: 461; additional peak at 414 $\{\mathbf{1} - (SMe)\}^+$. Anal. Calcd for $C_{17}H_{21}FeN_6S_3$: C, 44.25; H, 4.59; N, 18.21; Fe, 12.10; S, 20.85. Found: C, 44.12; H, 4.54; N, 18.38; Fe, 12.15; S, 20.82.

$[Fe^{III}(L^{Me\bullet})_2Cl]$ (2). In a Schlenk flask under argon $[H_3L^{Me}]CF_3SO_3$ (505 mg, 1.5 mmol) and anhydrous $FeCl_3$ (268 mg, 1.65 mmol) were dissolved in 15 mL of dry acetone. The dark red solution was cooled to −80 °C (dry ice/acetone bath), and 2 equiv of Et_3N (412 μL, 300 mg, 3 mmol) was added dropwise. After 15 min of stirring a third equivalent of Et_3N (206 μL) was added. The dark solution was stirred for 2 h. The −80 °C cold solution was filtered through a frit in order to get rid of some pale yellow degradation product. The frit was rinsed twice with 2 mL of dry toluene. The purple filtrate is pumped under vacuum to remove the acetone. After 24 h, filtration of the toluene solution yielded a dark microcrystalline material. Further recrystallization from CH_2Cl_2/toluene yielded ~70 mg of dark green X-ray quality crystals. Yield: 21%. Anal. Calcd for $C_{16}H_{18}ClFeN_6S_2$: C, 42.73; H, 4.03; N, 18.68; Fe, 12.42; Cl, 7.88. Found: C, 42.82; H, 4.11; N, 18.60; Fe, 12.30; Cl, 7.75.

Physical Measurements. Temperature-dependent (2−298 K) magnetic susceptibilities of powdered samples of complexes were measured with a SQUID magnetometer (MPMS Quantum Design) in an external magnetic field of 1.0 T. The experimental data were corrected for underlying diamagnetism by use of tabulated Pascal's constants. 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 α-Fe at 298 K. Infrared spectra (400−4000 cm^{-1}) of solid samples were recorded on a Perkin-Elmer 2000 FT-IR/FT-NIR spectrometer as KBr pellets. UV−vis spectra of solutions were measured on a Perkin-Elmer Lambda 19 spectrophotometer in the range 200−1200 nm. X-band EPR spectra were recorded on frozen solutions using a Bruker Elexsys E300 spectrometer with a standard or dual-mode cavity and an Oxford Instruments ESR 910 flow cryostat. Spin Hamiltonian simulations (spin total $S_t = {}^1/_2$) were performed with a homemade program.

X-ray Crystallographic Data Collection and Refinement of the Structures. Dark green single crystals of **1** and **2** were coated with perfluoropolyether and mounted in the nitrogen cold stream of a Nonius Kappa-CCD diffractometer equipped with a Mo-target rotating-anode X-ray source and a graphite monochromator (Mo Kα, λ = 0.71073 Å). Final cell constants were obtained from a least-squares fit of a subset of several thousand strong reflections. Data collection was performed by taking frames at 1.0° in ω. Crystal faces were determined and the corresponding intensity data were corrected for absorption using the Gaussian-type routine embedded in XPREP.[9] Crystallographic data of the compounds are listed in Table 1. The Siemens ShelXTL[9] software package was used for solution and artwork of the structure; ShelXL97[10] was used for the refinement. The structures were readily solved by direct and Patterson methods and subsequent difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. The crystallographic data for both compounds have been deposited at the Cambridge Crystallographic Data Centre using the numbers CCDC 219227 for **1** and CCDC 219228 for **2**.

Results and Discussion

Synthesis and Spectroscopic Characterization of Complexes. In an attempt to obtain complexes of iron analogous to those reported by Revenco and Gerbeleu et al. of nickel and cobalt[1−4] with ligands derived from *S*-methyl-1-phenylisothiosemicarbazide, $H_2[L^{Me}]$, we studied the reaction of $\{H_3[L^{Me}]\}I$ with $FeCl_3$ (1:1) in dry methanol at elevated temperatures in the presence of triethylamine. Upon cooling of the dark solution to 20 °C, dark green crystals of X-ray

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

(10) Sheldrick, G. M. *ShelXL97*; Universität Göttingen: Göttingen, 1997.

Table 1. Crystallographic Data for **1** and **2**

	1	**2**
chem formula	$C_{17}H_{21}FeN_6S_3$	$C_{16}H_{18}ClFeN_6S_2$
fw	461.43	449.78
space group	$P2_1/c$, No. 14	$P\bar{1}$, No. 2
a, Å	9.5163(4)	8.9628(6)
b, Å	9.6966(4)	9.8292(6)
c, Å	22.3302(8)	12.0455(6)
α, deg	90	108.72(1)
β, deg	98.50(1)	100.12(1)
γ, deg	90	98.56(1)
V, Å	2037.9(2)	965.13(10)
Z	4	2
T, K	100(2)	100(2)
ρ calcd, g cm^{-3}	1.504	1.548
reflns collected/$2\Theta_{max}$	68068/62.04	17694/62.02
unique reflns/$I > 2\sigma(I)$	6493/6062	6088/5220
no. of params/restr	253/1	243/0
μ(Mo Kα), cm^{-1}	10.62	11.49
R1^a/GOF^b	0.0250/1.047	0.0462/1.061
wR2^c ($I > 2\sigma(I)$)	0.0616	0.1050
residual density, e Å^{-3}	+0.44/−0.45	+1.67/−1.33

^{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 $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$.

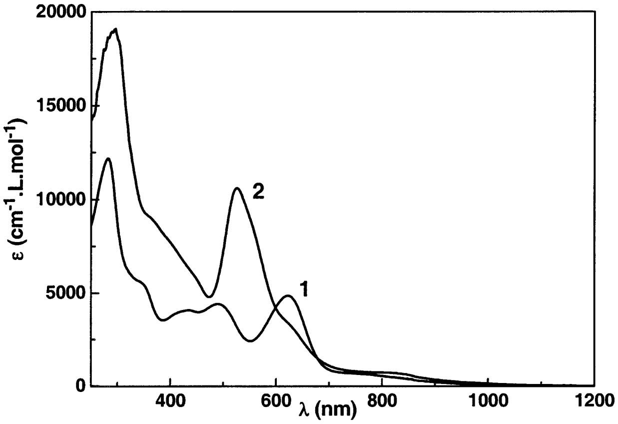

Figure 2. Electronic spectra of **1** and **2** in CH_2Cl_2 solution at 20 °C.

quality slowly precipitated. The crystal structure determination (not reported here) revealed that two different neutral compounds had cocrystallized, namely, $[Fe(L^{Me\bullet})_2(SCH_3)]$ (**1**) in 62% and $[Fe(L^{Me\bullet})_2I]$ in 38%.

Obviously, the methylthiolate ligand had originated from oxidative degradation of the ligand $H_2[L^{Me}]$ in basic solution at elevated temperature. Thus, avoiding all halide anions during the synthesis by using $[Fe^{III}(dmf)_6](ClO_4)_3$ and $[H_3(L^{Me})]ClO_4$ (in situ generated) as starting materials using anaerobic conditions allowed us to isolate a pure sample of **1** in low yield (15%). When the reaction was carried out at −80 °C using anhydrous $FeCl_3$ and $[H_3(L^{Me})]CF_3SO_3$ as starting materials we have obtained green single crystals of $[Fe^{III}(L^{Me\bullet})_2Cl]$ (**2**) in 21% yield. Note that since both reactions were carried out under anaerobic conditions, the required ligand oxidation ($(L^{Me})^{2-} \rightarrow (L^{Me\bullet})^{1-} + e$) was achieved by ferric ions which are reduced to Fe^{II} ions. Thus, the yields of **1** and **2** cannot exceed 33% based on total iron content.

The electronic spectra of **1** and **2** are shown in Figure 2. In the visible region both complexes display an intense ligand-to-ligand charge transfer band at 620 nm ($\epsilon = 0.5 \times 10^4$ M^{-1} cm^{-1}) for **1** and at 527 nm ($\epsilon = 1.1 \times 10^4$ M^{-1} cm^{-1}) for **2**. This absorption is tentatively assigned to a spin and dipole allowed transition between two approximately planar N,N-coordinated π radical ligands.[11] Very similar transitions have been reported for $[Fe(L^{ISQ})_2I]$ complexes where $(L^{ISQ})^{1-\bullet}$ is either the *o*-iminobenzosemiquinonate(1−)[12] radical anion (640 nm ($\epsilon = 1.0 \times 10^4$ M^{-1} cm^{-1})) or its thio analogue ($\lambda_{max} = 550$ nm ($\epsilon = 3.3 \times 10^4$)).[13]

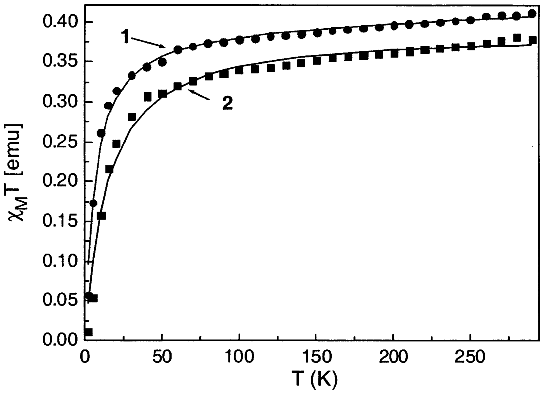

Figure 3. Temperature-dependence of the product of the molar magnetic susceptibility multiplied by the temperature, $\chi_M T$, for solid samples of **1** and **2**. Solid lines represent best fits. Fit parameters are given in the text.

Temperature-dependent magnetic susceptibility measurements on solid samples of **1** and **2** revealed that the molecular species in **1** and **2** possess an $S_t = 1/2$ ground state. Figure 3 shows the temperature-dependence of the product $\chi_M T$ (χ_M = molar magnetic susceptibility). The solid lines represent spin Hamiltonian simulations for $S_t = 1/2$ systems including some weak intermolecular antiferromagnetic exchange coupling between molecules as expressed by a Weiss constant θ of −6.2 K for **1** and −14.6 K for **2**. In both cases a small temperature-independent paramagnetism (TIP) of 0.60×10^{-4} emu for **1** and 0.19×10^{-4} emu for **2**, respectively, was also included. The fit yielded a g_{iso} value of 2.06 for **1** and **2**, respectively.

Figure 4 displays the X-band EPR spectra of frozen CH_2Cl_2 solutions of **1** and **2** at 30 K which confirm the $S_t = 1/2$ ground states. Both spectra show well-resolved powder lines in the $g = 2$ region with large g-anisotropy (rhombic signals) which arises from spin−orbit interactions and indicate significant spin density in a d orbital of the respective ferric ion. The spectra were satisfactorily simulated with g_x, g_y, g_z values of 2.167, 2.047, 2.017 for **1** and 2.207, 2.057, 2.023 for **2**.

The zero-field Mössbauer spectra of solid samples of **1** and **2** were recorded at 80 K and are shown in Figure 5. Both compounds exhibit a single quadrupole doublet with

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(11) (a) Herebian, D.; Bothe, E.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2001**, *123*, 10012. (b) Sun, X.; Chun, H.; Hildenbrand, K.; Bothe, E.; Weyhermüller, T.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 4295. (c) Herebian, D.; Wieghardt, K.; Neese, F. *J. Am. Chem. Soc.* **2003**, *125*, 10997.

(12) (a) Chun, H.; Weyhermüller, T.; Bill, E.; Wieghardt, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2489. (b) Chun, H.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2003**, *42*, 5612.

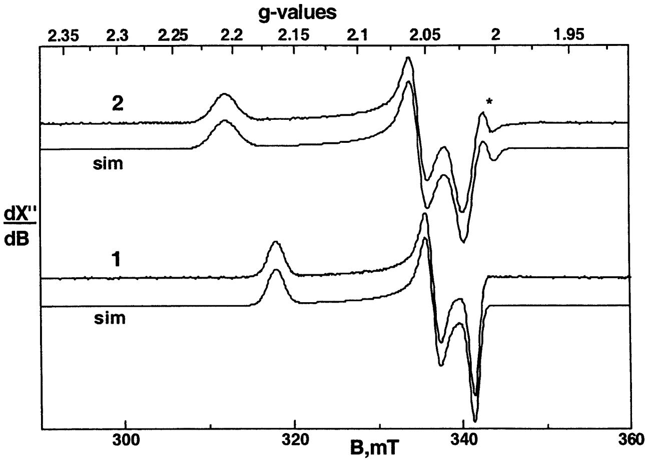

Figure 4. X-band EPR spectra of frozen CH_2Cl_2/toluene (1:1) solutions of **1** and **2** at 30 K. (Conditions for **1** and **2**, respectively: frequency 9.638 GHz and 9.634 GHz; power 0.0126 mW and 0.2 mW; modulation 5 G in both cases). *g*-values from simulations are given in the text. The asterisk denotes a small (0.5%) paramagnetic impurity ($S = {}^1/_2$).

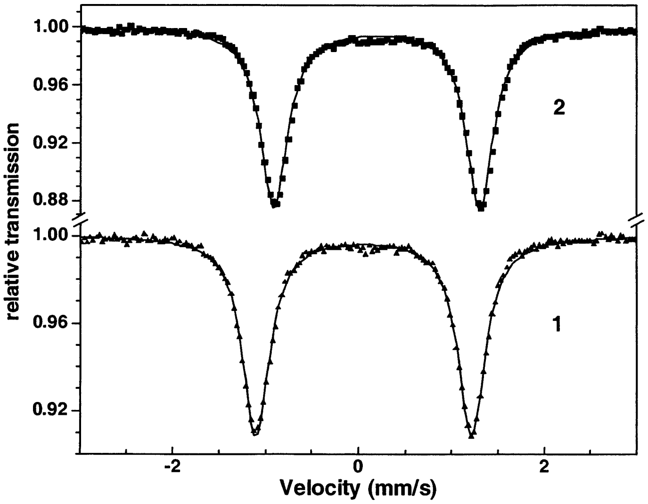

Figure 5. Zero-field Mössbauer spectra of **1** and **2** at 80 K. Simulation parameters (Lorentzian line shapes) are given in Table 2.

Table 2. Mössbauer Parameters of Complexes at 80 K[a]

complex	S_t[b]	S_{Fe}[c]	δ, mm s^{-1} [d]	$\lvert\Delta E_Q\rvert$, mm s^{-1} [e]	ref
1	$^1/_2$	$^3/_2$	0.06	2.32	this work
2	$^1/_2$	$^3/_2$	0.20	2.21	this work
$[Fe^{III}(O_2S_2C_2)_2I]^{2-}$	$^3/_2$	$^3/_2$	0.30	3.50	14
$[Fe^{III}(L_O^{ISQ})_2I]$	$^1/_2$	$^3/_2$	0.24	2.80	12a
$[Fe^{III}(L_S^{ISQ})_2I]$	$^1/_2$	$^3/_2$	0.11[d]	3.41[f]	13b
$[Fe^{III}(L_O^{ISQ})_2Cl]$	$^3/_2$	$^5/_2$	0.45	1.26	12
$[Fe^{II}(pyS_4)]_2$	0	0	0.44	0.43	15
$[Fe^{II}(pyS_4)PR_3]$	0	0	0.34	0.69	15
$[Fe^{II}(pyS_4)(CO)]$	0	0	0.19	0.88	15

[a] Abbreviations: $(L_O^{ISQ})^{1-\bullet}$ = *o*-iminobenzosemiquinonate(1−); $(L_S^{ISQ})^{1-\bullet}$ = *o*-iminothionebenzosemiquinonate(1−); $(pyS_4)^{2-}$ = 2,6-bis(2-mercaptophenylthiomethyl)pyridine. [b] Ground state of molecule. [c] Local spin state of iron ion. [d] Isomer shifts vs α-Fe at 298 K. [e] Quadrupole splitting. [f] Measured at 4.2 K, ref 13b.

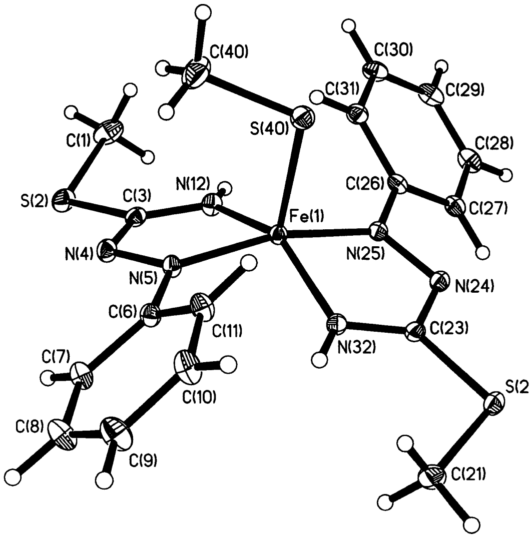

Figure 6. Structure of a neutral molecule in crystals of **1** (thermal ellipsoids are drawn at the 50% level).

isomer shift, δ, and quadrupole splitting, ΔE_Q, parameters of 0.06 mm s^{-1} and 2.32 mm s^{-1}, respectively, for **1**, and 0.20 mm s^{-1} and 2.21 mm s^{-1}, respectively, for **2**. Table 2 summarizes some pertinent Mössbauer spectroscopic data for ferric complexes. An isomer shift in the range 0.06−0.30 mm s^{-1} and a large quadrupole splitting 2.3−3.5 mm s^{-1} in five-coordinate complexes are indicative of a local intermediate spin ferric ion ($S_{Fe} = {}^3/_2$).[14] Thus, the Mössbauer spectra of **1** and **2** nicely agree with the notion that a local intermediate spin ferric ion is coupled strongly antiferromagnetically to two ligand π radical anions $(L^{Me\bullet})^{1-}$ generating the observed doublet ground state of **1** and **2**. The data reported for $[Fe^{III}(L_O^{ISQ})_2I]$[12] and $[Fe^{III}(L_S^{ISQ})_2I]$[13] are similar. Interestingly, $[Fe^{III}(L_O^{ISQ})_2Cl]$,[12] the exact analogue of **2**, possesses a quartet ground state ($S_t = {}^3/_2$) originating from a high spin ferric ion ($S_{Fe} = {}^5/_2$) coupled antiferromagnetically to two π radical anions $(L_O^{ISQ})^{1-\bullet}$. Its Mössbauer data are clearly different from those of **2**.

The observation that the isomer shift values of **1** and **2** differ by 0.14 mm s^{-1} is due to differing covalency of an apical Fe^{III}−S bond in **1** vs an Fe−Cl bond in **2**. For example, we have previously shown[15] that variation of only the sixth ligand X in $[Fe^{II}(pyS_4)X]$ complexes where X is either a bridging thiolate, a phosphine, or a carbonyl ligand brings about an isomer shift variation of 0.25 mm s^{-1} (Table 2). Significantly, the *g* values of the EPR spectrum of **1** cannot originate from a low spin ferric ion ($S_{Fe} = {}^1/_2$, d^5) because the smallest *g* value should then be <2, which is clearly not the case.

Crystal Structures. The crystal structures of **1** and **2** have been determined by X-ray crystallography at 100 K with high precision. Figures 6 and 7 show the neutral molecules in crystals of **1** and **2**, respectively. Table 3 summarizes important bond lengths and angles. The average bond distance has an error not larger than ±0.01 Å (3σ!). This allows an unambiguous determination of the protonation and oxidation levels of the ligands in **1** and **2**.

Both crystals consist of mononuclear, five-coordinate neutral molecules of $[Fe(L^{Me\bullet})_2X]$ (X = $^-SCH_3$ in **1** and Cl^-

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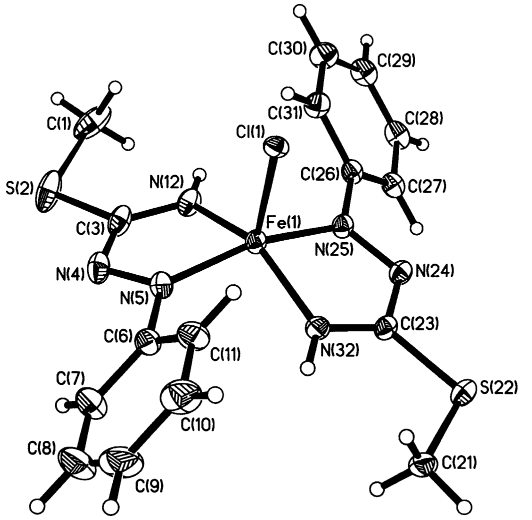

Figure 7. Structure of a neutral molecule in crystals of **2** (thermal ellipsoids are drawn at the 50% level).

Table 3. Selected Bond Distances (Å) and Angles (deg)

	1	**2**
Fe−X	2.2313(3)	2.2863(6)
Fe−N12	1.8944(9)	1.892(2)
Fe−N5	1.8758(9)	1.882(2)
Fe−N25	1.8937(9)	1.892(2)
Fe−N32	1.8837(9)	1.889(2)
N12−C3	1.320(1)	1.307(3)
C3−N4	1.348(1)	1.350(3)
N4−N5	1.341(1)	1.335(3)
N5−C6	1.422(1)	1.423(3)
C3−S2	1.754(1)	1.751(2)
S2−C1	1.805(1)	1.793(4)
N32−C23	1.318(1)	1.313(3)
C23−N24	1.343(1)	1.352(3)
N24−N25	1.347(1)	1.339(3)
N25−C26	1.420(1)	1.422(3)
S22−C23	1.755(1)	1.749(2)
C21−S22	1.802(1)	1.802(3)
N5−Fe−N32	94.24(4)	94.60(9)
N5−Fe−N25	164.18(4)	160.04(9)
N32−Fe−N25	79.21(4)	79.11(8)
N5−Fe−N12	79.26(4)	79.05(9)
N32−Fe−N12	145.69(4)	146.75(9)
N25−Fe−N12	97.97(4)	95.77(8)
N5−Fe−S40	100.26(3)	99.99(6)[a]
N32−Fe−S40	106.17(3)	105.35(6)[a]
N25−Fe−S40	95.41(3)	99.94(6)[a]
N12−Fe−S40	108.14(3)	107.89(7)[a]
C40−S40−Fe	107.22(5)	

[a] The atom S40 is to be replaced by the atom Cl1.

in **2**). The iron ions are in a square-base pyramidal environment of FeN_4S in **1** and FeN_4Cl in **2**. The coordinated sulfur atom and the chloride ligand occupy an apical position, respectively; the two N,N-coordinated $(L^{Me\bullet})^{1-}$ monoanions are in trans positions with respect to each other occupying four basal binding sites. The metrical details of the $Fe(L^{Me\bullet})_2$ unit are within experimental error identical in both compounds.

The average Fe−N bond distances of 1.887(1) Å in **1** and 1.889(3) Å in **2** clearly indicate the presence of an intermediate spin ferric ion in both complexes where the antibonding $d_{x^2-y^2}$ orbital is not occupied. In $[Fe(L_O^{ISQ})_2I]$[12] ($S_t = {}^1/_2$, $S_{Fe} = {}^3/_2$) a similar average Fe−N bond length is found at 1.885(2) Å. In $[Fe(L_O^{ISQ})_2Cl]$ ($S_t = {}^3/_2$; $S_{Fe} = {}^5/_2$) the average Fe−N bond distance is 2.041 Å.[12]

The geometrical features of the two five-membered chelate rings Fe−N−C−N−N in each compound are identical within experimental error. The two C−N and especially the N−N bond length are indicative of the presence of the π radical anions $(L^{Me\bullet})^{1-}$ and not its reduced dianion $(L^{Me})^{2-}$ or its oxidized neutral ligand $(L^{Me,ox})^0$ as shown in Figure 1. Indeed, the N−N bond at 1.34 ± 0.01 Å in **1** and **2** is intermediate between an N−N single bond as in, for example, hydrazine at 1.44 Å and a genuine N═N double bond at ∼1.24 Å in diimines R−N═N−R. Similarly, the two C−N bonds are intermediate between C−N single (∼1.48 Å) and double bonds (1.30 Å). The dimensions of the chelate rings in **1** and **2** are identical to those reported for $[Ni^{II}(L^{Me\bullet})_2]$[1] and $[Co^{III}(L^{Me\bullet})_2I]$,[3] both of which are diamagnetic and shown in Figure 1.

It is therefore clear that **1** and **2** contain each two N,N-coordinated π radical anions $(L^{Me\bullet})^{1-}$, which renders the central iron ion a d^5 ferric ion, the local spin state of which is $S_{Fe} = {}^3/_2$. An antiferromagnetic coupling to the two radical spins yields then the observed $S_t = {}^1/_2$ ground state for **1** and **2**, respectively.

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Supporting Information Available: Complete listings of atom coordinates, bond lengths and bond angles, anisotropic thermal parameters, and calculated positional parameters of hydrogen atoms for complexes **1** and **2**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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