Inorganic Chemistry

Article

Molecular and Electronic Structures of Iron(II)/(III) Complexes Containing N,S-Coordinated, Closed-Shell *o*-Aminothiophenolato(1−) and *o*-Iminothiophenolato(2−) Ligands

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The coordination chemistry of the ligands *o*-aminothiophenol, H(abt), 4,6-di-*tert*-butyl-2-aminothiophenol, H[L^{AP}], and 1,2-ethanediamine-*N,N'*-bis(2-benzenethiol), H$_4$('N$_2$S$_2$'), with FeCl$_2$ under strictly anaerobic and increasingly aerobic conditions has been systematically investigated. Using strictly anaerobic conditions, the neutral, air-sensitive, yellow complexes (μ-S,S)[Fe^{II}(abt)$_2$]$_2$ (**1**), (μ-S,S)[Fe^{II}(L^{AP})$_2$]$_2$·8CH$_3$OH (**2**), and (μ-S,S)[Fe^{II}('H$_2$N$_2$S$_2$')]$_2$·CH$_3$CN (**3**) containing high spin ferrous ions have been isolated where (abt)$^{1-}$, (L^{AP})$^{1-}$, and ('H$_2$N$_2$S$_2$')$^{2-}$ represent the respective N,S-coordinated, aromatic *o*-aminothiophenolate derivative of these ligands. When the described reaction was carried out in the presence of trace amounts of O$_2$ and [PPh$_4$]Br, light-green crystals of [PPh$_4$][Fe^{II}(abt)$_2$(itbs)]·[PPh$_4$]Br (**4**) were isolated. The anion [Fe^{II}(abt)$_2$(itbs)]$^-$ contains a high spin ferrous ion, two N,S-coordinated *o*-aminophenolate(1−) ligands, and an S-bound, monoanionic *o*-iminothionebenzosemiquinonate(1−) π radical, (itbs)$^-$. Complex **4** possesses an $S_t = {}^3/_2$ ground state. In the absence of [PPh$_4$]Br and presence of a base NEt$_3$ and a little O$_2$, the ferric dimer (μ-NH,NH)[Fe^{III}(L^{AP})(L^{IP})]$_2$ (**5a**) and its isomer (μ-S,S)[Fe^{III}(L^{AP})(L^{IP})]$_2$ (**5b**) formed. (L^{IP})$^{2-}$ represents the aromatic *o*-iminothiophenolate(2−) dianion of H[L^{AP}]. The structures of compounds **2**, **4**, and **5a** have been determined by X-ray crystallography at 100(2) K. Zero-field Mössbauer spectroscopy of **1**, **2**, **3**, and **4** unambiguously shows the presence of high spin ferrous ions: The isomer shift at 80 K is in the narrow range 0.85–0.92 mm s^{-1}, and a large quadrupole splitting, $|\Delta E_Q|$, in the range 3.24–4.10 mm s^{-1}, is observed. In contrast, **5a** and **5b** comprise both intermediate spin ferric ions ($S_{Fe} = {}^3/_2$) which couple antiferromagnetically in the dinuclear molecules yielding an $S_t = 0$ ground state.

Introduction

The coordination chemistry of *o*-aminothiophenolato ligands with iron ions has been fairly extensively studied since the original paper by Larkworthy and Philips et al.[1] in 1968 who reported the dimeric complex (μ-S,S)[Fe^{II}(abt)$_2$]$_2$ where (abt)$^{1-}$ represents the N,S-coordinated, aromatic monoanion *o*-aminothiophenolate(1−). Since then a number of ferrous and ferric complexes of this kind have been reported.[2−14]

Sellmann et al.[15,16] described the facile synthesis, crystal structures, and spectroscopic properties of stable *o*-amino-thiophenolato complexes of high-valent Fe^{IV} and even Fe^V.

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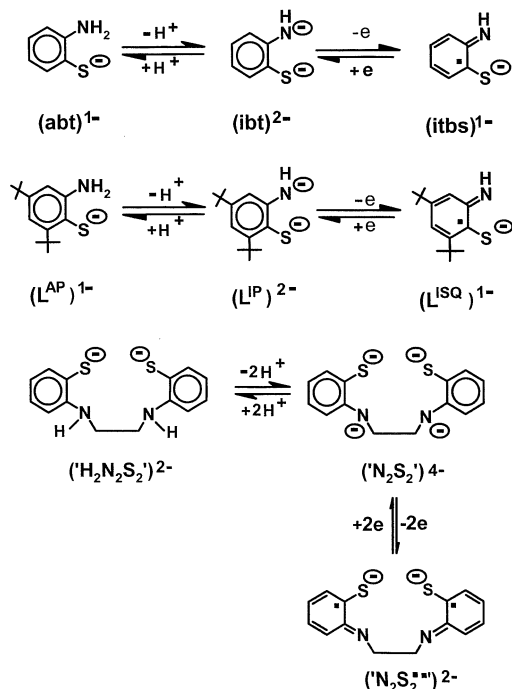
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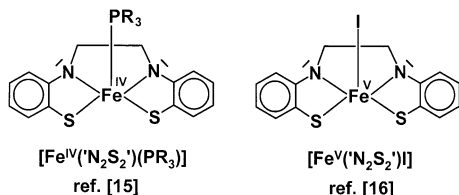(6) Sellmann, D.; Käppler, O. *Z. Naturforsch.* **1987**, *42b*, 1291.

Structures of Fe(II)/(III) Complexes

Scheme 1. Ligand and Abbreviations

(abt)$^{1-}$ (ibt)$^{2-}$ (itbs)$^{1-}$

(L^{AP})$^{1-}$ (L^{IP})$^{2-}$ (L^{ISQ})$^{1-}$

('H$_2$N$_2$S$_2$')$^{2-}$ ('N$_2$S$_2$')$^{4-}$

('N$_2$S$_2$$^{\bullet\bullet}$')$^{2-}$

In these latter two species, the deprotonated *o*-iminothiophenolate(2−) dianion was proposed to be present.

[Fe^{IV}('N$_2$S$_2$')(PR$_3$)]
ref. [15]

[Fe^V('N$_2$S$_2$')I]
ref. [16]

In contrast, in a recent publication we have shown[17] that *o*-aminothiophenolates are redox noninnocent ligands in the sense that they can be N,S-coordinated to transition metal ions (i) as closed-shell, aromatic *o*-aminothiophenolates(1−), (ii) as aromatic *o*-iminothiophenolate(2−) dianions, and, contrary to common wisdom, also (iii) as open-shell *o*-iminothionebenzosemiquinonate(1−) monoanions (Scheme 1). Thus, we have established that it is experimentally possible to distinguish between the two electronic structures **A** and **B** by using high-quality, single crystal X-ray crystallography.

A   B

The most distinctive structural features of an N,S-coordinated *o*-iminothionebenzosemiquinonato(1−) π radical are the experimentally observed, short C−S and C−N bond lengths at 1.72 ± 0.01 and 1.36 ± 0.01 Å, respectively, which are observed at 1.76 ± 0.01 and 1.40 ± 0.01 Å in the aromatic dianions (L^{IP})$^{2-}$ or (ibt)$^{2-}$ shown in Schemes 1 and

Scheme 2. Bond Lengths in N,S-Coordinated Anions

(L^{AP})$^{1-}$ (L^{IP})$^{2-}$ (L^{ISQ})$^{1-}$

1.46   1.41   1.36 1.36
1.76   1.76   1.42 1.41 1.42
                   1.36   1.72

av. C−C: av. C−C:
1.39 Å   1.39 Å

2. In addition, N,S-coordinated (L^{ISQ})$^{1-}$ and (itbs)$^{1-}$ radicals display a quinoid type distortion of the six-membered ring which is not observed in their closed-shell analogues. This distortion comprises two alternating short C−C distances at 1.37 ± 0.01 Å and four longer ones at ~1.415 ± 0.01 Å, whereas in the closed-shell, aromatic mono- and dianions, the six C−C bond lengths are equidistant at 1.39 ± 0.01 Å (Scheme 2).

In the past, many authors have not explicitly considered the presence of *o*-iminothionebenzosemiquinonate(1−) π radicals in a given coordination compound but have invariably derived the formal oxidation state of the central metal ion by assuming the closed-shell *o*-iminothiophenolate dianion to be present. This practice leads to a situation where the formal oxidation number and the physical or spectroscopic oxidation state differ by one unit.[17]

As it is possible to determine the true d^n electron configuration of the central metal ion and measure its physical or spectroscopic oxidation state spectroscopically (UV−vis, EPR, magnetic circular dichroism (MCD), or X-ray absorption near edge (XANE) spectroscopy) and/or magnetochemically, we decided to (re)investigate the coordination chemistry of iron with *o*-aminothiophenol derived ligands. This appeared to be very appealing because Mössbauer spectroscopy gives independent, valuable information about the d^n electron configuration in a given complex. We will show in this work and a subsequent paper that physical or spectroscopic oxidation states >III of the central iron ions have not been reached in this chemistry.
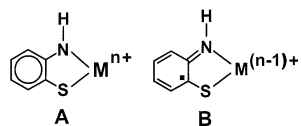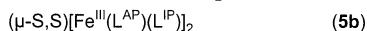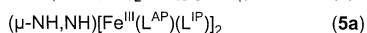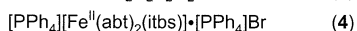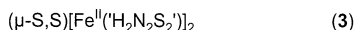
In order to avoid solubility problems often encountered in compounds containing the unsubstituted *o*-aminothiophenolates, we decided to use Sellmann's ligands 4,6-di-*tert*-butyl-2-aminothiophenol,[6] H[L^{AP}], and 1,2-ethanediamine-*N*,*N*′-bis(2-benzenethiol),[19] H$_2$('H$_2$N$_2$S$_2$').

In this paper, the first part of two successive papers, we will describe the synthesis and spectroscopic characterization of iron(II)/(III) complexes containing N,S-coordinated, closed-shell *o*-aminothiophenolate(1−) or *o*-iminothiophenolato(2−) ligands. In the second part (Ghosh, P.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.*, in press), we will then discuss compounds containing N,S-coordinated open-shell *o*-iminothionebenzosemiquinonate(1−) π radical ligands. Scheme 3 summarizes the complexes prepared here.

Experimental Section

The ligand 4,6-di-*tert*-butyl-2-aminothiophenol (2-mercapto-3,5-di-*tert*-butylaniline), H[L^{AP}], was prepared by using the elegant route

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Scheme 3. Complexes Prepared in This Study

Complexes:

(μ-S,S)[Fe^{II}(abt)$_2$]$_2$	**(1)**
(μ-S,S)[Fe^{II}(L^{AP})$_2$]$_2$	**(2)**
(μ-S,S)[Fe^{II}('H$_2$N$_2$S$_2$')]$_2$	**(3)**
[PPh$_4$][Fe^{II}(abt)$_2$(itbs)]·[PPh$_4$]Br	**(4)**
(μ-NH,NH)[Fe^{III}(L^{AP})(L^{IP})]$_2$	**(5a)**
(μ-S,S)[Fe^{III}(L^{AP})(L^{IP})]$_2$	**(5b)**

described by Sellmann and Käppler[6] with a slight modification. In contrast to the original procedure, we have not prepared the zinc(II) complex as a means for purification but oxidized the crude solution containing the ligand with air instead which yields the disulfide ($C_{14}H_{22}NS$)$_2$ in quantitative yield as yellow crystalline and air-stable solid. ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 1.23$ (s, 18H), 1.31 (s, 18H); 4.27 (4H), 6.56 (d, 2H), 6.76 (d, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) $\delta = 31.08$, 31.86, 34.80, 37.34, 110.74, 114.43, 151.17, 153.42, 153.92. 1,2-Ethanediamine-N,N'-bis(2-benzenethiol) has been prepared as described in ref 19.

Syntheses of Complexes. (μ-S,S)[Fe^{II}(abt)$_2$]$_2$ (1). This very air-sensitive complex has been described previously.[1] We have used a simplified route for its preparation. To a deaerated methanolic solution (60 mL) of 2-aminothiophenol (0.50 g; 4.0 mmol) and triethylamine (0.45 g; 4.0 mmol) was added under strictly anaerobic conditions (glovebox) FeCl$_2$·4H$_2$O (0.40 g; 2.0 mmol). The reaction mixture was heated to reflux under an Ar atmosphere for 3 h during which time a pale yellow, air-sensitive precipitate formed which was filtered off. IR(KBr disk): ν_{as}(NH$_2$) 3269, 3255 cm^{-1}; ν_s(NH$_2$) 3104, 3060 cm^{-1}. Anal. Calcd for C$_{24}$H$_{24}$Fe$_2$N$_4$S$_4$: C, 47.38; H, 3.98; N, 9.21; S, 21.08. Found: C, 47.1; H, 4.0; N, 9.1; S, 21.3.

(μ-S,S)[Fe^{II}(L^{AP})$_2$]$_2$·8CH$_3$OH (2). To a solution of 4,6-di-*tert*-butyl-2-aminothiophenol (H[L^{AP}]) (0.50 g; 2.0 mmol) and triethylamine (0.2 g; $\sim$2.0 mmol) in dry CH$_3$OH (60 mL) was added under strictly anaerobic conditions (glovebox, Ar) FeCl$_2$·4H$_2$O (0.20 g; 1.0 mmol). The yellow reaction mixture was stirred at 20 °C for 15 min and stored in a glovebox for 4 days within which time yellow crystals of **2** were obtained. Yield: 0.70 g (70%). IR(KBr disk): ν_{as}(NH$_2$) 3298, 3267; ν_s(NH$_2$) 3208 cm^{-1}. Anal. Calcd for C$_{56}$H$_{88}$Fe$_2$N$_4$S$_4$ (after drying in vacuo): C, 63.62; H, 8.39; N, 5.30; S, 12.13; Fe, 10.56. Found: C, 63.5; H, 8.4; N, 5.2; S, 12.3; Fe, 10.6.

(μ-S,S)[Fe^{II}('H$_2$N$_2$S$_2$')]$_2$·CH$_3$CN (3). To a degassed solution of the ligand 1,2-ethanediamine-N,N'-bis(2-benzenethiol) (0.60 g; 2.2 mmol) in dry acetonitrile (40 mL) was added under an Ar blanketing atmosphere FeCl$_2$ (0.254 g; 2.0 mmol). Triethylamine (0.355 g) was added dropwise with stirring at ambient temperature under strictly anaerobic conditions (glovebox). Within 2 h of stirring, a yellow, microcrystalline solid formed which was collected by filtration, washed with acetonitrile, and dried. The material is very air-sensitive and must be stored under Ar. Yield: 0.58 g (84%). Anal. Calcd for C$_{28}$H$_{28}$N$_4$S$_4$Fe$_2$·CH$_3$CN: C, 51.36; H, 4.45; N, 9.98; S, 18.28. Found: C, 51.5; H, 4.3; N, 10.4; S, 18.0. IR(KBr disk): ν(N$-$H) 3264 cm^{-1}.

[PPh$_4$][Fe^{II}(abt)$_2$(itbs)]·[PPh$_4$]Br (4). To a solution of the ligand H[L^{AP}] (0.38 g; 3.0 mmol) and triethylamine (0.3 g; 3.0 mmol) in *aerated* tetrahydrofurane (60 mL) were added under an Ar protecting atmosphere FeCl$_2$·4H$_2$O (0.20 g; 1.0 mmol) and [PPh$_4$]Br (0.42 g; 2.0 mmol). The mixture was stirred at ambient temperature for 10 min and stored in a closed vessel under Ar for 2 days. During this time, yellowish-green crystals of **4** grew on the walls of the flask along with an amorphous yellow powder of probably **1**. After

decanting the THF solvent, the crystals of **4** were separated manually by using a needle and transferred to a vial in a glovebox. Yield: 0.70 g (60%). Anal. Calcd for C$_{66}$H$_{57}$BrFeN$_3$P$_2$S$_3$: C, 66.84; H, 4.84; N, 3.54; Br, 6.74; S, 8.11; Fe, 4.71. Found: C, 66.8; H, 4.7; N, 3.5; Br, 6.2; S, 8.1.

(μ-NH,NH)[Fe^{III}(L^{AP})(L^{IP})]$_2$ (5a). To a solution of the ligand H[L^{AP}] (0.50 g; 2.1 mmol) in dry O$_2$-saturated CH$_3$CN (50 mL) was added under an argon blanketing atmosphere FeCl$_2$ (0.13 g; 1.0 mmol). Triethylamine (0.20 g; 2.0 mmol) was added to this yellow reaction mixture whereupon a rapid color change to green was observed. After the solution was stirred for 1 h at ambient temperature, a light blue-green precipitate of **5a** formed which was collected by filtration and dried under argon. Yield: 0.40 (76%). Single crystals suitable for X-ray crystallography of **5a**·2CH$_3$CN· CH$_2$Cl$_2$ were grown from a solution of CH$_2$Cl$_2$ (40 mL) and CH$_3$CN (20 mL) containing 100 mg of **5a** by slow evaporation of the solvent under argon. IR(KBr disk): ν(N$-$H) 3208, 3146, 3175, 3122, 3076, 3055. Anal. Calcd for C$_{56}$H$_{86}$Fe$_2$N$_4$S$_4$: C, 63.74; H, 8.21; N, 5.31; S, 12.15; Fe, 10.62. Found: C, 64.0; H, 8.2; N, 5.4; S, 12.2; Fe, 10.6.

(μ-S,S)[Fe^{III}(L^{AP})(L^{IP})]$_2$·2CH$_3$CN·CH$_3$OH (5b). When the same reaction as described for **5a** was carried out in dry, O$_2$-saturated CH$_3$CN (30 mL) and dry CH$_3$OH (10 mL) containing Li[OCH$_3$] (3 mmol), a brown precipitate of **5b** was obtained. Yield: 0.47 g (80%). IR(KBr disk): ν(N$-$H) 3314, 3280, 3264. After drying **5b** in vacuo for 12 h at 45 °C, the elemental analysis (C, H, N, S, Fe) was nearly identical to that of **5a**.

X-ray Crystallographic Data Collection and Refinement of the Structures. A dark brown single crystal of **2**, a yellow crystal of **4**, and a deep green specimen of **5a** were coated with perfluoropolyether, picked up with a glass fiber, and immediately mounted in the nitrogen cold stream of the diffractometers to prevent loss of solvent. Intensity data were collected at 100 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Final cell constants were obtained from a least-squares fit of a subset of several thousand strong reflections. Data collection was performed by hemisphere runs taking frames at 0.3° (Siemens SMART) and 1.0° (Nonius Kappa-CCD) in ω. A semiempirical absorption correction using the program SADABS[20] was performed on the data set of **5a**, and intensity data of **4** were corrected with MulScanAbs[21] while data of **2** were left uncorrected. Crystallographic data of the compounds and diffractometer types used are listed in Table 1. The Siemens ShelXTL[22] software package was used for solution, refinement, and artwork of the structure. The structures were readily solved by direct methods and difference Fourier techniques. All non-hydrogen atoms except some atoms in disordered parts were refined anisotropically, and hydrogen atoms attached to carbon atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Hydrogens attached to nitrogen atoms were, where possible, located from the difference map and refined with restrained N$-$H distances using the SADI option. Disordered solvent molecules in **2** and **5a** were refined using a split atom model with restrained distances. The bromide anion in **4** was split over two positions with refined occupation factors of about 0.85 and 0.15 giving both positions the equal displacement parameters.

Physical Measurements. Electronic spectra of complexes were recorded with an HP 8452 A diode array spectrophotometer

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

Table 1. Crystallographic Data for **2**·8CH₃OH, **4**, and **5a**·2CH₃CN·CH₂Cl₂

	2	**4**	**5a**
chem formula	$C_{64}H_{120}Fe_2N_4O_8S_4$	$C_{66}H_{57}BrFeN_3P_2S_3$	$C_{61}H_{94}Cl_2Fe_2N_6S_4$
fw	1313.58	1186.03	1222.26
space group	$P\bar{1}$, No. 2	$P2_12_12_1$, No. 19	$P\bar{1}$, No. 2
a, Å	10.7231(12)	12.5998(4)	10.6430(8)
b, Å	11.727(2)	19.5165(8)	10.6610(8)
c, Å	16.112(2)	23.3203(11)	17.0322(12)
α, deg	83.38(2)	90	76.64(2)
β, deg	71.77(2)	90	72.79(2)
γ, deg	71.40(2)	90	66.92(2)
V, Å	1823.6(4)	5734.6(4)	1683.6(2)
Z	1	4	1
T, K	100(2)	100(2)	100(2)
ρ calcd, g cm^{-3}	1.196	1.374	1.205
diffractometer	Nonius Kappa-CCD	Nonius Kappa-CCD	Siemens SMART
reflns collected/θ_{max}	13233/24.99	49899/27.50	18536/33.19
unique reflns/[$I > 2\sigma(I)$]	6335/4571	13137/11149	11050/8025
no. params/restraints	365/21	689/0	381/3
μ(Mo Kα), cm^{-1}	5.62	11.69	6.74
R1^a/GOF^b	0.0711/1.063	0.0600/1.037	0.0544/1.034
wR2^c ($I > 2\sigma(I)$)	0.1627	0.1465	0.1641

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

(range: 190−1100 nm). 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 and where appropriate for temperature-independent paramagnetism, TIP. 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.

Results and Discussion

Syntheses and Characterization of Complexes. The reaction of the ligand *o*-aminothiophenol, H[abt], or 4,6-di-*tert*-butyl-2-aminothiophenol, H[L^{AP}], or 1,2-ethanediamine-*N,N*′-bis(2-benzenethiol), H₂(H₂N₂S₂), and 2 or 1 equiv of triethylamine in dry methanol or acetonitrile with FeCl₂ under strictly anaerobic conditions at ambient temperature affords the yellow, microcrystalline, extremely air-sensitive complexes (μ-S,S)[Fe^{II}(abt)₂]₂ (**1**), (μ-S,S)[Fe^{II}(L^{AP})₂]₂ (**2**), and (μ-S,S)[Fe^{II}('H₂N₂S₂')]₂ (**3**), respectively. These compounds consist of two N,S-coordinated, aromatic *o*-aminothiophenolato(1−) ligands and a high spin ferrous ion. Two such monomeric units are connected via two thiolato bridges rendering the Fe^{II} ions five-coordinate (FeN₂S₃).

Complex **1** has been described previously[1] as an insoluble, yellow powder. From variable-temperature (70−310 K) magnetic susceptibility measurements, it was concluded[1] that two high spin ferrous ions ($S_{Fe} = 2$) are antiferromagnetically coupled with $J = -11.1$ cm^{-1}; converted according to the notation of eq 1, $g = 2.07$, yielding the diamagnetic ground state $S_t = 0$. We have repeated these measurements in the range 4−300 K, and from a fit of the data to the Hamiltonian, eq 1, the following parameters have been established: $J = -47 \pm 4$ cm^{-1}, $g = 2.0$ (fixed), $D_1 = D_2 = 10 \pm 5$ cm^{-1}; $E/D = 0$ (fixed), and a paramagnetic impurity of $S = \frac{5}{2}$ of
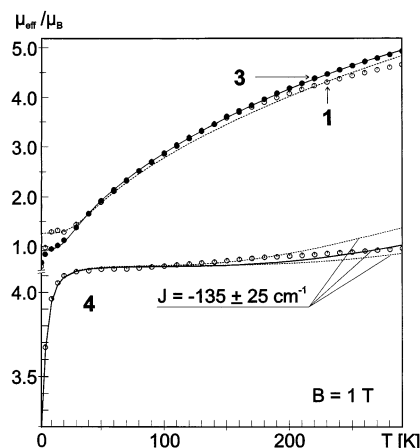

Figure 1. Temperature dependence of the magnetic moment, μ_{eff}, of dinuclear **1** and **3** (top) and mononuclear **4** (bottom). The parameters for the best fit are given in the text.

4.5% (or 5.6% for $S = 2$). We note that the present (see Figure 1) and the previous experimental data[1] of **1** in the range 80−300 K are in good agreement. The discrepancy of J values is due to errors in the fitting procedure in ref 1.

$$H = -2J\vec{S}_1 \cdot \vec{S}_2 + \sum_{i=1}^{2}[D_i(S_{z,i}^2 - \frac{1}{3}S_i(S_i + 1)] + g_i\mu_B \cdot \vec{S}_i \cdot \vec{B}$$

(1)

The structure of **1** can be composed of either two *cis*-FeN₂S₂ or two *trans*-FeN₂S₂ monomers which are bridged in both instances by two μ-thiophenolato groups.


1
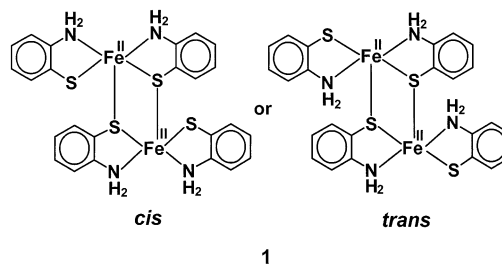
In order to obtain a more soluble analogue of **1**, the dimeric yellow complex (μ-S,S)[Fe^{II}(L^{AP})$_2$]$_2$·8CH$_3$OH (**2**) was synthesized by using the described protocol but with the ligand 4,6-di-*tert*-butyl-2-aminothiophenol. The crystal structure determination of **2** (see later) confirms the dimeric nature of this species. The magnetic moment of **2** at 295 K is 4.2 μ_B per dimer which corresponds nicely to the value of 4.0 μ_B determined for **1** at this temperature.

2
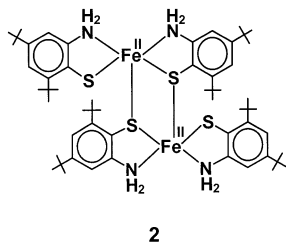
By using 1,2-ethanediamine-*N,N*′-bis(2-benzenethiol) as starting material in the preparation, yellow microcrystals of (μ-S,S)[Fe^{II}(′H$_2$N$_2$S$_2$′)]$_2$·CH$_3$CN (**3**) were obtained. The magnetic moment of 5.5 μ_B at 295 K indicates the dimeric nature of **3**. Figure 1 shows the temperature dependence of the magnetic moment per dimer and a best fit which was obtained with $g_{Fe} = 2.18 \pm 0.2$, $J = -35 \pm 2$ cm^{-1} ($S_1 = S_2 = 2$), $|D| = 10 \pm 5$ cm^{-1}, a paramagnetic impurity $S = {}^5/_2$ of 2% (or 2.5% for $S = 2$), and $\chi_{TIP} = 300 \times 10^{-6}$ emu.


3
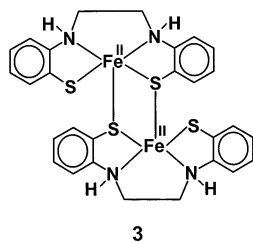
Since **1**, **2**, and **3** each contain a high spin ferrous ion and the ligands are in their fully reduced forms, namely N,S-coordinated *o*-aminothiophenolate, we decided to study the reaction products under more aerobic (oxidizing) conditions. To this end, we first used dioxygen saturated solvents but performed the reactions under an argon blanketing atmosphere (the solvents were not purged with argon). Thus, from an aerated tetrahydrofuran solution of the ligand H[L^{AP}] and NEt$_3$ and FeCl$_2$·4H$_2$O (3:3:1) to which [PPh$_4$]Br had been added, yellow-green crystals of [PPh$_4$][Fe^{II}(abt)$_2$(itbs)]·[PPh$_4$]Br (**4**) grew within 2 days under Ar at 20 °C on the wall of the vessel in ∼70% yield. In addition, a small amount of yellow, microcrystalline **1** precipitated which was decanted off with the solvent. The yellow-green crystals were then manually collected with a long needle under anaerobic conditions.

4
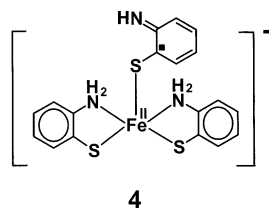
Complex **4** is air-sensitive and was stored under argon in a refrigerator. The crystal structure determination (see later) clearly establishes the presence of the mononuclear mono-anion [Fe^{II}(abt)$_2$(itbs)]$^-$ containing a high spin ferrous ion, two N,S-coordinated *o*-aminothiophenolato(1−) anions, (abt)$^{1-}$, and, in addition, a monodentate S-coordinated iminothione-benzosemiquinonate(1−) radical, (itbs)$^{1-\bullet}$.

The temperature dependence of the magnetic moment of **4** (3−290 K) shown in Figure 1 (bottom) was modeled successfully by using the same spin Hamiltonian, eq 1, as shown. The following parameters were obtained from a best fit: a high spin ferrous ion ($S_{Fe} = 2$) is antiferromagnetically coupled to a ligand radical ($S_{rad} = {}^1/_2$) with $J = -135 \pm 25$ cm^{-1}; $g_{Fe} = 2.12 \pm 0.1$, $g_{rad} = 2.0$ (fixed), $|D|_{3/2} = 5.0$ cm^{-1} (fixed) yielding the observed $S_t = {}^3/_2$ ground state of **4**. Thus, trace amounts of oxygen have generated a ligand radical anion under the described reaction conditions.

By using slightly different reaction conditions as already described for the synthesis of **4**, we have discovered that it is also possible to selectively oxidize the Fe^{II} to Fe^{III} ions. Thus, the reaction of the ligand H[L^{AP}] and FeCl$_2$ (2:1) in dry acetonitrile which was saturated with dioxygen with 2 equiv of triethylamine induces a color change from yellow to green, and a bluish-green precipitate of (μ-NH,NH)-[Fe^{III}(L^{AP})(L^{IP})]$_2$ (**5a**) formed in 76% yield.

5a
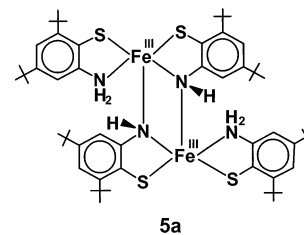
The protonation and oxidation level of the ligands in **5a** as one (L^{AP})$^{1-}$ and one (L^{IP})$^{2-}$ is corroborated by infrared spectroscopy (ν_{as}, ν_s(NH$_2$)- and ν(N−H)-stretching vibrations are observed) and its crystal structure determination (see a following section). The electron rich, N,S-coordinated di-anion (L^{IP})$^{2-}$ acts as bridging ligand via the imido group to form a dinuclear complex (FeN$_3$S$_2$ polyhedron).

When this reaction was carried out in an acetonitrile/methanol mixture using lithium methoxide as a base, a brown precipitate of presumably (μ-S,S)[Fe^{III}(L^{AP})(L^{IP})]$_2$·2CH$_3$CN·CH$_3$OH (**5b**) was obtained in excellent yields. Figure 2 shows the differing electronic spectra of **5a** and **5b** in CH$_2$Cl$_2$ solution under anaerobic conditions. We have not been able to obtain single crystals of **5b** for an X-ray structure determination. Therefore, the proposed and shown (μ-S,S)[Fe^{III}(L^{AP})(L^{IP})]$_2$ structure is tentative.
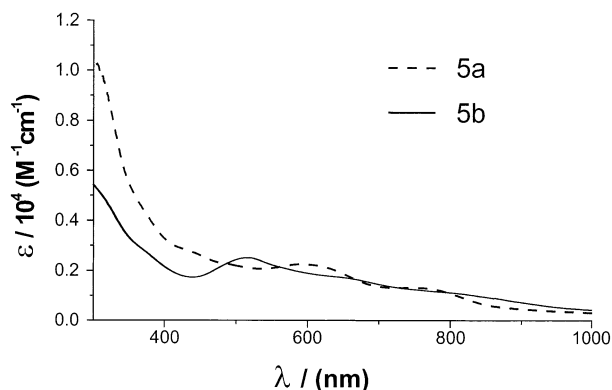

5b
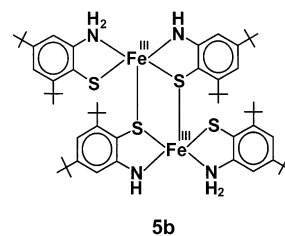
Figure 2. Electronic spectra of **5a** and **5b** in CH₂Cl₂ solution under an argon atmosphere.

Figure 4. Structure of the monoanionic complex [Fe^{II}(abt)₂(itbs)]⁻ in crystals of **4**.
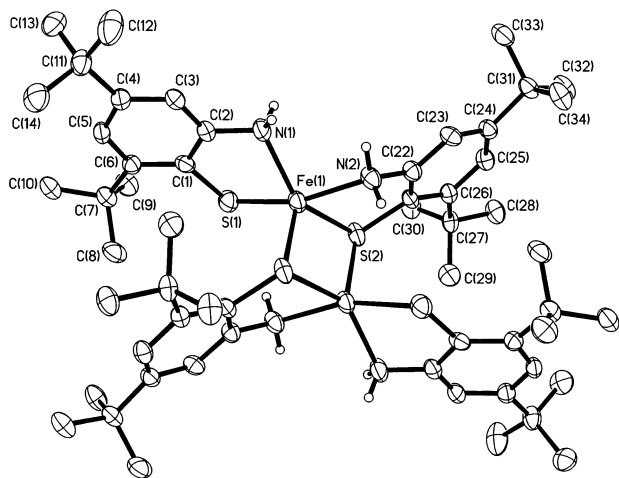

Figure 3. Structure of the dimer in crystals of **2**.

In solution (CH₂Cl₂), both **5a** and **5b** are very sensitive toward dioxygen. The resulting products are described in a subsequent paper.

Crystal Structure Determination. The structures of complexes **2**, **4**, and **5a** have been determined by X-ray crystallography at 100(2) K. As pointed out previously,[17] the geometric features of N,S-coordinated ligands $(L^{AP})^{1-}$, $(L^{IP})^{2-}$, and $(L^{ISQ})^{1-}$ differ significantly (Scheme 2) and allow the assignment of the protonation and oxidation level of a ligand in a given complex.

Figure 3 shows the structure of the dinuclear bis(μ-thiolato)diferrous complex **2**. Clearly, each iron ion is N,S-bound to two $(L^{AP})^{1-}$ ligands (in *cis* position relative to each other). The two R−NH₂ groups per monomer are not equivalent. Therefore, the IR spectrum of **2** displays *two* antisymmetric and *two* symmetric N−H stretching frequencies (see Experimental Section). This renders the central iron ions divalent. The rather long Fe−N and Fe−S bond distances are indicative of a high spin configuration (S_{Fe} = 2) (Table 2) in excellent agreement with the magnetic susceptibility measurements and the Mössbauer spectrum (see in a following section). Similar structures are proposed for complexes **1** and **3**.

Complex **4** contains in one quarter of a unit cell two tetraphenylphosphonium cations, an uncoordinated bromide anion, a water molecule of crystallization, and the mono-
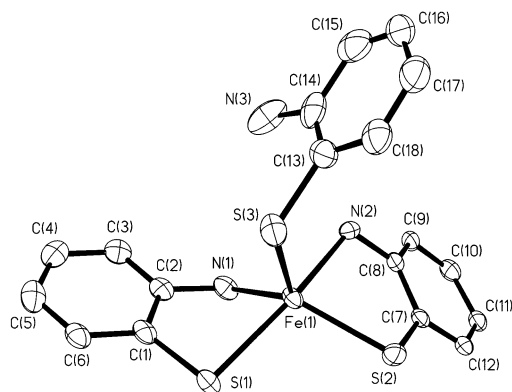
Table 2. Selected Bond Distances (Å)

Complex 2			
Fe1−N1	2.134(4)	S2−C21	1.795(4)
Fe1−N2	2.229(4)	N2−C22	1.451(6)
Fe1−S1	2.382(2)	C21−C22	1.406(6)
Fe1−S2	2.394(1)	C21−C26	1.417(6)
Fe1−S2*	2.397(2)	C22−C23	1.382(6)
Fe1−Fe1*	2.919(2)	C23−C24	1.384(6)
S1−C1	1.790(5)	C24−C25	1.386(6)
N1−C2	1.447(6)	C25−C26	1.396(6)
C1−C2	1.401(6)	C3−C4	1.374(6)
C1−C6	1.419(6)	C4−C5	1.408(6)
C2−C3	1.378(7)	C5−C6	1.385(6)
Complex 4			
Fe1−N1	2.242(4)	S2−C7	1.753(4)
Fe1−N2	2.268(4)	N2−C8	1.444(5)
Fe1−S3	2.351(1)	C7−C12	1.402(6)
Fe1−S2	2.377(1)	C7−C8	1.411(6)
Fe1−S1	2.441(1)	C8−C9	1.393(6)
S1−C1	1.771(5)	C9−C10	1.379(6)
N1−C2	1.443(6)	C10−C11	1.392(6)
C1−C6	1.389(7)	C11−C12	1.383(6)
C1−C2	1.409(6)	S3−C13	1.747(5)
C2−C3	1.378(7)	N3−C14	1.356(8)
C3−C4	1.394(7)	C13−C14	1.329(8)
C4−C5	1.392(8)	C13−C18	1.446(8)
C5−C6	1.376(7)	C14−C15	1.569(9)
		C15−C16	1.28(1)
		C16−C17	1.44(1)
		C17−C18	1.33(1)
Complex 5a			
Fe1−N2	1.928(2)	C3−C4	1.384(3)
Fe1−N1	2.013(2)	C4−C5	1.408(3)
Fe1−N2*	2.118(2)	C5−C6	1.401(3)
Fe1−S2	2.206(1)	C21−C22	1.402(3)
Fe1−S1	2.211(1)	C21−C26	1.427(3)
Fe1−Fe1*	2.7192(7)	C22−C23	1.394(3)
S1−C1	1.771(2)	C23−C24	1.393(3)
S2−C21	1.770(2)	C24−C25	1.403(3)
N1−C2	1.458(3)	C25−C26	1.391(3)
N2−C22	1.423(3)		
C1−C2	1.400(3)		
C1−C6	1.423(3)		
C2−C3	1.394(3)		

anion [Fe^{II}(abt)₂(itbs)]⁻ as shown in Figure 4. The five-coordinate anion consists of two N,S-coordinated *o*-amino-thiophenolato(1−) ligands, bound in *cis*-position relative to each other, and a monodentate, S-bound *o*-iminothione-benzosemiquinonato(1−) π radical which is disordered in crystals of **4** as was judged from the comparatively large anisotropic thermal parameters of the one nitrogen and six carbon atoms of this ligand. From the fact that the Mössbauer
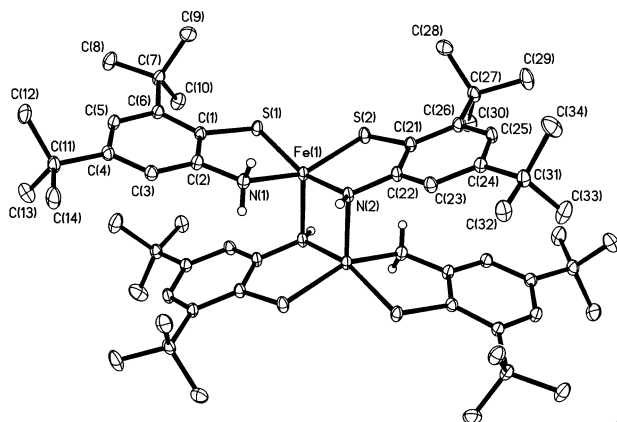
Figure 5. Structure of the dimer in crystals of **5a**.

spectrum of **4** displays *two* quadrupole doublets of very similar isomer shift and quadrupole splitting parameters, we conclude that the radical ligand $(L^{ISQ})^{1-}$ is statically disordered over two positions in a hydrophobic cavity generated by phenyl groups of two $[PPh_4]^+$ cations in the solid state. It has not been possible to resolve this disorder by a split atom model. The Fe—N and Fe—S bonds are long and indicative of a central high spin ferrous ion as in **2**.

The dimer in crystals of **5a** shown in Figure 5 has a different structure as compared to that of **2** (Figure 3). Two (μ-imido) bridges are observed, and the two N,S-chelating ligands differ in their respective level of protonation. Clearly, two terminal $(L^{AP})^{1-}$ ligands are present, as well as two dianionic, aromatic $(L^{IP})^{2-}$ ligands. The latter, electron richer dianion forms the bridges via the R—NH⁻ groups. The oxidation level of both ligands is clearly aromatic: the C—S bonds at 1.77 Å *and* the C—N bonds at 1.46 Å (terminal) and 1.42 Å (bridging) are long, and the six-membered carbon rings do not show quinoid type distortions but display six nearly equivalent C—C bonds. It is noted the C—C bond between the two carbon atoms which carry the sulfur donor atom and the *tert*-butyl group, respectively, is always at 1.41−1.42 Å irrespective of the protonation or oxidation level of the ligand. This is presumably a steric effect. This is true for all structures reported here and for those described previously.[17] The geometrical features of the bridging $(L^{IP})^{2-}$ ligand in **5a** are very similar to those reported for a terminal *o*-iminothiophenolate(2−) in square planar, diamagnetic $[(bpy)Pt^{II}(L^{IP})]$.[23]

These considerations render the iron ions in **5a** trivalent. The Fe—N and Fe—S bonds are significantly *shorter* than those in **2** and those expected for a high spin ferric ion. Therefore, the local spin states at the ferric ions in **5a** are either intermediate or low spin ($S_{Fe} = {}^3/_2$ or $^1/_2$) which are intramolecularly antiferromagnetically coupled yielding an $S_t = 0$ ground state.

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Table 3. Zero-Field Mössbauer Parameters of Complexes at 80 K

complex	δ, mm s⁻¹ [a]	$\lvert\Delta E_Q\rvert$, mm s⁻¹ [b]	S_{Fe} [c]	S_t [d]
1	0.91	4.10	2	0
2	0.85	3.68	2	0
3	0.87	3.24	2	0
4	0.92 (50%)	4.05	2	$^3/_2$
	0.88 (50%)	3.38	2	$^3/_2$
5a	0.33	0.93	$^3/_2$	0
5b	0.30	2.71	$^3/_2$	0

[a] Isomer shift vs α-Fe at 298 K. [b] Quadrupole splitting. [c] Local spin state of iron ion. [d] Ground state of molecule.
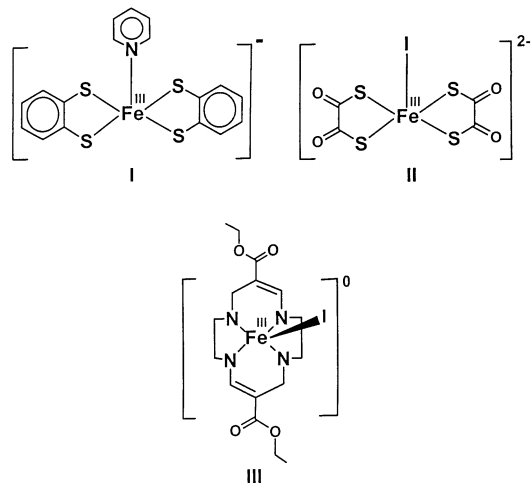
	I	II	III
δ, mm s⁻¹	0.33	0.30	0.18
ΔE_Q, mm s⁻¹	3.02	3.50	3.56
Ref.	24	25	26

Figure 6. Five-coordinate intermediate spin ferric complexes and their Mössbauer parameters at 80 K.

Zero-Field Mössbauer Spectroscopy. The zero-field Mössbauer spectra of all complexes have been recorded at 80 K; the isomer shift (vs α-Fe at 295 K) and quadrupole splitting parameters are given in Table 3.

The zero-field spectra of complexes **1**, **2**, and **3** display each a single doublet in the narrow isomer shift range 0.83− 0.92 mm s⁻¹ and quadrupole splitting range 3.38−4.10 mm s⁻¹. These values unequivocally indicate the presence of a high spin ferrous ion ($S_{Fe} = 2$) in each of these compounds. Complex **4** containing the mononuclear anion $[Fe^{II}(abt)_2(itbs)]^-$ displays two such doublets (ratio 1:1) at $\delta = 0.92$ and 0.88 mm s⁻¹, $\Delta E_Q = 4.05$ and 3.38 mm s⁻¹, which indicates the presence of two structurally slightly different iron(II) ions. As already pointed out, the S-coordinated $(itbs)^{1-}$ radical is disordered in solid **4**. Therefore, we suggest that the anion exists in two different conformations in the solid state. It is clear that both conformers contain a high spin ferrous ion.

The dinuclear complexes **5a** and **5b** both display a quadrupole doublet at a similar isomer shift of 0.33 and 0.30 mm s⁻¹, respectively, but significantly different quadrupole splittings of 0.93 and 2.71 mm s⁻¹. From magnetic susceptibility data, the X-ray structure analysis of **5a**, and from their electronic spectra, it is concluded that both complexes contain intermediate spin ferric ions ($S_{Fe} = {}^3/_2$) which couple antiferromagnetically in the dimers yielding the observed

diamagnetic ground state. Figure 6 summarizes some Mössbauer data for three genuine intermediate spin ferric complexes. These data resemble closely those of **5a** and **5b**.

Conclusion

We have shown in this part of our investigation of the reactivity of *o*-aminothiophenols with iron(II)/(III) ions under anaerobic, or dioxygen deficient, conditions that complexes containing N,S-coordinated, aromatic, closed-shell mono- and dianions, $(L^{AP})^{1-}$ or $(abt)^{1-}$, $(L^{IP})^{2-}$ or $(ibt)^{2-}$, are formed: complexes **1** and **2** are high spin ferrous species whereas **5a** and **5b** are intermediate spin ferric species. In one instance, **4**, an S-coordinated monodentate *o*-iminothionebenzosemi-quinonate(1−) π radical ligand has been identified. The aromatic tetradentate ligand $('H_2N_2S_2')^{2-}$ has been identified in the dimer $(\mu\text{-S,S})[Fe^{II}('H_2N_2S_2')]_2$ (**3**).

Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **2**, **4**, and **5a**. Figure S1 showing the Mössbauer spectra of complexes **1**−**4**, **5a**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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