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Transition-Metal Complexes with Sulfur Ligands. 62.[1] Hydrogen Evolution upon Reaction of Protons with Sulfur-Coordinated Fe(II) Complexes. Investigation of the H^+, H_2, and H^- Interactions with Iron 1,2-Benzenedithiolate Complexes

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Abstract: In search for model systems of iron hydrogenases, we investigated the interaction of iron 1,2-benzenedithiolate complexes with H^+, H_2, and H^-. The reaction of $[Fe^{II}('S_2')_2]^{2-}$ ($'S_2'^{2-}$ = 1,2-benzenedithiolate(2−)) with H^+ yielding $[Fe^{III}('S_2')_2]_2^{2-}$ and H_2 was examined in detail. A mechanism is suggested. H_2 activation by $[Fe('S_2')_2]_n^{2-}$ ($n = 1, 2$) was not observed. With an excess of $NaBH_4$, $[Fe^{III}('S_2')_2]_2^{2-}$ and $[Fe^{IV}('S_2')_2(PMe_3)_2]$ are reduced to the corresponding $[Fe^{II}('S_2')_2]^{2-}$ and $[Fe^{III}('S_2')_2(PMe_3)_2]^-$, respectively; the reduction of $[Fe^{IV}('S_2')_2(PMe_3)_2]$ with *n*-BuLi and $LiBEt_3H$ yields $[Fe^{II}('S_2')_2]^{2-}$, and no hydride complexes are found even when an excess of $LiBEt_3H$ is used.

Introduction

Hydrogenases[2,3] are the most efficient catalysts of hydrogen reactions. They catalyze the H^+/H_2 redox interconversion (eq 1) and the H/D exchange according to eq 2.

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad (1)$$

$$H_2 + D_2O \rightleftharpoons HD + HDO \qquad (2)$$

Under functional aspects, they can be divided into dissimilative (H_2 producing) and assimilative (H_2 consuming) hydrogenases, and with regard to their composition it can be distinguished between Fe/Fe and Fe/Ni hydrogenases. The active sites of both consist of metal centers predominantly coordinated by sulfur donors. For Fe/Ni hydrogenases, according to EPR spectroscopy, a change of Ni oxidation state during turnover is assumed.[4] The mechanisms of reactions 1 and 2 at the metal sulfur sites are unknown. Metal hydride [M(H)] and metal hydride thiol [M(H)(RSH)] as well as metal dithiol $[M(RSH)_2]$ intermediates were suggested.[4,5] Metal hydride complexes with sulfur ligands as potential model compounds to confirm or disprove any of the suggested mechanisms, however, are rare and generally contain transition metals of the second or third period.[6] The only examples with exclusively sulfur coordination are $[Ir(H)(TTN)_2](PF_6)_2$ (TTN = 1,4,7-trithiacyclononane),[7] $[Rh(H)(TTD)](BF_4)_2$ (TTD = 1,4,8,11-tetrathiacyclotetradecane),[8] and $[Mo(H)('S_2')_3]^{3-}$ ($'S_2'^{2-}$ = 1,2-benzenedithiolate(2−)).[9] The recently described $[Ni(H)(N(C_2H_4SR)_3)]^+$ in addition contains one amine donor.[10]

Fe/Fe hydrogenases are generally assumed to contain Fe_xS_x ($x = 2, 3, 4$) clusters as active sites,[11] and, e.g., for clostridium pasteurianum hydrogenase, three Fe_4S_4 cores can be extruded.[12] An unambiguous structural determination of the active sites by X-ray diffraction, however, is still lacking, and $[Fe_4S_4(SR)_4]^{n-}$ clusters usually do not show hydrogenase activity. $[Fe_4S_4(SR)_4]^{2-}$ rapidly decomposes after protonation in aqueous solution,[13] and to our knowledge the only reaction between an iron(II/III) sulfur complex and protons or SH functions producing dihydrogen is the reaction of $[Fe_4S_4(SPh)_4]^{3-}$ with thiols that leads to evolution of small amounts of H_2 (≤30% of the stoichiometric amount).[14] The generation of this cluster trianion, however, demands very strong reducing agents, for example, sodium acenaphthylenide.[15]

We now observed H_2 evolution when an Fe(II) salt, a sulfur ligand, and protons are combined in protic media. $FeCl_2$ and 1,2-benzenedithiolate(2−), $'S_2'^{2-}$, in methanol form $[Fe^{II}('S_2')_2]^{2-}$ that yields H_2 and the Fe(III) species $[Fe^{III}('S_2')_2]_2^{2-}$ upon reaction with protic acids. With regard to the iron sulfur centers of hydrogenases, this reaction can be considered a model reaction.

While tetracoordinate Fe(II) complexes usually are tetrahedral,[16] $[Fe^{II}('S_2')_2]^{2-}$ is uncommon with respect to its structure and magnetism:[17] It is square planar and has an unusual Fe(II) $S = 1$ intermediate spin state. X-ray structure analyses proved

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that, in its salts, $[Fe^{II}('S_2')_2]^{2-}$ is strictly mononuclear,[17,18] while the corresponding Fe(III) species forms dinuclear $[Fe^{III}('S_2')_2]_2^{2-}$ ions,[19,20] which in strongly polar solvents partially dissociate into mononuclear species.[19] The structure of $[Fe^{II}('S_2')_2]^{2-}$ contrasts theoretical considerations according to which dimer formation is expected for dithiolenes and related systems with d^5 and d^6 metal centers.[21]

The aim of our investigations was to gain closer insight into the reaction of $[Fe^{II}('S_2')_2]^{2-}$ with protons and possibly to obtain evidence for the intermediate formation of Fe–thiol or Fe–H species.

Experimental Section

Unless otherwise noted, all procedures were carried out under nitrogen at room temperature by using standard Schlenk techniques. All solvents were dried and distilled before use; deuteriated solvents were dried with activated 4-Å molecular sieves ($[d_6]$DMSO) or $LiAlH_4$ ($[d_8]$THF). 1,2-Benzenedithiol, $'S_2'-H_2$,[22] and $[Fe('S_2')_2(PMe_3)_2]$[23] were prepared as described in the literature; $FeCl_2{\cdot}4H_2O$, $FeCl_3$, NMe_4Cl, $NaBH_4$, $LiAlH_4$, and *n*-BuLi were purchased from Merck; NBu_4ClO_4 from Fluka; NaOMe, LiOMe, and $LiBEt_3H$ from Aldrich; H_2 and HCl gas from Messer Griesheim. Spectra were recorded on the following instruments: NMR, Jeol FT-JNM-GX 270; IR (KBr disks), Perkin Elmer 983; mass spectra, Varian MAT 212. Magnetic moments of solids were determined on a Johnson Matthey magnetic susceptibility balance at room temperature. GC analyses of hydrogen were performed with a Pye Unicam PU 4500 capillary chromatograph (Philips) equipped with a steel column (4 m) filled with activated carbon, 0.3–0.5 mm, using N_2 as carrier gas (40 mL/min) and a heat conductivity detector. ^{57}Fe Mössbauer investigations were carried out by using a constant acceleration spectrometer, which has been described before;[23] all velocity scales and isomer shifts are referred to the iron standard at 298 K. Cyclic voltammetry was performed with a PAR 264 A potentiostat with glassy carbon ROTEL A working, Ag/AgCl reference, and Pt counter electrodes. DMSO solutions were 10^{-4} M in complex and 0.1 M in NBu_4ClO_4 as supporting electrolyte. Potentials were referred to NHE via Cp_2Fe/Cp_2Fe^+ as an internal standard.

$(NMe_4)_2[Fe^{II}('S_2')_2]$, 1. A stirred solution of $FeCl_2{\cdot}4H_2O$ (1.70 g, 8.55 mmol) in 50 mL of THF was treated with a solution of LiOMe (1.33 g, 35 mmol) and $'S_2'-H_2$ (2.10 mL, 17.2 mmol) in 30 mL of methanol. After filtration, the air-sensitive red-yellow solution was layered with a solution of NMe_4Cl (1.97 g, 18.0 mmol) in 40 mL of methanol. Ochre-yellow crystals of **1** were separated after 3 days, washed with 50 mL of THF, and dried in vacuo for 3 h: yield 3.54 g (85%); ^{1}H NMR ($[d_6]$DMSO) δ 11.8 (4 H, s, C_6H_4), 3.0 (24 H, s, $N(CH_3)_4^+$), −9.0 (4 H, s, C_6H_4); $^{13}C\{^1H\}$ NMR ($[d_6]$DMSO) δ 349, 258 (1:2, C_6H_4), 54 ($N(CH_3)_4^+$). Anal. Calcd for $C_{20}FeH_{32}N_2S_4$ (484.59): C, 49.6; H, 6.7; N, 5.8. Found: C, 50.0; H, 6.9; N, 5.5.

$(NMe_4)_2[Fe^{III}('S_2')_2]_2$, 2. A solution of NaOMe (2.97 g, 55 mmol) and $'S_2'-H_2$ (3.31 mL, 27.0 mmol) in 40 mL of methanol was combined with a methanolic $FeCl_3$ (2.19 g, 13.5 mmol) solution (60 mL). Precipitated NaCl was removed by filtration, and the black-red solution was layered with NMe_4Cl (1.53 g, 14.0 mmol) in 40 mL of methanol. After 5 days, black crystals of **2** were filtered off, washed with 40 mL of methanol, and dried in vacuo for 1 day: yield 4.80 g (87%); ^{1}H NMR ($[d_6]$DMSO) δ 3.0 (12 H, s, $N(CH_3)_4^+$), −29, −34 (4 H each, both br s, C_6H_4); $^{13}C\{^1H\}$ NMR ($[d_6]$DMSO) δ 137 (C_6H_4), 55 ($N(CH_3)_4^+$), 15 (C_6H_4). Anal. Calcd for $C_{32}Fe_2H_{40}N_2S_8$ (820.89): C, 46.8; H, 4.9; N, 3.4. Found: C, 47.1; H, 5.0; N, 3.2.

Reactions of $[Fe^{II}('S_2')_2]^{2-}$ with H^+ to Yield $[Fe^{III}('S_2')_2]_2^{2-}$ and H_2. General Procedure. About 1.5 mmol of Fe(II) species A in 30–40 mL of solvent was introduced into a 50-mL Schlenk tube equipped with a septum inlet and connected to a gas burette. Oxidizing agent B (1 equiv) was injected in one portion to the stirred solution of species A, and gas evolution corrected for added volumes was recorded as a function of time. H_2 was determined by GC.

(a) A: $Na_2[Fe^{II}('S_2')_2]$ (1.63 mmol), generated in situ by combining a solution of NaOMe (360 mg, 6.7 mmol) and $'S_2'-H_2$ (0.40 mL, 3.3 mmol) in 10 mL of methanol with a methanolic $FeCl_2{\cdot}4H_2O$ (325 mg, 1.63 mmol) solution (20 mL). B: HCl in methanol (1.1 mL of a 1.5 M solution, 1.65 mmol).

After 1 day, the resulting black-red solution was layered with NMe_4Cl (200 mg, 1.8 mmol) in 10 mL of methanol. The precipitated black crystals of $(NMe_4)_2[Fe^{III}('S_2')_2]_2$, **2**, were separated after 5 days, washed with methanol, and dried in vacuo for 1 day: yield 510 mg (76%). Anal. Calcd for $C_{32}Fe_2H_{40}N_2S_8$ (820.89): C, 46.8; H, 4.9; N, 3.4. Found: C, 47.1; H, 5.0; N, 3.2.

(b) A: $FeCl_2{\cdot}4H_2O$ (370 mg, 1.86 mmol) in 30 mL of methanol. B: $Na_2'S_2'$ (1.9 mmol) and $Na'S_2'-H$ (1.9 mmol) by combining NaOMe (310 mg, 5.7 mmol) and $'S_2'-H_2$ (0.47 ml, 3.8 mmol) in 3 mL of methanol.

Workup and isolation of **2** were analogous to (a): yield 650 mg (85%). Anal. Calcd for $C_{32}Fe_2H_{40}N_2S_8$ (820.89): C, 46.8; H, 4.9; N, 3.4. Found: C, 46.7; H, 5.0; N, 3.1.

(c) A: $[Li(THF)_3]_2[Fe^{II}('S_2')_2]$, **3** (1210 mg, 1.55 mmol; synthesis see later), dissolved in 40 mL of THF in a Schlenk tube that had been heated in vacuo before. B: HCl in THF (2.35 mL of a 0.66 M solution, 1.55 mmol).

After 3 days, the deep red solution was concentrated to one-third in volume and kept at −30 °C for another 3 days. Black microcrystals of $[Li(THF)_3]_2[Fe^{III}('S_2')_2]_2$, **4**, were separated, washed with 20 mL of a cold 1:1 mixture of THF and *n*-hexane, and dried in vacuo for 1 day: yield 615 mg (71%); ^{1}H NMR ($[d_6]$DMSO) δ 3.6, 1.7 (12 H each, both s, THF), −29, −34 (4 H each, both br s, C_6H_4); ^{1}H NMR ($[d_8]$THF) δ −32.4, −37.2 (1:1, both s, C_6H_4).

Reaction c was monitored by ^{1}H NMR spectroscopy at 20 °C: **3** (40.2 mg, 0.051 mmol) was dissolved in 0.6 mL of $[d_8]$THF in an NMR tube. The ^{1}H NMR spectrum was recorded, gaseous HCl (1.15 mL, 0.05 mmol) was added with a syringe, and the NMR tube was sealed again. Spectra were recorded after 10 min, 45 min, 3 h, and 7 h. In an analogous NMR experiment, 2 equiv of HCl gas (1.45 mL, 0.065 mmol) were added to a solution of **3** (25.4 mg, 0.032 mmol) in 0.6 mL of $[d_8]$THF.

Investigations of Potential Reactions between H_2 and $[Fe^{III}('S_2')_2]_2^{2-}$ as well as $[Fe^{II}('S_2')_2]^{2-}$. (a) $Na_2[Fe^{III}('S_2')_2]_2$ (0.75 mmol) was generated in situ by combining a solution of NaOMe (325 mg, 6.0 mmol) and $'S_2'-H_2$ (0.37 mL, 3.0 mmol) in 15 mL of methanol with a methanolic $FeCl_3$ (245 mg, 1.5 mmol) solution (10 mL). NaOH in methanol (3.0 mL of a 2 M solution) was added, and after filtration the black-red solution was stirred for 3 days. (1) The solution was stirred under an atmosphere of hydrogen (1 bar). With NMe_4Cl (330 mg, 3.0 mmol) in 15 mL of methanol, exclusively **2** was isolated in 74% yield. (2) The solution was stirred under hydrogen at 50 bar of pressure. An ochre-colored solid byproduct was removed by filtration and not further identified. Composition and yield varied in different preparations. The filtrate was layered with NMe_4Cl (330 mg, 3.0 mmol) in 15 mL of methanol, and **2** was isolated in up to 60% yield.

(b) $FeCl_2{\cdot}4H_2O$ (190 mg, 0.95 mmol) in 15 mL of methanol was reacted with a solution of $'S_2'-H_2$ (0.23 mL, 1.9 mmol) and NaOMe (205 mg, 3.8 mmol) in 10 mL of methanol. The red-yellow solution was stirred under an atmosphere of hydrogen for 30 min. Subsequent layering with NMe_4Cl (210 mg, 1.9 mmol) in 10 mL of methanol yielded yellow crystals of **1** (61%), which were characterized by ^{1}H NMR spectroscopy.

$(NMe_4)_2[Fe^{II}('S_2')_2]$, 1, by Reduction of $[Fe^{III}('S_2')_2]_2^{2-}$ with $NaBH_4$. $Na_2[Fe^{III}('S_2')_2]_2$ (0.40 mmol) was generated in situ by reacting a solution of $FeCl_3$ (130 mg, 0.80 mmol) in 15 mL of methanol with a methanolic solution (10 mL) of NaOMe (180 mg, 3.3 mmol) and $'S_2'-H_2$ (0.20 mL, 1.6 mmol). The black-red solution was treated with $NaBH_4$ until the color had turned to red-yellow. The suspension was filtered when gas evolution had finished, and the filtrate was layered with NMe_4Cl (180 mg, 1.6 mmol) in 10 mL of methanol. Yellow crystals of **1** precipitated and were collected after 1 day, washed with 15 mL of methanol, and dried in vacuo for 1 day: yield 100 mg (26%). Anal. Calcd for $C_{20}FeH_{32}N_2S_4$ (484.59): C, 49.6; H, 6.7; N, 5.8. Found: C, 49.2; H, 6.7; N, 5.3.

$(NMe_4)[Fe('S_2')_2(PMe_3)_2]{\cdot}CH_3OH$, 6, by Reduction of $[Fe('S_2')_2(PMe_3)_2]$, 5. (a) **5** (420 mg, 0.86 mmol) was suspended in 30 mL of methanol. $NaBH_4$ was added until the initially blue-green suspension turned into a red-violet solution. After filtration, the air-sensitive solution was layered with NMe_4Cl (110 mg, 1.0 mmol) in 10 mL of methanol. Cooling to −30 °C for 14 days yielded black crystals of **6**, which were filtered off, washed with 5 mL of cold methanol, and dried in vacuo for 1 day: yield 330 mg (65%). Anal. Calcd for $C_{23}FeH_{42}NOP_2S_4$ (594.65): C, 46.5; H, 7.1; N, 2.4. Found: C, 46.3; H, 7.1; N, 2.3.

(b) In a Schlenk tube that had been heated in vacuo before, **5** (485 mg, 0.99 mmol) was suspended in 25 mL of THF and reacted with 1 equiv of *n*-BuLi (0.6 mL of a 1.6 M solution in *n*-hexane; an excess of *n*-BuLi has to be avoided). Unreacted **5** was filtered off, 5 mL of

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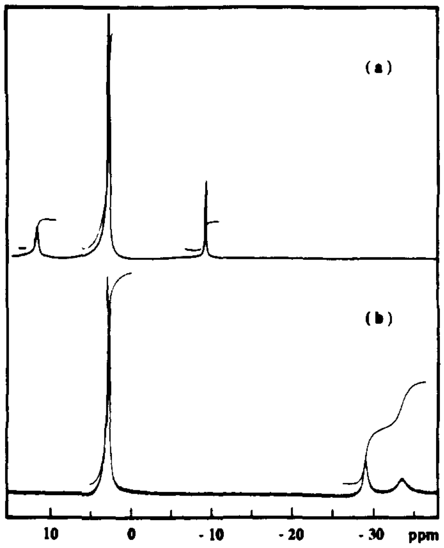
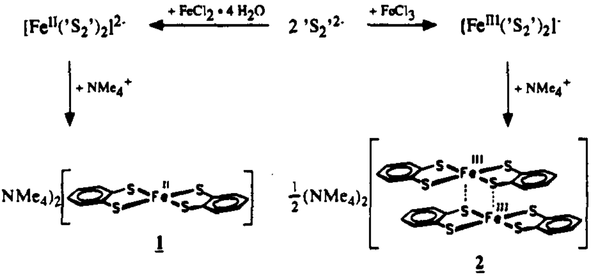


Figure 1. ^1H NMR spectra in $[d_6]DMSO$ (270 MHz) of (a) $(NMe_4)_2[Fe^{II}('S_2')_2]$, **1**; (b) $(NMe_4)_2[Fe^{III}('S_2')_2]_2$, **2**.

Scheme I



methanol was added, and the resulting red-violet solution was layered with NMe_4Cl (120 mg, 1.1 mmol) in 10 mL of methanol. After 5 days at −30 °C, the precipitated crystals of **6** were collected, washed with 5 mL of cold methanol, and dried in vacuo for 1 day: yield 320 mg (54%). Anal. Calcd for $C_{23}FeH_{42}NOP_2S_4$ (594.65): C, 46.5; H, 7.1; N, 2.4. Found: C, 46.2; H, 7.3; N, 2.3.

$[Li(THF)_3]_2[Fe^{II}('S_2')_2]$, 3, by Reduction of $[Fe('S_2')_2(PMe_3)_2]$, 5. In a Schlenk tube that had been heated in vacuo before, $LiBEt_3H$ (6.5 mL of a 1.0 M solution in THF) was added at −30 °C to a suspension of **5** (1.05 g, 2.15 mmol) in 40 mL of THF. After 1 h at 20 °C, the resulting yellow solution was cooled to −30 °C again, layered with 25 mL of *n*-hexane, and kept at −30 °C for 5 days. The precipitated large yellow needles of **3** were separated, washed with 10 mL of a cold mixture of THF and *n*-hexane (1:1), and dried in vacuo for 30 min: yield 1.35 g (80%); ^1H NMR ($[d_6]DMSO$) δ 11.6 (4 H, s, C_6H_4), 3.6, 1.7 (24 H each, both s, THF), −9.9 (4H, s, C_6H_4); ^1H NMR ($[d_8]THF$) δ 4.4, −9.2 (1:1, both s, C_6H_4). Anal. Calcd for $C_{36}FeH_{56}Li_2O_6S_4$ (782.82): C, 55.2; H, 7.2; S, 16.4. Found: C, 55.7; H, 7.3; S, 16.6.

Analogous results were obtained when 2 equiv of *n*-BuLi or 2 and 4 equiv of $LiBEt_3H$ were used.

Results

The previously reported $AsPh_4^+$ and PPh_4^+ salts of $[Fe^{II}('S_2')_2]^{2-}$ are almost insoluble in all common solvents and prevented further investigations in homogeneous phase.[17,24] More soluble is $(NMe_4)_2[Fe^{II}('S_2')_2]$, **1**, but the reported synthesis[24] yielded only microcrystals that were extremely air sensitive and often got oxidized even when very careful precautions were taken. For these reasons, a modified synthesis of **1** was developed. It allowed the growth of large ochre-yellow crystals, which can be handled more easily. An analogous synthesis of crystalline $(NMe_4)_2[Fe^{III}('S_2')_2]_2$, **2**, was worked out (Scheme I).

1 and **2** were characterized by NMR and Mössbauer spectroscopy; structural, spectroscopic, and magnetic properties of $(NEt_4)_2[Fe^{III}('S_2')_2]_2$ were reported[19] when this work was in progress and confirmed our own results.

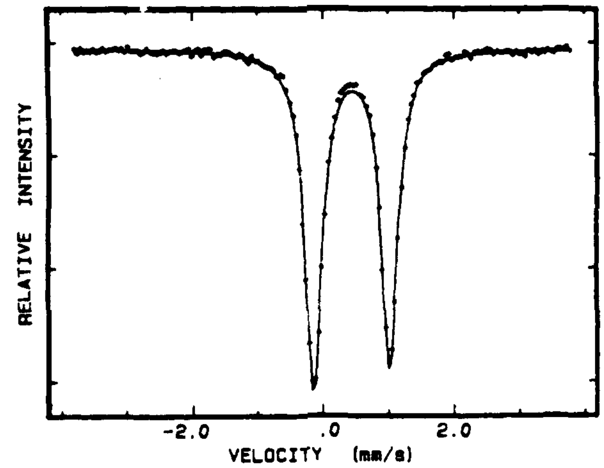


Figure 2. Zero-field Mössbauer spectrum of **1** at 4.2 K. The solid line is a least-squares fit with Lorentzian line shape. Isomer shift δ, mm/s (T, K): 0.441 (1) (4.2), 0.435 (1) (85), 0.387 (1) (200), 0.367 (4) (293). Quadrupole splitting ΔE_Q, mm/s (T, K): 1.161 (1) (4.2 and 85), 1.135 (1) (200), 1.117 (7) (293). Line widths Γ, mm/s (T, K): 0.307 (2), 0.300 (2) (4.2); 0.266 (1), 0.259 (1) (85); 0.264 (3), 0.260 (3) (200); 0.556 (11) (293).

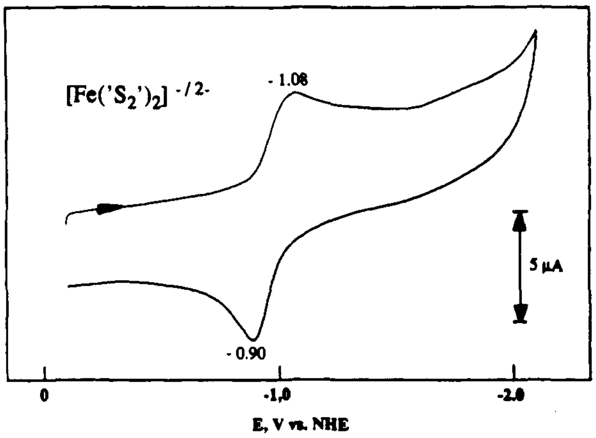


Figure 3. Cyclic voltammogram of **2**, 1 × 10^{-4} M, 0.10 M NBu_4ClO_4, DMSO. Scan rate 0.100 V s^{-1}.

1 and **2** are readily soluble in DMSO, DMF, and MeCN, moderately soluble in MeOH and acetone, and almost insoluble in THF. The ^1H and ^{13}C NMR signals of the aromatic protons and carbon atoms of the $'S_2'$ units in **1** and **2** are shifted paramagnetically. Figure 1 displays the ^1H NMR spectra of **1** and **2**, illustrating the unambiguous differentiation of both species.

In solid state (295 K), **1** has a magnetic moment of 2.8 μ_B, consistent with two unpaired electrons; the magnetic moment of **2** (2.3 μ_B/dimer) is indicative of two low-spin Fe(III) centers and partial antiferromagnetic coupling through the S bridges. Mössbauer investigations revealed for **1** a slightly asymmetric quadrupole doublet at temperatures between 4.2 and 293 K. The isomer shift δ displays normal temperature dependence, and the quadrupole splitting ΔE_Q is almost temperature independent. Figure 2 displays the zero-field spectrum of **1** at 4.2 K; selected data are given. The isomer shift value of **1** (0.441 (1) mm/s at 4.2 K, 0.367 (4) mm/s at 293 K) fits the shift range characteristic for Fe(II) $S = 1$ compounds (0.30–0.50 mm/s at 293 K).[25] The room temperature δ and ΔE_Q values of **2** ($\delta = 0.245(1)$ mm/s; $\Delta E_Q = 2.696$ (1) mm/s) consist with corresponding data of related systems.[26]

Cyclovoltammetry of **2** in DMSO in the range from 0 to −2.1 V vs NHE revealed one quasi-reversible Fe(III)/Fe(II) redox couple at −0.99 V (Figure 3).

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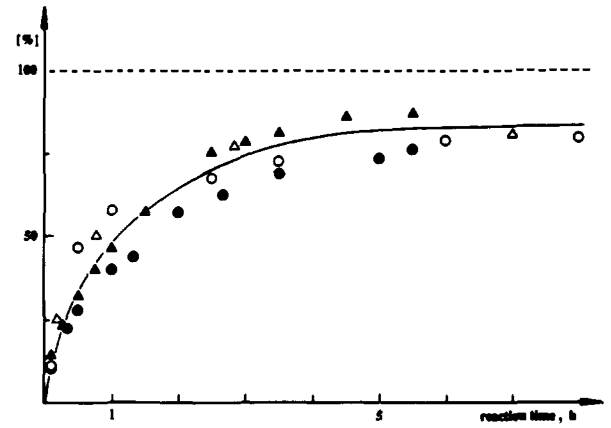

Figure 4. Evolution of H_2 and formation of $[Fe^{III}('S_2')_2]_2^{2-}$ as function of time: percent H_2 according to eq 3, ○; to eq 4, ●; and to eq 5, ▲; percent $[Fe^{III}('S_2')_2]_2^{2-}$ according to the ^1H NMR experiment in analogy to eq 5, △.

In order to isolate and fully characterize the reaction products of the protonation of $[Fe^{II}('S_2')_2]^{2-}$, homogeneous reaction conditions were maintained as far as possible. Therefore, $[Fe^{II}('S_2')_2]^{2-}$ was generated in situ in MeOH and subsequently reacted with a stoichiometric amount of HCl (eq 3). Gas evolution was measured by volumetry. After addition of HCl to the yellow-red solution of $[Fe^{II}('S_2')_2]^{2-}$, a blue-grey solid immediately precipitated and the color of the resulting suspension became deeper red. After 6 h, the precipitate had vanished, the color of the reaction solution had changed to black-red, and about 80% of the stoichiometric quantity of gas was evolved. With NMe_4^+, **2** was isolated in about 80% yield and characterized by ^1H NMR spectroscopy and elemental analysis. H_2 was proved qualitatively by GC. The blue-grey intermediate species that had precipitated rapidly decomposed in vacuo and could not be further characterized. H_2 evolution as a function of time is shown in Figure 4. Identical results were obtained, when 2 equiv of HCl instead of 1 was used. In control experiments, addition of HCl to methanolic $Na_2'S_2'$ or $FeCl_2$ solutions did not yield any gas evolution.

$$\begin{aligned}&FeCl_2{\cdot}4H_2O + 2Na_2'S_2' \xrightarrow[-2NaCl]{} \\ &\quad Na_2[Fe^{II}('S_2')_2] \xrightarrow{+1HCl/MeOH/1\ min} \{intermediate\} \xrightarrow[-NaCl]{6h} \\ &\quad \tfrac{1}{2}H_2 + Na[Fe^{III}('S_2')_2] \xrightarrow[-NaCl]{+NMe_4Cl} \tfrac{1}{2}\underset{\textbf{2}}{(NMe_4)_2[Fe^{III}('S_2')_2]_2}\end{aligned} \qquad (3)$$

Two principally different pathways can be discussed for the reduction of H^+ by $[Fe^{II}('S_2')_2]^{2-}$: (1) primary attack of H^+ at the thiolate donors, yielding intermediate SH species or (2) primary attack of H^+ at the Fe center, yielding iron hydride species. In order to distinguish between these alternatives, $FeCl_2$ was reacted with an equimolar mixture of $Na_2'S_2'$ and $Na'S_2'$–H (eq 4).

$$\begin{aligned}&FeCl_2{\cdot}4H_2O + Na_2'S_2' + Na'S_2'\text{–}H \xrightarrow[-2NaCl]{MeOH/1\ min} \\ &\{intermediate\} \xrightarrow{6h} \tfrac{1}{2}H_2 + Na[Fe^{III}('S_2')_2] \xrightarrow[-NaCl]{+NMe_4Cl} \tfrac{1}{2}\textbf{2}\end{aligned} \qquad (4)$$

Exactly the same reaction course as described above was observed. Again, a blue-grey intermediate precipitated and H_2 evolution took place; quantity and rate correlated with the results obtained when reaction 3 was carried out (Figure 4), and **2** could be isolated in 86% yield.

In order to exclude alternative 2 and the possibility that an intermediate Fe–H species rapidly reacts with protons of the solvent under evolution of H_2, reaction 5 was carried out in aprotic THF.

Again, the precipitating and redissolving blue-grey intermediate was observed and H_2 evolution correlated with the previous results (Figure 4). The resulting Fe(III) complex was isolated as $[Li(THF)_3]_2[Fe^{III}('S_2')_2]_2$, **4**, in 70% yield and characterized by ^1H NMR spectroscopy (Experimental Section).

$$\begin{aligned}&\underset{\textbf{3}}{[Li(THF)_3]_2[Fe^{II}('S_2')_2]} + 1HCl \xrightarrow[-LiCl]{THF} \{intermediate\} \rightarrow \\ &\qquad \tfrac{1}{2}H_2 + \tfrac{1}{2}\underset{\textbf{4}}{[Li(THF_3)_2[Fe^{III}('S_2')_2]_2}\end{aligned} \qquad (5)$$

The reaction of 1 equiv of **3** with 1 equiv of H^+ in analogy to eq 5 was also performed by using HCl gas in $[d_8]$THF and monitored by ^1H NMR spectroscopy in order to obtain evidence for either SH or FeH bond formation. The inhomogeneity of the sample after rapid precipitation of the blue-grey intermediate upon HCl addition and the paramagnetism of the compounds caused broadening of the THF signals and made a definite identification of signals between 0 and 5 ppm impossible. The signals of the aromatic protons of **3** and **4** at −9.2, −32.4, and −37.2 ppm, however, could be monitored.

Remarkably, about 50% of educt **3** was still unprotonated 10 min after HCl addition though precipitation of the blue-grey intermediate occurred rapidly and **4** was already detectable. During the next 3 h, the ^1H NMR signal intensities of educt **3** decreased and those of product **4** increased slowly. Besides **3** and **4**, another species displaying a doublet of low intensity at 7.1 ppm was observed; the splitting pattern of this signal indicated the presence of small amounts of free $'S_2'$–H_2. After 3 h and complete redissolution of the blue-grey precipitate, the signals of this species had disappeared; except small amounts of educt **3**, only product **4** was present. Moreover, it was found that formation of product **4** as a function of time correlated with H_2 evolution observed in the reactions according to eqs 3–5 (Figure 4).

When in another ^1H NMR experiment **3** was reacted with 2 equiv of HCl gas in $[d_8]$THF, educt **3** had disappeared completely 10 min after protonation. The signals of product **4** and free $'S_2'$–H_2 (δ 7.1 (4 H, d, C_6H_4), 4.3 (2 H, s, SH)) could be detected immediately after H^+ addition. Only in this experiment, an extra signal being weak and very broad is observed at −12 ppm. The species causing this signal could not be identified so far, but on the base of the experiments in methanol, the measured H_2 evolutions, and the preceding experiment, we assume it is a paramagnetic iron species containing only one $'S_2'^{2-}$ ligand and not a hydride complex. Thus, the experiments in methanol and the ^1H NMR experiments in $[d_8]$THF did not yield evidence for Fe hydride species, and the only SH species that could be detected was free $'S_2'$–H_2.

The results show that, upon interaction of protons with $[Fe^{II}('S_2')_2]^{2-}$, H_2 and $[Fe^{III}('S_2')_2]_2^{2-}$ are formed. In order to test whether the reverse reaction was possible as well, we tried to achieve a reduction of $[Fe^{III}('S_2')_2]_2^{2-}$ by H_2; base was added in order to remove potentially originating protons (eq 6).

$$[Fe^{III}('S_2')_2]^- + H_2 \not\xrightarrow[-H_2O]{OH^-/MeOH/3 days} [Fe^{II}('S_2')_2]^{2-} \qquad (6)$$

Neither under standard conditions nor under high pressure of H_2 (20 °C, 50 bar) a reaction could be observed, and with NMe_4^+ unreacted **2** was the only species that could be isolated in up to 74% yield along with slight amounts of decomposition products.

Though $[Fe^{II}('S_2')_2]^{2-}$, formally a 14-e$^-$ complex, readily adds CO to give $[Fe('S_2')_2(CO)_2]^{2-}$,[27,28] it does not react with H_2 in order to give hydride complexes, for example, $[Fe(H)_2('S_2')_2]^{2-}$.

We finally attempted to synthesize such a species by hydride addition to higher valent $Fe('S_2')_2$ complexes. When $[Fe^{III}('S_2')_2]_2^{2-}$ was generated in situ and reacted with an excess of $NaBH_4$ (eq 7), no hydride complexes but yellow crystals of the Fe(II) complex **1** were precipitated with NMe_4^+.

$$FeCl_3 + 2Na_2'S_2' + NaBH_{4\,exc} \xrightarrow[MeOH/-5NaCl]{+2NMe_4Cl} \textbf{1} + H_2 + \text{other products} \qquad (7)$$

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Reduction of $(\mathrm{NBu_4})_2[\mathrm{Fe^{III}('S_2')_2}]_2$ by $\mathrm{NaBH_4}$ or $\mathrm{N_2H_4}$ had been observed before, but the resulting extremely air sensitive yellow complexes could not be characterized then.[27,29]

Reaction of the Fe(IV) complex $[\mathrm{Fe('S_2')_2(PMe_3)_2}]$, **5**, with $\mathrm{NaBH_4}$ according to eq 8 yielded $[\mathrm{Fe('S_2')_2(PMe_3)_2}]^-$. Direct syntheses and characterization of **5** and $(\mathrm{NMe_4})[\mathrm{Fe('S_2')_2(PMe_3)_2}]\cdot\mathrm{CH_3OH}$, **6**, were previously reported.[23]

$$\underset{\mathbf{5}}{[\mathrm{Fe^{IV}('S_2')_2(PMe_3)_2}]} + \mathrm{NaBH_4}\ _{\mathrm{exc}} \xrightarrow[\mathrm{MeOH/-NaCl}]{+\mathrm{NMe_4Cl}} \underset{\mathbf{6}}{(\mathrm{NMe_4})[\mathrm{Fe^{III}('S_2')_2(PMe_3)_2}]\cdot\mathrm{CH_3OH}} \quad (8)$$

The reduction stops at the Fe(III) stage even when a large excess of $\mathrm{NaBH_4}$ is applied. In aprotic solvents and with $\mathrm{LiBEt_3H}$ as well as *n*-BuLi as hydride sources, the Fe(II) stage was reached but the $\mathrm{PMe_3}$ ligands were removed (eq 9).

$$\mathbf{5} + \mathrm{R} \xrightarrow[\mathrm{THF/-2PMe_3}]{+20\text{ or }-30\ {}^\circ\mathrm{C}} \underset{\mathbf{3}}{[\mathrm{Li(THF)_3}]_2[\mathrm{Fe^{II}('S_2')_2}]} \quad (9)$$

$$\mathrm{R} = x\mathrm{LiBEt_3H}\ (x = 2,3,4)\text{ or }2(n\text{-BuLi})$$

Neither further reduction nor an Fe–H species was achieved when an excess of $\mathrm{LiBEt_3H}$ was used or the temperature was lowered. The resulting $[\mathrm{Fe^{II}('S_2')_2}]^{2-}$ was isolated and characterized as $[\mathrm{Li(THF)_3}]^+$ salt **3**.

By using only 1 equiv of *n*-BuLi, **5** was reduced to give the corresponding Fe(III) species that was isolated as **6** (eq 10).

$$\mathbf{5} + 1(n\text{-BuLi}) \xrightarrow{\mathrm{THF}} \mathrm{Li}[\mathrm{Fe^{III}('S_2')_2(PMe_3)_2}] \xrightarrow[\mathrm{MeOH/-LiCl}]{+\mathrm{NMe_4Cl}} \mathbf{6} \quad (10)$$

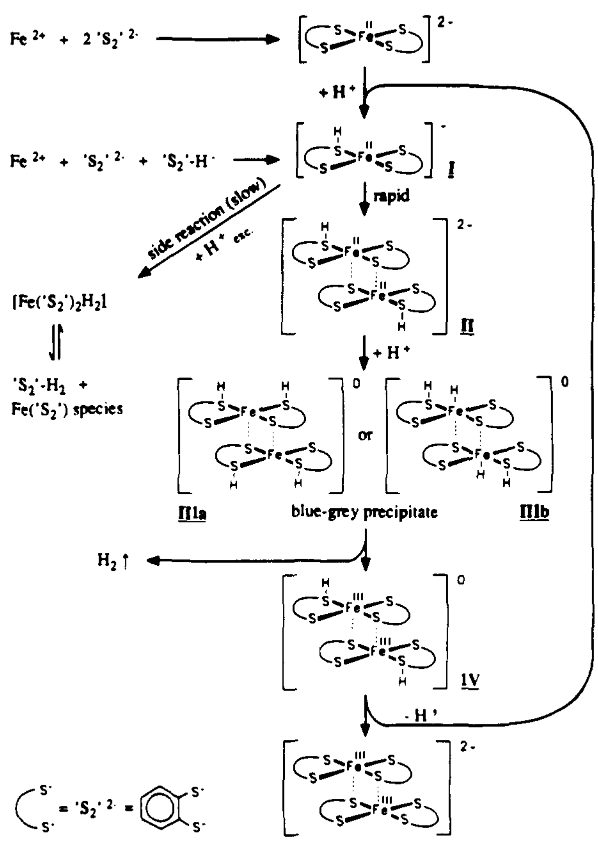
Discussion and Conclusions

The results show the possibility of achieving $\mathrm{H_2}$ evolution by reaction of protons with iron sulfur ligand complexes. In the course of the reaction, the Fe(II) complex $[\mathrm{Fe^{II}('S_2')_2}]^{2-}$ is oxidized stoichiometrically to give the Fe(III) species $[\mathrm{Fe^{III}('S_2')_2}]^-$ (or $[\mathrm{Fe^{III}('S_2')_2}]_2{}^{2-}$, respectively).

Reduction of protons by Fe(II) complexes is a remarkable reaction per se, It becomes possible because the redox potential of the $[\mathrm{Fe('S_2')_2}]^{2-/-}$ couple (–0.99 V vs NHE) is very negative. A selection of standard potentials E° illustrates the strong dependence of $\mathrm{Fe^{II}/Fe^{III}}$ redox couples upon the nature of the ligands: $[\mathrm{Fe(phen)_3}]^{2+/3+}$ (+1.12 V); $[\mathrm{Fe(bpy)_3}]^{2+/3+}$ (+0.96 V); $[\mathrm{Fe(H_2O)_6}]^{2+/3+}$ (+0.77 V at low pH); $[\mathrm{Fe(CN)_6}]^{4-/3-}$ (+0.36 V); $[\mathrm{FeCl_4}]^{2-/-}$ (+0.34 V); $[\mathrm{Fe(EDTA)}]^{2-/-}$ (–0.12 V).[30] All potentials listed are preferably positive, and the contrasting rather negative E° of $\mathrm{Fe^{II}/Fe^{III}}$ in alkaline aqueous solution (–0.53 V) is due to the low solubility of $\mathrm{Fe(OH)_3}$. In fact, the $\mathrm{Fe^{II}/Fe^{III}}$ redox potentials cited are considerably more positive than that of the $[\mathrm{Fe('S_2')_2}]^{2-/-}$ couple, even when the influence of different solvents is taken into account. Thiolate donors appear to enhance the electron density at Fe(II) centers to such an extent that Fe(II) thiolate complexes become strongly reducing. Negative redox potentials (vs NHE) are also reported for $\mathrm{Fe^{II}/Fe^{III}}$ in $[\mathrm{Fe(S_2C_6H_3CH_3)_2}]^{2-/-}$ (–0.59 V)[31] and $[\mathrm{Fe}(o\text{-}(\mathrm{SCH_2})_2\mathrm{C_6H_4})_2]^{2-/-}$ (–0.78 V)[16a] and for the $\mathrm{Fe_4S_4}$ cluster couples $[\mathrm{Fe_4S_4(SPh)_4}]^{2-/3-}$ (–0.76 V)[15] or $[\mathrm{Fe_4S_4(SCH_2CH_2COO^-)_4}]^{6-/7-}$ (–0.58 V).[32] Considering the very different structures and electronic states of these complexes and $[\mathrm{Fe('S_2')_2}]^{2-/-}$, the coordination of thiolate donors to Fe centers evidently is the major reason for the negative redox potentials.

We suggest that the thiolate donors are also the sites of the first chemical interaction when $[\mathrm{Fe^{II}('S_2')_2}]^{2-}$ reacts with $\mathrm{H^+}$. This can be deduced from the identical reaction course when either $\mathrm{FeCl_2}$ is reacted with $\mathrm{'S_2'{-}H^-}$ (eq 4) or $[\mathrm{Fe^{II}('S_2')_2}]^{2-}$ with 1 (or 2) equiv of $\mathrm{H^+}$ (eq 3). It is also indicated by the immediate formation of free $\mathrm{'S_2'{-}H_2}$ observed in ^{1}H NMR spectroscopy when **3** is reacted with 2 equiv of HCl.

Scheme II



According to the ^{1}H NMR spectra in which the signals of $[\mathrm{Fe^{II}('S_2')_2}]^{2-}$ and $[\mathrm{Fe^{III}('S_2')_2}]^-$ can be unambiguously assigned, 50% of $[\mathrm{Fe^{II}('S_2')_2}]^{2-}$ remained unreacted even a few minutes after the addition of 1 equiv of $\mathrm{H^+}$. Later in the course of the reaction, this unreacted $[\mathrm{Fe^{II}('S_2')_2}]^{2-}$ disappeared practically completely, while the signals of $[\mathrm{Fe^{III}('S_2')_2}]^-$ increased. When 2 equiv of HCl was added, however, $[\mathrm{Fe^{II}('S_2')_2}]^{2-}$ immediately and completely dissappeared.

These observations indicate that $[\mathrm{Fe^{II}('S_2')_2}]^{2-}$ is always diprotonated even when only 1 equiv of $\mathrm{H^+}$ is available; that is, as soon as one proton is added, addition of a second proton is favored. With regard to acid–base reactions and dissociation constants, such a behavior is uncommon and not compatible with equilibria according to eq 11.

$$[\mathrm{Fe('S_2')_2}]^{2-} \underset{-\mathrm{H^+}}{\overset{+\mathrm{H^+}}{\rightleftharpoons}} [\mathrm{Fe('S_2')_2H}]^- \underset{-\mathrm{H^+}}{\overset{+\mathrm{H^+}}{\rightleftharpoons}} [\mathrm{Fe('S_2')_2H_2}] \quad (11)$$

It rather suggests that primarily generated $[\mathrm{Fe('S_2')_2H}]^-$ very rapidly is converted into another species, which then adds the second proton. The resulting compound must be the blue-grey precipitate that must also contain all protons having been added, because no protonated species can be observed in solution but only slight amounts of free 1,2-benzenedithiol that increase when 2 equiv or an excess of $\mathrm{H^+}$ are added.

All observations can be plausibly explained when the following sequence of reaction steps and intermediates is assumed (Scheme II).

$[\mathrm{Fe^{II}('S_2')_2}]^{2-}$ is monoprotonated to give I that forms the dinuclear species II. II must have a different—and as the experiments indicate, a higher—proton affinity in comparison to I and even to $[\mathrm{Fe^{II}('S_2')_2}]^{2-}$, such that it is easily further protonated, yielding either the dithiol species IIIa or the hydride/thiol species IIIb. IIIa or IIIb eliminates $\mathrm{H_2}$ and yields the Fe(III) complex IV in which dissociation of the remaining SH bonds is favored

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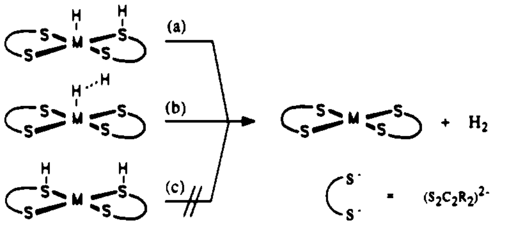
by the (higher) oxidation state compared to I or II. The resulting protons are then available for protonation of as yet unreacted $[Fe^{II}('S_2')_2]^{2-}$.

When 2 equiv or an excess of protons are added, the side reaction in which a second proton adds to I becomes more important. The resulting $[Fe('S_2')_2H_2]$ is labile and dissociates, yielding free $'S_2'-H_2$.

Theoretical calculations for the evolution of hydrogen at transition-metal sulfur centers were carried out for mononuclear bis(dithiolenes). They favor the heterolytic elimination of H_2 from metal hydride species according to either eq 12a or 12b rather than a concerted H_2 elimination from a dithiol species (eq 12c), which is thermally forbidden.[33]

The results described above and the mechanism of Scheme II show that such systems are only seemingly simple and that the evolution of H_2 at them can involve considerably more steps than hitherto regarded. The results further show that it is possible to generate dihydrogen in protic media at iron sulfur centers whose formation does not require strongly reducing conditions.



(12)

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Proton NMR Study of High-Spin Iron(III) Isobacteriochlorins. The Effects of Five- vs Six-Coordination and Comparisons with Homologous Porphyrin and Chlorin Complexes

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Abstract: The two stereoisomers of free base 2,3,7,8-tetrahydro-2,3,7,8,12,13,17,18-octaethylporphyrin (octaethylisobacteriochlorin, H_2(OEiBC)), H_2(*ttt*-OEiBC) and H_2(*tct*-OEiBC), were separated to >90% purity with medium pressure liquid chromatography. These two macrocycles and *trans*-7,8-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrin (*trans*-octaethylchlorin, H_2(*t*-OEC)) were used to prepare or generate in solution the following high-spin ($S = 5/2$) Fe(III) compounds: Fe(*ttt*-OEiBC)Cl, Fe(*tct*-OEiBC)Cl, $[Fe(ttt\text{-OEiBC})(DMSO)_2]^+[CF_3SO_3]^-$, $[Fe(tct\text{-OEiBC})(DMSO)_2]^+[CF_3SO_3]^-$, Fe(*t*-OEC)Cl, and $[Fe(t\text{-OEC})(DMSO)_2]^+[CF_3SO_3]^-$. The isobacteriochlorin complexes are models for the siroheme active sites in the resting states of *E. coli* NADPH sulfite reductase and spinach ferredoxin nitrite reductase. Along with several specifically deuterated derivatives, the model complexes were studied by ^1H and ^2H NMR spectroscopy. (The six-coordinate complexes, reported here for the first time, were also characterized by UV-vis and EPR spectroscopy.) The OEiBC spectra are well enough resolved to show, for example, separate resonances for nearly all of the individual protons (not counting methyl protons) of the two C_s stereoisomers of Fe(*tct*-OEiBC)Cl. For both ligation states, the change from *ttt*-OEiBC to *tct*-OEiBC results in only minor changes in contact shift patterns. The range of contact shifts exhibited by pyrrole methylene protons, pyrroline protons, and meso protons is *far greater* for the OEiBC complexes than for the corresponding *t*-OEC complexes. Nevertheless, the estimated amount of unpaired spin density in pyrrole rings is essentially the same, at parity of axial ligation, across the series OEP, *t*-OEC, *ttt*-OEiBC. For both types of hydroporphyrin complexes, the change from five- to six-coordination induces diagnostic changes in meso and pyrroline proton isotropic shifts. Thus, pyrroline ^1H NMR resonances, which are relatively sharp, can be used to elucidate whether high-spin Fe(III) hydroporphyrin prosthetic groups in green heme and siroheme enzymes are five- or six-coordinate. T_1 relaxation times at 293 K for pyrrole methylene protons (~2 ms) and for meso protons (~0.3 ms) are qualitatively the same across the series OEP, *t*-OEC, *ttt*-OEiBC. For the hydroporphyrin complexes, the order of decreasing T_1 relaxation times is pyrrole methylene > pyrroline H ~ pyrroline methylene > meso. The pyrroline H and pyrroline methylene T_1's are measurably longer for the six-coordinate derivatives.

Introduction

Iron chlorins (e.g., heme-*d*,[3] sulfheme,[4] and the green heme in myeloperoxidase[5]) and isobacteriochlorins (e.g., heme-d_1[6] and siroheme[7]) are now widely recognized as important prosthetic groups in so-called green heme and siroheme proteins. Many of the physicochemical techniques that have been used to study the structure and dynamics of heme proteins (i.e., those containing iron porphyrins), such as X-ray crystallography and resonance Raman, EPR, MCD, Mössbauer, and NMR spectroscopy, have been recently applied to green heme and siroheme proteins and

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