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Transition-Metal Complexes with Sulfur Ligands. 57.[1] Stabilization of High-Valent Fe(IV) Centers and Vacant Coordination Sites by Sulfur π-Donation: Syntheses, X-ray Structures, and Properties of $[Fe("S_2")_2(PMe_3)_n]$ ($n = 1, 2$) and $(NMe_4)[Fe("S_2")_2(PMe_3)_2]\cdot CH_3OH$ ($"S_2"^{2-}$ = 1,2-Benzenedithiolate(2–))

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Abstract: The iron(IV) complexes $[Fe("S_2")_2(PMe_3)_2]$ (**1**) and $[Fe("S_2")_2(PMe_3)]$ (**2**) as well as the related iron(III) complex $(NMe_4)[Fe("S_2")_2(PMe_3)_2]\cdot CH_3OH$ (**4**) ($"S_2"^{2-}$ = 1,2-benzenedithiolate(2–)) were synthesized and characterized as potential models for FeS oxidoreductases. X-ray structure determination shows that **1** (orthorhombic, $P2_12_12_1$, $a = 2075.7$ (6) pm, $b = 1202.4$ (2) pm, $c = 875.0$ (2) pm, $Z = 4$, $R = R_w = 0.059$) contains six-coordinate iron in a strongly distorted octahedral environment; the two phosphine P atoms occupy trans positions, and the P–Fe–P angle is only 159.7 (1)°; the FeS_4 unit is planar with two long ($Fe–S_{av} = 229.8$ (3) pm) and two short ($Fe–S_{av} = 219.1$ (3) pm) iron–sulfur bonds. In **2** (monoclinic, $P2_1/n$, $a = 1218.3$ (3) pm, $b = 730.7$ (4) pm, $c = 1998.6$ (4) pm, $\beta = 104.20$ (2)°, $Z = 4$, $R/R_w = 0.062/0.046$) four basal sulfur and one apical phosphorus donors surround five-coordinate iron in a tetragonal pyramid; all four Fe–S bonds are short ($d_{av} = 218.5$ (3) pm). In **4** (triclinic, $P\bar{1}$, $a = 880.5$ (3) pm, $b = 931.3$ (3) pm, $c = 1793.9$ (5) pm, $\alpha = 91.99$ (2)°, $\beta = 91.83$ (2)°, $\gamma = 94.40$ (3)°, $Z = 2$, $R/R_w = 0.078/0.070$) two methanol molecules are bound to one of the two independent anions via S···H–O bridges. Both anions are centrosymmetric, the iron centers are pseudooctahedrally surrounded by four sulfur and two trans phosphorus atoms, and the Fe–S distances range from 224.8 (2) to 227.3 (2) pm. Comparison of the structural data reveals that the $"S_2"$ ligands in all three complexes function as "innocent" dianionic dithiolates, and the iron atoms in **1**, **2**, and **4** have to be regarded as Fe(IV) and Fe(III) centers. This conclusion could be corroborated by Mössbauer, NMR, EPR, UV, and IR investigations as well as magnetic moments. Cyclovoltammetry further revealed two reversible one-electron steps for **1**, **2**, and **4** each, due to Fe(IV/III) and Fe(III/II) redox couples. The model character of the new complexes for [FeS] centers in redox enzymes is discussed. In the iron–benzenedithiolate systems a linear correlation exists between Fe–S bond lengths and formal electron count. In conclusion, it could be shown that Fe–S bond lengths and the stabilization of vacant coordination sites as well as high oxidation states in Fe/$"S_2"$ complexes depend on sulfur π-donation.

Introduction

The active sites of numerous electron transferases and oxidoreductases contain iron in a coordination sphere dominated by sulfur.[2] In order to elucidate the enzymatic processes on a molecular level, metal–sulfur ligand complexes are required which can serve as both functional and structural model compounds. The characteristic properties that are closely associated with metal–sulfur centers, for example, uncommon structures,[3] redox behavior,[4] and stabilization of unusual metal oxidation states[5] as well as vacant coordination sites and electron deficiency,[6] are as important as the understanding of elementary reactions, for example, electron transfer, substrate addition/product release, or protonation/deprotonation.

In this context we have investigated Fe complexes with 1,2-benzenedithiolate(2–) ($"S_2"^{2-}$). The planar, mononuclear Fe(II) complex $[Fe("S_2")_2]^{2-}$ [7] readily coordinates CO to give $[Fe("S_2")_2(CO)_2]^{2-}$;[8] oxidation of this dianion causes loss of CO and formation of the dinuclear Fe(III) complex $[Fe("S_2")_2]_2^{2-}$.[8,9] Beside $[\mu\text{-}N_2H_4\{Fe("S_2")_2\}_2]^{2-}$,[10] this is the only example in the Fe/$"S_2"$ system with an oxidation state of higher than +2. In order to gain information about the sulfur interactions on high-valent iron centers, we now investigated the system Fe/$"S_2"^{2-}$/PMe_3 and synthesized Fe(IV) and Fe(III) complexes with planar $Fe("S_2")_2$ units and phosphine coligands. All species including the five-coordinate $[Fe("S_2")_2(PMe_3)]$ are mononuclear and contrast with theoretical considerations[11] revealing that dithiolene complexes with low metal d electron configurations should tend to dimerize.

The term dithiolene was created for 1,2-dithio ligands with sulfur donors connected via unsaturated C–C bonds in order to express that the dithiolate and dithiodiketone forms are strongly related and differ by two electrons only (eq 1). Dithiolenes are

I II (1)

regarded as typical "noninnocent" ligands[12] which are assumed

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to exhibit the dithiolate form I in low-valent anionic complexes but should be oxidized partially to the dithiodiketone form II when coordinated to formally high-valent metal ions.

1,2-Benzenedithiolate and 1,2-ethylenedithiolate (I, R = H), which is the parent compound of all dithiolene ligands, are related systems, because in both cases unsaturated C–C bonds connect the sulfur donors. It might be much easier, however, to achieve the oxidation I → II than the analogous oxidation III → IV, where the formation of dithio-*o*-benzoquinone requires breaking up of the aromatic system of III (eq 2).[13] Here the question arises

(2)

III IV

whether 1,2-benzenedithiolate is a noninnocent dithiolene type or an innocent dianionic dithiolate ligand even when coordinated to high-valent Fe(IV) centers. Is the unusual oxidation state of the iron centers stabilized by the potential dithiolene character of the ligands or by the sulfur donors only?

Structurally characterized Fe(IV) complexes are rare and predominantly sulfur coordinated.[14-19] In this paper we report the syntheses and crystal structures as well as electrochemical and physical properties of the Fe(IV) and Fe(III) compounds [Fe(“S_2”)$_2$(PMe$_3$)$_x$]^n (n = 0, x = 1, 2; n = −1, x = 2). Bonding in these complexes is discussed in detail, and considerable differences to conventional dithiolene systems are pointed out. Additionally, the biological significance of the new compounds is elucidated with regard to elementary reactions, for example, substrate coordination/decoordination and reversible redox behavior, taking place in iron–sulfur redox enzymes.

Experimental Section

General Methods. Unless otherwise noted, all reactions and operations were carried out under nitrogen at room temperature by using standard Schlenk techniques. Solvents were dried and distilled before use. Starting materials were prepared according to literature methods: 1,2-benzenedithiole, “S_2”-H_2,[20] PMe$_3$,[21] and [Fe(“S_4”)(CO)(PMe$_3$)] (“S_4”$^{2-}$ = dianion of 1,2-bis((2-mercaptophenyl)thio)ethane).[22] $FeCl_2 \cdot 4H_2O$, $FeCl_3$, and NMe_4Cl were purchased from Merck, and NBu_4ClO_4 and NaOMe were purchased from Fluka and Aldrich Chemical Co., respectively. Irradiation reactions were carried out with a 25 W Hg high-pressure lamp (Fa. Original Quarzlampen GmbH, Hanau, Germany). Spectra were recorded on the following instruments: NMR, Jeol FT-JNM-GX 270; EPR, Bruker ER 220 D LR and Jeol PE-3X; IR (KBr discs or CaF_2 cuvettes), Perkin Elmer 983; UV–vis–NIR, Beckman DK 2A and Shimadzu UV-3100; mass spectra, Varian MAT 212. Magnetic moments of solids were determined on a Johnson Matthey magnetic susceptibility balance at room temperature. Cyclic voltammetry was performed with a PAR 264 A potentiostat by using a three electrode cell with glassy carbon ROTEL A working, Ag/AgCl reference, and Pt counter electrodes. The solutions were saturated with N_2 for 8 min before measurement. Potentials were referred to NHE via Cp_2Fe/Cp_2Fe^+ as standard. ^{57}Fe Mössbauer investigations were carried out with powder samples of about 100 mg in 19-mm diameter polyethylene containers. The spectrometer consisted of a constant-acceleration electromechanical drive and a Nuclear Data ND 2400 multichannel analyzer operating in the multiscaling mode. The γ-source consisted of 30 mCi of ^{57}Co in rhodium at room temperature. A 25-μm iron-foil absorber was used for calibration. All velocity scales and isomer shifts are referred to the iron standard at 298 K; for conversion to the sodium nitroprusside scale +0.257 mm·s^{-1} have to be added. Variable-temperature measurements between 80 and 300 K were performed by using a custom-made cryostat (iron/constantan thermocouple, Thor cryogenics E 3010-II temperature controller; temperature stability, ±0.10 K); measurements at 4.2 K were carried out by using a helium cryostat.

Preparation of Compounds. [Fe(“S_2”)$_2$(PMe$_3$)$_2$], 1, from $FeCl_2 \cdot 4H_2O$. A stirred solution of $FeCl_2 \cdot 4H_2O$ (705 mg, 3.55 mmol) in 30 mL of methanol was treated with a solution of NaOMe (810 mg, 15 mmol) and “S_2”-H_2 (0.87 mL, 7.1 mmol) in 15 mL of methanol. Upon addition of PMe$_3$ (1.4 mL, ca. 14 mmol), the red solution immediately turned into a yellow-brown suspension. The solid was removed by filtration, and air was bubbled through the filtrate for 10 min. The color immediately changed from brown to red-violet and finally to dark green. Black-green microcrystals of **1** precipitated, which were filtered off, washed with 40 mL of methanol, and dried in vacuo for 1 day: yield, 1.60 g (92%).

The crude product (940 mg, 1.9 mmol) was suspended in 40 mL of toluene. After addition of PMe$_3$ (0.5 mL, ca. 5 mmol), the mixture was refluxed for 15 min and filtered while hot. Slow cooling to 20 °C yielded black cubes of **1**, which were separated after 3 days, washed with toluene and *n*-hexane, and dried in vacuo for 6 h: yield, 530 mg. Anal. Calcd for $C_{18}FeH_{26}P_2S_4$ (488.46): C, 44.26; H, 5.37; S, 26.26. Found: C, 44.44; H, 5.47; S, 26.36.

1 from $FeCl_3$. A solution of NaOMe (700 mg, 13 mmol) and “S_2”-H_2 (0.74 mL, 6.0 mmol) in 20 mL of methanol was combined with a solution of $FeCl_3$ (485 mg, 3.0 mmol) in 30 mL of methanol. Addition of PMe$_3$ (1.2 mL, ca. 12 mmol) and filtration gave a red-violet solution. Bubbling air through this solution for ca. 5 min yielded a dark-green suspension. The black-green microcrystals of **1** were collected by filtration, washed with 40 mL of methanol, and dried in vacuo for 1 day: yield, 1.26 g (86%). Anal. Calcd for $C_{18}FeH_{26}P_2S_4$ (488.46): C, 44.26; H, 5.37. Found: C, 44.04; H, 5.27.

[Fe(“S_2”)$_2$(PMe$_3$)], 2, from 1. A gentle stream of N_2 was bubbled through the boiling blue-green toluene solution (35 mL) of **1** (630 mg, 1.29 mmol) for 2 h. The solution did not change in color and was filtered while hot, whereupon **2** crystallized in black needles and some unreacted **1** in big black cubes. The crystals were collected, washed with toluene and *n*-hexane, and dried in vacuo for 8 h. Manual separation of needles and cubes yielded 60 mg of educt **1** and 240 mg (45%) of **2**. Running the reaction on a larger scale, the product/educt ratio deteriorates; refluxing the toluene solution for a longer time, e.g., 3 h, led to decomposition and unidentifiable products, respectively. Anal. Calcd for $C_{15}FeH_{17}PS_4$ (412.38): C, 43.69; H, 4.16; S, 31.10. Found: C, 43.91; H, 4.24; S, 31.59.

2 from Irradiation of [Fe(“S_4”)(CO)(PMe$_3$)], 3. 3 (500 mg, 1.07 mmol) was dissolved in 100 mL of THF and irradiated for 2.5 h, while N_2 bubbled through the initially red-colored reaction solution. The reaction monitored by IR spectroscopy was finished when the ν(CO) absorption had vanished. The deep blue-green solution was evaporated to dryness, and the residue was extracted with hot toluene. The extracts were filtered and evaporated to dryness again yielding **2** which was characterized by IR and ^{1}H NMR spectroscopy.

[Fe(“S_2”)$_2$(PMe$_3$)$_2$], 1, by Reaction of 2 with PMe$_3$. To a suspension of **2** (170 mg, 0.41 mmol) in 10 mL of toluene PMe$_3$ (0.20 mL, ca. 2 mmol) was added. The blue-green suspension was refluxed for 5 min and filtered while hot. After 2 days at 20 °C black cubes and plates of **1** were separated, washed with toluene and *n*-hexane, and dried in vacuo for 1 day: yield, 120 mg (60%). Anal. Calcd for $C_{18}FeH_{26}P_2S_4$ (488.46): C, 44.26; H, 5.37. Found: C, 44.50; H, 5.71.

(NMe$_4$)[Fe(“S_2”)$_2$(PMe$_3$)$_2$]·CH_3OH, 4. NaOMe (425 mg, 7.9 mmol) and “S_2”-H_2 (0.48 mL, 3.9 mmol) dissolved in 10 mL of methanol were added to a solution of $FeCl_3$ (310 mg, 1.9 mmol) in 20 mL of methanol and stirred for 10 min. After addition of PMe$_3$ (0.40 mL, ca. 4 mmol), the resulting air-sensitive dark-violet reaction mixture was filtered and layered with a solution of NMe_4Cl (250 mg, 2.3 mmol) in 10 mL of methanol. Cooling to −30 °C for 10 days yielded black crystals of **4** which were filtered off, washed with 10 mL of cold methanol, and dried in vacuo for 1 day: yield, 890 mg (79%). Anal. Calcd for $C_{23}FeH_{42}NOP_2S_4$ (594.65): C, 46.46; H, 7.12; N, 2.36; S, 21.57. Found: C, 46.73; H, 6.72; N, 2.18; S, 21.59.

X-ray Structure Determinations. Black prisms of [Fe(“S_2”)$_2$(PMe$_3$)$_2$] (**1**) were grown by slow cooling of a toluene solution from 110 °C to 20 °C; [Fe(“S_2”)$_2$(PMe$_3$)] (**2**) was obtained in black needles according to the same procedure, and black columnar crystals of (NMe$_4$)[Fe(“S_2”)$_2$(PMe$_3$)$_2$]·CH_3OH (**4**) formed after storage of a methanolic Na[Fe(“S_2”)$_2$(PMe$_3$)$_2$] solution layered with NMe_4Cl in methanol for 10 days at −30 °C. The single crystals were sealed under N_2 in glass

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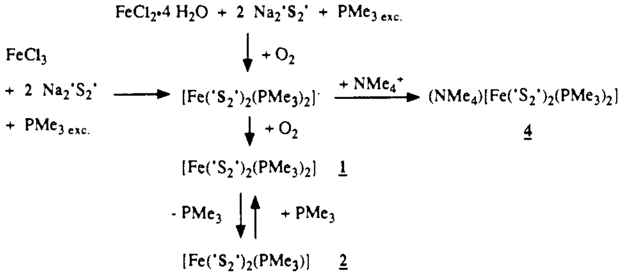
Table I. Crystallographic Data for **1**, **2**, and **4**

compound	[Fe(“S$_2$”)$_2$(PMe$_3$)$_2$], **1**	[Fe(“S$_2$”)$_2$(PMe$_3$)], **2**	(NMe$_4$)[Fe(“S$_2$”)$_2$(PMe$_3$)$_2$]·CH$_3$OH, **4**
formula	$C_{18}FeH_{26}P_2S_4$	$C_{15}FeH_{17}PS_4$	$C_{23}FeH_{42}NOP_2S_4$
mol wt	488.46	412.38	594.65
cryst dimens, mm	0.50 × 0.30 × 0.30	0.60 × 0.20 × 0.20	0.40 × 0.25 × 0.25
space group	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
cell dimensions			
a, pm	2075.7 (6)	1218.3 (3)	880.5 (3)
b, pm	1202.4 (2)	730.7 (4)	931.3 (3)
c, pm	875.0 (2)	1998.6 (4)	1793.9 (5)
α, deg	90.00 (0)	90.00 (0)	91.99 (2)
β, deg	90.00 (0)	104.20 (2)	91.83 (2)
γ, deg	90.00 (0)	90.00 (0)	94.40 (3)
V, pm^3	2184 (1) × 10^6	1724 (1) × 10^6	1464 (1) × 10^6
Z	4	4	2
d_{calcd}, g/cm^3	1.49	1.59	1.35
μ, cm^{-1}	12.1	14.2	9.1
wavelength, pm	71.073	71.073	71.073
meas temp, K	200	200	200
R/R_w	0.059/0.059	0.062/0.046	0.078/0.070

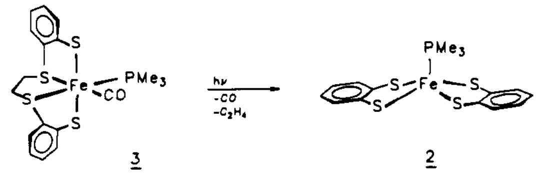
Scheme I



capillaries. The structures were solved by direct methods (SHELXTL PLUS). Non-hydrogen atoms were refined anisotropically, the aromatic hydrogen atoms were calculated for ideal geometry and restricted during refinement, the methyl hydrogen atoms were calculated for ideal tetrahedra and rotated around the central carbon atom during refinement, and the isotropic H atoms were refined with common temperature factors. The hydroxyl H-atom of the methanol molecule in 4 was located from the difference fourier map and fixed. 4 contains two independent half molecules, each completed by the symmetry of the crystal. Table I summarizes crystallographic data.

Results

Synthesis and Characterization of [Fe(“S$_2$”)$_2$(PMe$_3$)$_2$] (1), [Fe(“S$_2$”)$_2$(PMe$_3$)] (2), and (NMe$_4$)[Fe(“S$_2$”)$_2$(PMe$_3$)$_2$]·CH$_3$OH (4). The novel 1,2-benzenedithiolate complex [Fe(“S$_2$”)$_2$(PMe$_3$)$_2$] (**1**) forms in a one-step synthesis when either $FeCl_2 \cdot 4H_2O$ or $FeCl_3$ is reacted with Na$_2$“S$_2$” and PMe$_3$ in the presence of O_2. An intermediate in the reaction sequence must be the iron(III) species [Fe(“S$_2$”)$_2$(PMe$_3$)$_2$]$^-$. This could be confirmed by reacting $FeCl_3$ with Na$_2$“S$_2$” and PMe$_3$ in the absence of O_2 and isolation of (NMe$_4$)[Fe(“S$_2$”)$_2$(PMe$_3$)$_2$]·CH$_3$OH (**4**). When **1** is heated in boiling toluene, one PMe$_3$ can reversibly be decoordinated. Removal of PMe$_3$ by gaseous nitrogen yields five-coordinate [Fe(“S$_2$”)$_2$(PMe$_3$)] (**2**) (Scheme I). Although CO easily coordinates to [Fe(“S$_2$”)$_2$]$^{2-}$ yielding [Fe(“S$_2$”)$_2$(CO)$_2$]$^{2-}$,[8] the analogous complex [Fe(“S$_2$”)$_2$(PMe$_3$)$_2$]$^{2-}$ could not be obtained. **2** also forms according to eq 3.



3   2   (3)

UV irradiation of the thioether–thiolate Fe(II) complex [Fe(“S$_4$”)(CO)(PMe$_3$)] (**3**) (“S$_4$”$^{2-}$ = dianion of 1,2-bis((2-mercaptophenyl)thio)ethane) leads not only to cleavage of the Fe–CO bond but also to an intramolecular redox reaction: The tetradentate “S$_4$” ligand is desalkylated, and the iron center is oxidized to Fe(IV). Sulfur desalkylation reactions were previously observed also with [Fe(“S$_4$”)][23] and [Mo(“S$_4$”)(CO)$_2$(PMe$_3$)].[24]

1 and **2** are soluble in CHCl$_3$, CH$_2$Cl$_2$, THF, acetone, and toluene; ionic 4 is soluble in THF, acetone, and DMSO. Trans bis-adducts of iron bis-1,2-dithiolates are novel. In the extensively examined iron dithiolene systems usually monoadducts are found;[25-35] when bis-adducts formed, they were anionic and cis configurated with bidentate N, P, or As donor ligands.[32-35]

1, **2**, and 4 are paramagnetic. In solid state, the magnetic moments (295 K) of neutral **1** and **2** are 2.75 μ_B each, consistent with two unpaired electrons in low-spin Fe(IV) (d^4, $S = 1$) systems. For instance, room-temperature magnetic moments of 2.83 and 2.74 μ_B were measured for (PPh$_4$)$_2$[Fe(S$_2$C$_2$(CN)$_2$)$_3$] and (PPh$_4$)$_2$[Fe(S$_2$C$_2$(CN)$_2$)$_2$(S$_2$CC(CN)$_2$)], respectively.[36] In contrast, neutral XR$_3$ (X = P, As, Sb) monoadducts of iron bisdithiolenes, for example, [Fe(S$_2$C$_2$(CF$_3$)$_2$)$_2$(XPh$_3$)], are usually diamagnetic.[27,32,37] In solution (Evans' method,[38] CDCl$_3$, 295 K) magnetic moments of 4.2 μ_B for **1** and 3.6 μ_B for **2** are observed indicating low-spin/high-spin equilibria. The magnetic moment of solid 4 (2.00 μ_B at 295 K) well agrees with the characteristic value of ~2.1 μ_B for d^5 low-spin systems.[39]

The ^{1}H NMR spectra of **1** and **2** display signals which are isotropically shifted to high fields and well separated for the nonequivalent protons; in 4, NMe$_4^+$, and PMe$_3$ signals overlap, while the broad resonances of the aromatic protons appear also at high field (Table II). ^{31}P NMR data could be obtained only in the case of 4; **1** and **2** decomposed during the long time required for recording.

Resolved EPR spectra of **1** and **2** at 295 or 30 K could not be obtained, neither in the solid state nor in diluted toluene solutions. Only very broad signals of low intensity (**1**, δH ~ 500 G; **2**, δH ~ 300 G) with g values between 2.0 and 2.1 were observed. This is not uncommon for d^4 systems with short spin–lattice relaxation

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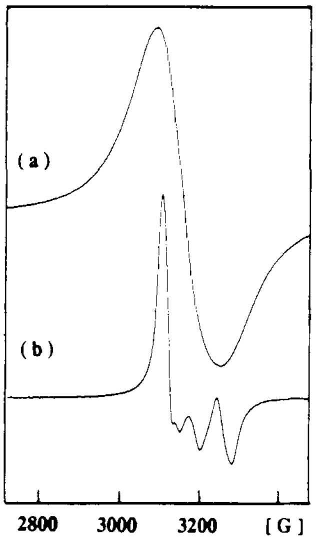

Figure 1. EPR spectra (9.29 GHz, 100 KHz modulation of the magnetic field) of solid **4** (a) at 295 K (power, 2.00 mW; identical spectrum at 63 μW) and (b) at 30 K (power, 200 μW).

times and large zero-field splittings.[40] The EPR spectrum of solid 4 at 295 K displays a slightly asymmetric singlet (g = 2.100, δH = 160 G) showing neither ^{31}P nor ^{1}H hyperfine splitting. At 30 K the signal splits anisotropically (Figure 1) and gives rise to more than three anisotropic g values, indicating at least two different species. They could be confirmed by X-ray analysis (see below) showing that solvated as well as unsolvated anions exist in crystalline 4.

Solution EPR spectra in acetone could not be obtained. Lack of hyperfine splittings and the g value distinctly deviating from the free electron value of 2.002 may indicate that the delocalization of the odd electron in 4 is restricted to the FeS$_4$ unit.

The strongest and most characteristic IR absorptions of **1**, **2**, and 4 are δ(PCH) (**1**, 935 cm^{-1}; **2**, 944 cm^{-1}; 4, 937 cm^{-1}) and the typical δ of ortho-disubstituted benzene rings (**1**, 745 cm^{-1}; **2**, 738 cm^{-1}; 4, 742 cm^{-1}). No evidence for a partial dithiodiketone character of the benzenedithiolate carbon–sulfur bonds could be found, because IR absorptions assigned to ν(C=S) at ca. 1110 and ca. 860 cm^{-1} in typical dithiolene complexes[4a,5a] are not present in the spectra of **1**, **2**, and **4**.

The mass spectra (FD and EI) of **1**, **2**, and **4** each display a [Fe("S$_2$")$_2$(PMe$_3$)]$^+$ signal at m/e = 412. For **1** and 4 no molecular ions could be observed, and the monoadduct **2** seems to be the most stable species under mass spectroscopical conditions.

High-intensity low-energy electron transitions (λ > 700 nm, ϵ > 15.000 L mol^{-1} cm^{-1}) are characteristic in particular of high-valent metal dithiolenes.[13] They are assigned to π–π^* transitions between molecular orbitals which are generally assumed to be highly delocalized over metal, sulfur, and unsaturated C–C bonds.[13] These absorptions are usually absent in dianionic dithiolenes.[4a] **1**, **2**, as well as **4** show transitions in the respective region above 700 nm, but their intensity is much smaller than in high-valent dithiolene complexes (Table II). Despite their different coordination numbers, **1** and **2** show remarkably similar spectra indicating that they are dominated mainly by transitions in the FeS$_4$ unit.

Table II lists selected spectroscopic and magnetic data for **1**, **2**, and **4**.

X-ray Structure Determinations

The crystal structure determinations revealed that **1**, **2**, and 4 are strictly mononuclear complexes. **4** consists of discrete NMe$_4^+$ cations and [Fe("S$_2$")$_2$(PMe$_3$)$_2$]$^-$ anions. Distances shorter than van der Waals contacts could not be found between the iron species in any of the compounds. Crystallographic data of **1**, **2**, and **4** are summarized in Table I, and selected bond distances and angles are listed in Table III.

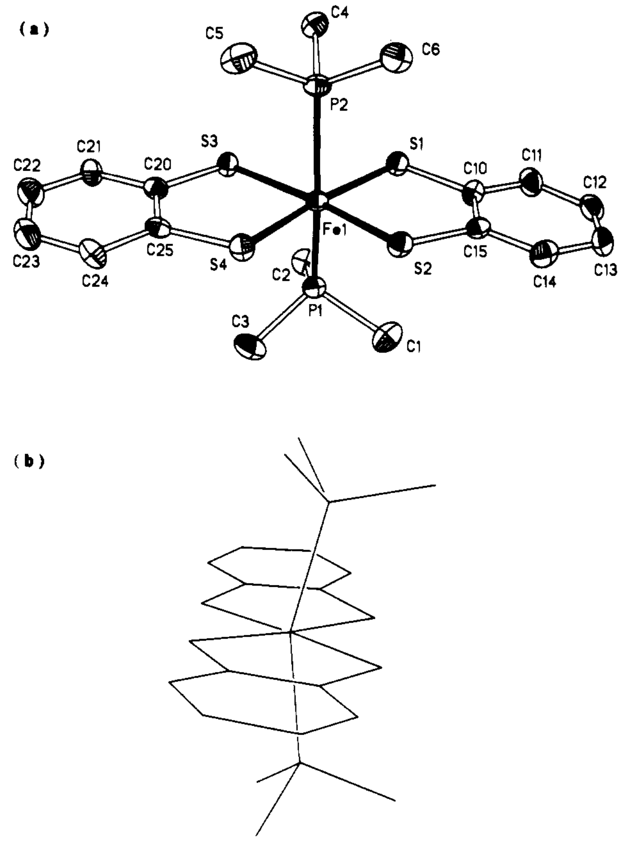

Figure 2. (a) Molecular structure (H atoms omitted) of [Fe("S$_2$")$_2$(PMe$_3$)$_2$] (**1**) and (b) side view of a schematic molecule.

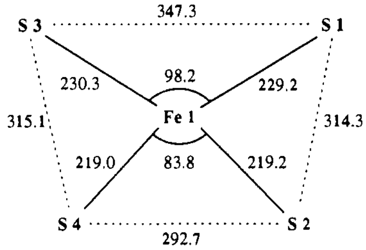

Figure 3. Trapezoidal distortion of the planar FeS$_4$ unit in **1** (distances, pm; angles, deg).

The iron atom in [Fe("S$_2$")$_2$(PMe$_3$)$_2$] (**1**) is coordinated by four sulfur atoms of two chelating "S$_2$"$^{2-}$ ligands and by two trans PMe$_3$ phosphorus atoms (Figure 2a). The resulting pseudooctahedron is strongly distorted because the P2-Fe1-P1 angle of only 159.7 (1)° deviates more than 20° from linearity (Figure 2b).

A second distortion from octahedral symmetry is found in the Fe("S$_2$")$_2$ unit. A common feature of planar metal bisdithiolenes is almost equal intra- and interligand S-S distances such that the MS$_4$ unit form regular squares with S-M-S angles all being close to 90° and all M-S distances being identical.[41] In **1**, the FeS$_4$ unit is planar within ±1 pm; the FeS$_4$ plane, however, does not form a square but a trapezoid as illustrated in Figure 3.

The S1-Fe1-S3 (98.2 (1)°) and S4-Fe1-S2 (83.8 (1)°) angles significantly deviate from 90°, while both intraligand S-Fe-S angles (89.0 (1)°) are almost rectangular. The Fe-S bonds confining the larger S-Fe-S angle are more than 10 pm longer (230.3 (2) and 229.2 (3) pm) than Fe1-S2 (219.2 (3) pm) and Fe1-S4 (219.0 (3) pm). In other words, each bidentate "S$_2$"$^{2-}$ ligand coordinates by forming one long and one short Fe–S bond. The trapezoidal deformation of the FeS$_4$ unit causes no structural irregularities within the ligands themselves; that means all C–S

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Table II. Selected Spectroscopic and Magnetic Data of **1**, **2**, and **4**

complex	μ_{eff}, μ_B	EPR, $\langle g\rangle^a$	NMR^b δ, ppm	UV-vis-NIR^c λ(ε), nm (L mol^{-1} cm^{-1}·10^3)
[Fe("S_2")$_2$(PMe$_3$)$_2$] **1**	2.75^d	2.0–2.1^{d,f}	$^1H^h$ −21.0 (18 H, s, CH_3)	330 (15.7), 480 (sh, 3.4), 505 (3.6), 655 (6.0), 720 (sh, 5.0), 1190 (1.0), 1440 (1.6)
	4.2^e		−32.8 (4 H, s ar)	
			−42.8 (4 H, s, ar)	
[Fe("S_2")$_2$(PMe$_3$)] **2**	2.75^d	2.0–2.1^{d,g}	$^1H^h$ −29.8 (4 H, s, ar)	315 (sh, 15.8), 360 (sh, 7.4), 480 (5.1), 580 (sh, 4.8), 645 (8.6), 730 (sh, 5.2), 1210 (0.7), 1510 (0.8)
	3.6^e		−34.1 (4 H, s, ar)	
			−44.5 (9 H, s, CH_3)	
(NMe$_4$)[Fe("S_2")$_2$(PMe$_3$)$_2$]·CH_3OH **4**	2.00^d	2.100^{d,f}	$^1H^i$ 4.1 (1 H, m, CH_3OH)	360 (19.0), 480 (sh, 7.2), 510 (13.2), 550 (sh, 5.4), 1080 (0.2), 1320 (0.1)
			3.15 (3 H, d, CH_3OH)	
			3.0 (30 H, s, sh, N(CH_3)$_4$ and P(CH_3)$_3$)	
			−30 (4 H, s (br), ar)	
			−36 (4 H, s (br), ar)	
			$^{31}P^i$ −70	

^{a} Frequency: 9.29 GHz, 100 kHz modulation of the magnetic field. ^{b} 270 MHz. ^{c} Acetone solutions, 5 × 10^{-4} M, sh = shoulder. ^{d} Solid, 295 K. ^{e} $CDCl_3$ solution, Evans' method. ^{f} Power: 2.0 mW. ^{g} Power: 200 μW. ^{h} In $CDCl_3$. ^{i} In DMSO-d_6.

bonds are identical within standard deviations, and the two intraligand S–S distances (314.3 and 315.1 pm) show no anomality either. The trapezoidal deformation gives rise to a long S1–S3 (347.3 pm) and a very short S2–S4 (292.7 pm) interligand distance. The short distance is still much larger than a S–S single bond (av 205 pm for cyclo-S_x, x = 6,8,10,12,18,20[42]) and certainly nonbonding. Due to the eclipsed arrangement of the *trans*-PMe$_3$ methyl groups, the overall symmetry of **1** in solid state is C_{2v}.

In [Fe("S_2")$_2$(PMe$_3$)] (**2**) five-coordinate iron is surrounded by four sulfur atoms (maximum deviation from a common S_4 plane is ±1 pm) and one apical phosphorus atom forming a square pyramid. The iron center is located 22.8 pm above the basal S_4 plane (Figure 4). An analogous displacement (23 pm) is observed in [Fe($S_2C_2(CF_3)_2$)$_2$(AsPh$_3$)].[18]

Within the standard deviations the four Fe–S distances are identical (av 218.5 (3) pm). They are approximately as long as the "short" Fe–S bonds in **1** (av 219.1 (3) pm) and somewhat longer than the corresponding average distances in [Fe($S_2C_2Ph_2$)$_2$(P(OMe)$_3$)] (216.6 pm)[19] and [Fe($S_2C_2(CF_3)_2$)$_2$(AsPh$_3$)] (214.8 pm).[18] Again, the Fe–P bond in **2** does not stand perpendicular on but is inclined to the S_4 plane as was observed for the two PMe$_3$ groups in **1** (Figure 4b). Likewise, differences between interligand S···S distances (311.7 and 299.4 pm) and S–Fe–S angles (91.1 (1)° and 86.4 (1)°) cause a trapezoidal distortion of the basal S_4 plane. The interligand S···S distances difference of ~11 pm, however, is smaller when compared to the structure of six-coordinate **1** showing a difference of ~55 pm. Trapezoidal distortions in FeS$_4$ entities of dimensions as observed in **2** were previously reported for [Fe($S_2C_2(CF_3)_2$)$_2$(AsPh$_3$)],[18] displaying identical Fe–S bond lengths but a long (308.7 (2) pm) and a short (295.2 (2) pm) interligand S···S distance. The latter was discussed also as a nonbonding interaction. The Fe–P distance in **2** (224.0 (3) pm) is significantly shorter than the Fe–P bond lengths in **1** (232.7 (3) and 232.2 (3) pm), in agreement with theoretical considerations.[43,44]

Because **2** is five-coordinate but mononuclear, intermolecular interactions in the solid state were examined. In the crystal lattice, the molecules of **2** are stacked in columns parallel to the *b* axis. Within each stack, the complexes are oriented in the same direction; the iron atoms, however, stay strictly five-coordinate; the shortest intermolecular Fe–P, Fe–Fe, or Fe–S distance observed is 462.5 pm for Fe–S and excludes Fe–S–Fe bridges between adjacent molecules. Slight interstack S···S interactions (358–382 pm), however, exist between sulfur atoms of neighboring molecules with dimensions in the range of sulfur–sulfur van der Waals contacts (~370 pm).[45] A stacking as observed for **2** is not found in the related [Fe($S_2C_2(CF_3)_2$)$_2$(AsPh$_3$)][18] and [Fe($S_2C_2Ph_2$)$_2$(P(OMe)$_3$)];[19] in **2** it may be due to the flat dithiolate ligands and the small PMe$_3$ group, which are sterically much less demanding than the bulky dithiolenes and AsPh$_3$.

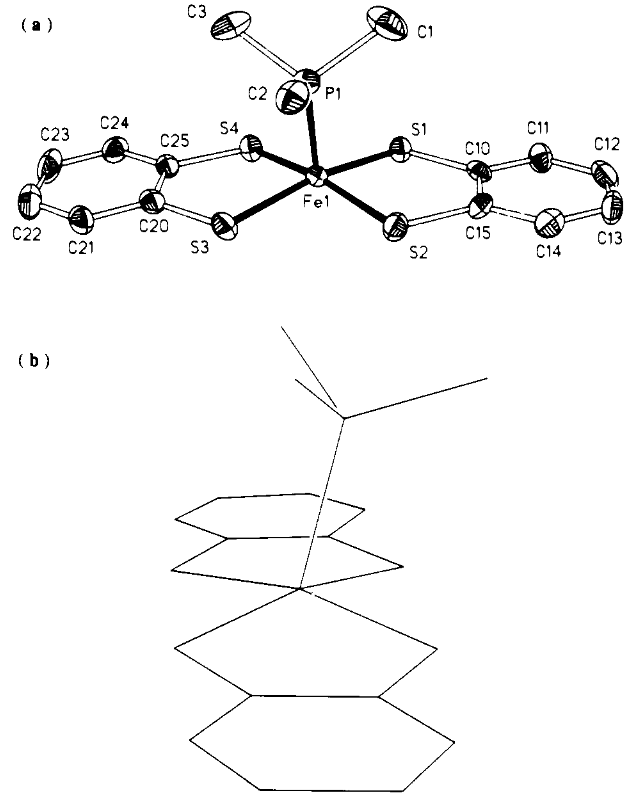

Figure 4. (a) Molecular structure (H atoms omitted) and (b) schematical side view of [Fe("S_2")$_2$(PMe$_3$)] (**2**).

The unit cell of (NMe$_4$)[Fe("S_2")$_2$(PMe$_3$)$_2$]·CH_3OH (**4**) contains two different, independent halves of complex molecules, each completed by the symmetry of the crystal. One [Fe("S_2")$_2$(PMe$_3$)$_2$]$^-$ anion is solvated by two methanol molecules via hydrogen bridges to trans sulfur atoms, while the other anion is unsolvated. Both species exhibit approximately the same molecular geometry and distances. Figure 5 shows a view only of the solvated anion; selected distances and angles of both independent anions are listed in Table III.

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Table III. Selected Interatomic Distances (pm) and Angles (deg) for **1**, **2**, and **4**

[Fe(“S_2”)$_2$(PMe$_3$)$_2$], **1**			
Fe(1)–S(1)	229.2 (3)	Fe(1)–S(2)	219.2 (3)
Fe(1)–S(3)	230.3 (2)	Fe(1)–S(4)	219.0 (3)
Fe(1)–P(1)	232.7 (3)	Fe(1)–P(2)	232.2 (3)
S(1)–C(10)	175.4 (9)	S(2)–C(15)	174.0 (10)
S(3)–C(20)	174.0 (10)	S(4)–C(25)	174.3 (9)
C(15)–C(14)	139.2 (14)	C(15)–C(10)	140.0 (13)
C(14)–C(13)	140.2 (15)	C(13)–C(12)	138.3 (16)
C(12)–C(11)	138.0 (14)	C(11)–C(10)	141.9 (14)
C(25)–C(24)	142.0 (14)	C(25)–C(20)	140.4 (13)
C(24)–C(23)	138.9 (14)	C(23)–C(22)	140.6 (16)
C(22)–C(21)	136.9 (15)	C(21)–C(20)	141.5 (13)
S(1)···S(2)	314.3	S(1)···S(3)	347.3
S(2)···S(4)	292.7	S(3)···S(4)	315.1
S(1)–Fe(1)–S(2)	89.0 (1)	S(1)–Fe(1)–S(3)	98.2 (1)
S(2)–Fe(1)–S(3)	172.8 (1)	S(1)–Fe(1)–S(4)	172.8 (1)
S(2)–Fe(1)–S(4)	83.8 (1)	S(3)–Fe(1)–S(4)	89.0 (1)
S(1)–Fe(1)–P(1)	83.1 (1)	S(2)–Fe(1)–P(1)	97.5 (1)
S(3)–Fe(1)–P(1)	83.5 (1)	S(4)–Fe(1)–P(1)	97.0 (1)
S(1)–Fe(1)–P(2)	83.7 (1)	S(2)–Fe(1)–P(2)	97.6 (1)
S(3)–Fe(1)–P(2)	83.2 (1)	S(4)–Fe(1)–P(2)	98.0 (1)
P(1)–Fe(1)–P(2)	159.7 (1)		
[Fe(“S_2”)$_2$(PMe$_3$)], **2**			
Fe(1)–P(1)	224.0 (3)	Fe(1)–S(1)	218.6 (3)
Fe(1)–S(2)	218.3 (2)	Fe(1)–S(3)	218.5 (3)
Fe(1)–S(4)	218.7 (2)	S(1)–C(10)	175.9 (6)
S(2)–C(15)	175.3 (8)	S(3)–C(20)	175.1 (7)
S(4)–C(25)	174.9 (8)	C(25)–C(24)	139.5 (9)
C(25)–C(20)	139.7 (11)	C(24)–C(23)	136.6 (11)
C(23)–C(22)	140.5 (12)	C(22)–C(21)	136.8 (10)
C(21)–C(20)	138.5 (12)	C(15)–C(14)	140.1 (9)
C(15)–C(10)	140.0 (10)	C(14)–C(13)	137.6 (11)
C(13)–C(12)	138.4 (12)	C(12)–C(11)	137.2 (9)
C(11)–C(10)	139.7 (11)		
S(1)···S(2)	308.7	S(1)···S(4)	299.4
S(2)···S(3)	311.7	S(3)···S(4)	309.5
P(1)–Fe(1)–S(1)	106.1 (1)	P(1)–Fe(1)–S(2)	87.6 (1)
S(1)–Fe(1)–S(2)	89.9 (1)	P(1)–Fe(1)–S(3)	86.5 (1)
S(1)–Fe(1)–S(3)	167.4 (1)	S(2)–Fe(1)–S(3)	91.1 (1)
P(1)–Fe(1)–S(4)	104.2 (1)	S(1)–Fe(1)–S(4)	86.4 (1)
S(2)–Fe(1)–S(4)	168.2 (1)	S(3)–Fe(1)–S(4)	90.1 (1)
(NMe$_4$)[Fe(“S_2”)$_2$(PMe$_3$)$_2$]·CH$_3$OH, **4**			
[Fe(“S_2”)$_2$(PMe$_3$)$_2$]$^-$·2CH$_3$OH			
Fe(1)–P(1)	231.9 (2)	Fe(1)–S(1)	227.3 (2)
Fe(1)–S(2)	226.3 (2)	S(1)–C(10)	176.6 (6)
S(2)–C(15)	176.0 (6)	C(15)–C(14)	139.2 (8)
C(15)–C(10)	140.8 (8)	C(14)–C(13)	138.1 (10)
C(13)–C(12)	138.1 (10)	C(12)–C(11)	138.2 (9)
C(11)–C(10)	138.5 (9)	O(1)–C(35)	140.5 (13)
O(1)–H(1D)	84.2	H(1D)···S(1)	243.7
S(1)···S(2)	318.7	S(1)···S(2A)	322.6
P(1)–Fe(1)–S(1)	92.9 (1)	P(1)–Fe(1)–S(2)	87.4 (1)
S(1)–Fe(1)–S(2)	89.3 (1)	S(1)–Fe(1)–P(1A)	87.1 (1)
S(2)–Fe(1)–P(1A)	92.6 (1)	S(1)–Fe(1)–S(2A)	90.7 (1)
O(1)–H(1D)···S(1)	168.7		
[Fe(“S_2”)$_2$(PMe$_3$)$_2$]$^-$			
Fe(2)–P(2)	232.5 (2)	Fe(2)–S(3)	225.7 (2)
Fe(2)–S(4)	224.8 (2)	S(3)–C(20)	175.8 (7)
S(4)–C(25)	174.9 (7)	C(25)–C(24)	141.1 (10)
C(25)–C(20)	140.0 (10)	C(24)–C(23)	137.3 (13)
C(23)–C(22)	138.6 (15)	C(22)–C(21)	135.0 (13)
C(21)–C(20)	140.9 (10)		
S(3)···S(4)	317.4	S(3)···S(4A)	319.8
P(2)–Fe(2)–S(3)	87.0 (1)	P(2)–Fe(2)–S(4)	91.1 (1)
S(3)–Fe(2)–S(4)	89.6 (1)	S(3)–Fe(2)–P(2A)	93.0 (1)
S(4)–Fe(2)–P(2A)	88.9 (1)	S(3)–Fe(2)–S(4A)	90.4 (1)

[a] Estimated standard deviations are given in parentheses.

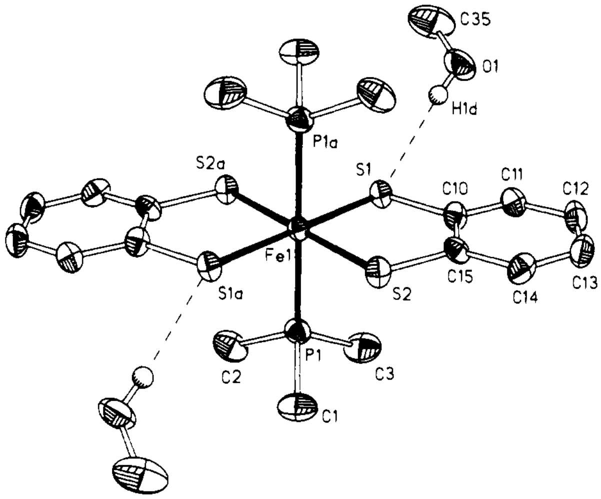

Figure 5. Molecular structure (H atoms omitted with the exception of H1d) of the anion [Fe(“S_2”)$_2$(PMe$_3$)$_2$]$^-$·2CH$_3$OH.

Both anions possess crystallographically imposed centrosymmetry. The iron atoms are each surrounded pseudooctahedrally by four sulfur and two trans phosphorus atoms. The S_4 units are nearly square-planar showing inter- and intraligand S···S distances between 317.4 and 322.6 pm; the Fe–S bonds cover the range from 224.8 (2) to 227.3 (2) pm. Structural data of six-coordinate Fe(III) and Fe(IV) bis-dithiolene bis-adducts were not yet reported; in the square-pyramidal Fe(III) monoadduct (NBu$_4$)[Fe(S$_2$C$_2$(CF$_3$)$_2$)$_2$(OPPh$_3$)][46] or the binuclear (NBu$_4$)$_2$[μ-N$_2$H$_4$-{Fe(“S_2”)$_2$}$_2$][10] the average Fe–S distances of 222 and 223 pm, respectively, are significantly shorter than in **4**. Average Fe–S bond lengths of 223 and 222 pm, respectively, are also reported for the planar FeS$_4$ units of dimeric [Fe(”S_2”)$_2$]$_2^{2-}$[47] with square-pyramidal pentacoordinate iron and the analogous Fe(III) 1,2-toluenedithiolate.[48]

The approximately identical Fe–P distances of neutral **1** and anionic **4** show that the additional electron in **4** occupies a molecular orbital which is nonbonding with respect to iron and phosphorus. This is consistent with the lack of ^{31}P hyperfine splitting in the EPR spectra of **4**.

The bridging methanolic hydrogen atom, H1d, in [Fe(“S_2”)$_2$(PMe$_3$)$_2$]$^-$·2CH$_3$OH was located from a difference fourier map. It yielded a O1–H1d distance of 84.2 pm, a H1d–S1 contact of 243.7 pm, and an almost linear O1–H1d–S1 angle of 168.7°. Comparable X–H···S (X = N, O) bridges were found in Fe$_4$S$_4$-type ferredoxines (ca. 240 pm) and discussed to be very strong interactions.[49] In **4** no strong influence of the hydrogen bonds on Fe–S bond lengths can be observed. Fe1–S1 (227.3 (2) pm) and Fe1–S2 (226.3 (2) pm) distances do not significantly differ in the solvated anion and are only marginally longer than the corresponding bond lengths in the unsolvated anion (Fe2–S3 = 225.7 (2) pm and Fe2–S4 = 224.8 (2) pm). The sharp methanol signals in the ^{1}H NMR spectrum of **4** indicate that in solution the hydrogen bridges are not maintained (cf. Table II).

Comparative Discussion of 1, 2, and 4: Is 1,2-Benzenedithiolate an Innocent or Noninnocent Ligand? The partial oxidation of nonaromatic dithiolene ligands to the corresponding dithiodiketones was concluded from IR studies and from comparison of structural data of low- and high-valent metal dithiolene complexes. In low-valent anionic complexes C–S bond lengths close to the values for C–S single bonds and C=C double bond distances were found, indicating dithiolate character of the ligands; in high-valent neutral species, however, comparatively shorter C–S and larger C–C distances suggested partial ligand oxidation to the dithiodiketone form as illustrated in eq 1. Examples are [Ni(S$_2$C$_2$(CN)$_2$)$_2$]$^{n-}$ (n = 1, 2)[50] and [Ni(S$_2$C$_2$Ph$_2$)$_2$]$^{-,0}$[51,52] complexes. This view was

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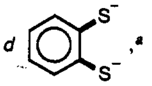
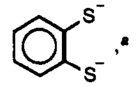
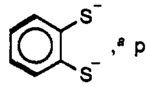
Table IV. Average C_{ar}–S and $(C–C)_{ar}$ Distances in **1**, **2**, **4**, $[Fe(“S_2”)_2]^{2-}$, and bzo$_2$-18S6

compound	d  ,^{a} pm	d  ,^{a} pm	d  ,^{a} pm	ref
$[Fe(“S_2”)_2(PMe_3)_2]$, **1**	174.4 (10)	140.2 (13)	138.5 (15)	this work
$[Fe(“S_2”)_2(PMe_3)]$, **2**	175.3 (7)	139.9 (11)	137.1 (10)	this work
$(NMe_4)[Fe(“S_2”)_2(PMe_3)_2]{\cdot}CH_3OH$, **4**	176.3 (6)^b	140.8 (8)^b	138.2 (10)^b	this work
	175.4 (7)^c	140.0 (10)^c	136.2 (13)^c	
$(AsPh_4)_2[Fe(“S_2”)_2]$, **6**	176.3 (8)	139.9 (15)	138.7 (12)	7
bzo$_2$-18S6	177.2 (5)	138.9 (8)	137.3 (8)	54

^{a} C–S and C–C bonds regarded are marked with thick lines. ^{b} For $[Fe(“S_2”)_2(PMe_3)_2]^-{\cdot}2CH_3OH$. ^{c} For $[Fe(“S_2”)_2(PMe_3)_2]^-$.

Table V. Isomer Shifts (δ), Quadrupole Splittings (ΔE_Q) and Line Widths (Γ) of **1**, **2**, and **4** at Different Temperatures

compound	T, K	δ,^{a} mm/s	ΔE_Q, mm/s	Γ, mm/s
$(NMe_4)[Fe(“S_2”)_2(PMe_3)_2]{\cdot}$ CH_3OH, **4**	271	0.224 (3)	1.615 (6)	0.369 (14), 0.334 (11)
	92	0.293 (1)	1.669 (2)	0.381 (4), 0.318 (3)
$[Fe(“S_2”)_2(PMe_3)_2]$, **1**	271	0.093 (1)	1.595 (3)	0.289 (4)
	86	0.168 (1)	1.536 (2)	0.294 (2)
	4.2	0.165 (1)	1.523 (2)	0.301 (4)
$[Fe(“S_2”)_2(PMe_3)]$, **2**	4.2	0.115 (1)	3.033 (1)	0.308 (2)

^{a} Relative to iron at room temperature.

supported by EPR of paramagnetic monoanionic nickel dithiolene complexes. They suggested a $[Ni^{II}$ (radical ligand)$_2]^-$ description, and as one consequence metal high valency in these systems was declared a myth.[53] Due to the aromatic system, an oxidation of 1,2-benzenedithiolate to give dithio-*o*-benzoquinone is expected to be less favorable, although it cannot be excluded a priori. In order to decide whether 1,2-benzenedithiolate acts as a dithiolene type noninnocent ligand or as an innocent dianionic dithiolate, the relevant C–S and $(C–C)_{ar}$ distances of **1**, **2**, **4**, and additionally of dianionic $[Fe(“S_2”)_2]^{2-}$[7] (**6**) as well as of dibenzo-18-crown-S6, bzo$_2$-18S6,[54] containing the “S_2” entity in an exclusively organic environment, were analyzed (Table IV).

The comparison of the compounds in Table IV shows that average C–S distances in **1**, **2**, **4**, and **6** cover the small range from 174.4 (10) to 176.3 (8) pm and are identical within the standard deviations. They agree with those found for the benzenedithiolate fragment in bzo$_2$-18S6 where partial oxidation to a dithiodiketone can be excluded. The C–C distances within the C_6 rings seem to differ slightly, but this holds for all complexes including bzo$_2$-18S6 and demonstrates that it is rather due to the ortho disubstitution than to the oxidation state of the Fe centers. In conclusion, the X-ray data yield no evidence that 1,2-benzenedithiolate is a noninnocent ligand in iron complexes. It shows no tendency to oxidize partially to a dithio-*o*-benzoquinone, and the stabilization of the iron oxidation state of +IV in **1** and **2** must have other reasons.

Mössbauer Spectroscopy

Although the term oxidation state is a purely formal concept, it is useful for the description of relative localizations of electrons. In order to further confirm the assignment of Fe(IV) centers in **1** and **2**, Mössbauer spectra were recorded. Table V lists the relevant data; characteristic spectra are shown in Figure 6.

The zero-field spectra of **1** at temperatures between 4.2 and 271 K display symmetrical quadrupole doublets. The doublet of **2** shows a slight inequivalence of the absorption signal areas, although the line widths Γ are equal. This is probably due to small effects of anisotropy caused by the needle shape of the microcrystals. In the case of **4**, the areas of amplitudes are equal, but the line widths are different as a consequence of the superimposition of two spectra which are only slightly different with respect to their isomer shifts δ and quadrupole splittings ΔE_Q. This is caused by the fact that crystals of **4** contain anions which differ with respect to solvation, as was shown above. The isomer shifts δ of **1** and **4** display normal temperature dependence.

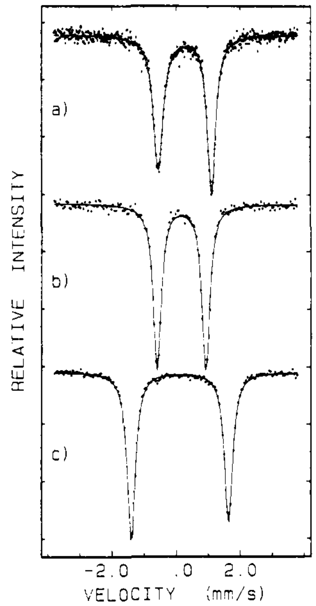


Figure 6. Zero-field Mössbauer spectra of (a) **4** at 92 K, (b) **1** at 4.2 K, and (c) **2** at 4.2 K. The full lines are least-squares fits with Lorentzian line shapes.

The δ values of **1** and **2** (Table V) compare with the data reported for other Fe(IV) compounds with $S = 1$ states,[36,55-57] ranging from +0.01 to +0.24 mm/s at room temperature and from +0.11 to +0.31 mm/s at 4.2 K. It may be noted that this shift region does not overlap with any other δ range of iron ($S = 1$) compounds[58] and is characteristic when the magnetism of the species is known. There are only a few Fe(IV) compounds, and most of them contain FeS_6 cores;[36,55,56] others are, for example, arsine complexes[57] and Fe(IV) porphyrin centers, which appear to be present in the oxidized forms of certain peroxidases.[59]

Due to the screening effect of p- and d-orbitals on the s-orbitals, the isomer shifts of Fe(IV) compounds are smaller than those of corresponding Fe(III) complexes, because loss of one 3d electron, when Fe(III) d^5 is oxidized to Fe(IV) d^4, causes a higher relative

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Table VI. Selected Electrochemical Parameters

complex	E_{pc},[a,c] V	E_{pa},[b,c] V	ΔE_p,[d] V	E,[e] V	I_{pa}/I_{pc}[f]	
[Fe("S_2")$_2$(PMe_3)$_2$], **1**	−0.314	−0.252	0.062	−0.28	1.1	first reduction
	−1.091	−1.012	0.079	−1.05	1.1	second reduction
	−0.330	−0.264	0.066	−0.30	0.9[g]	oxidation
(NMe_4)[Fe("S_2")$_2$(PMe_3)$_2$]·CH_3OH, **4**	−1.103	−1.019	0.084	−1.06	1.1	reduction
[Fe("S_2")$_2$(PMe_3)], **2**	−0.309	−0.246	0.063	−0.28	1.1	first reduction
	−1.072	−0.975	0.097	−1.02	1.1	second reduction
	0.648	0.714	0.066	0.68	0.7[g]	oxidation

[a] CV, reduction peak. [b] CV, oxidation peak. [c] Scan rates: 0.020, 0.050, 0.100 V/s. [d] $E_{pa} - E_{pc}$. [e] (Formal) redox potential. [f] Peak current ratio. [g] I_{pc}/I_{pa}. Acetone, 1 × 10^{-4} M solutions, 0.10 M NBu_4ClO_4, room temperature.

s electron density at the iron center. This was previously illustrated, for example, for $(PPh_4)_3[Fe^{III}(S_2C_2(CN)_2)_3]$[60] and $(PPh_4)_2[Fe^{IV}(S_2C_2(CN)_2)_3]$[36] showing room-temperature isomer shifts of 0.29 and 0.012 mm/s, respectively. It is also found for the neutral Fe(IV) complex **1** and the corresponding anionic Fe(III) complex **4** (Table V). On the contrary to that and regardless of the charge, the δ values of $[Fe(S_2C_6Cl_4)_2]_2^{n}$ (n = 0, 2−) are identical (0.23 mm/s each at 295 K),[61] demonstrating that both compounds contain iron in the same electronic state, and this clearly cannot be Fe(IV).

1, **2**, and **4** possess sizable quadrupole splittings (Table V); ΔE_Q of **1** agrees remarkably well with those of $(PPh_4)_2[Fe(S_2C_2(CN)_2)_3]$ and $(PPh_4)_2[Fe(S_2C_2(CN)_2)_2(S_2CC(CN)_2)]$ (1.53 and 1.58 mm/s at 297 K, respectively),[36] which contain also six-coordinate Fe(IV) (S = 1) centers. Pseudooctahedral **1** and **4** display almost identical ΔE_Q values due to their very similar molecular geometries; an analogous behavior was found for $[Fe(S_2C_2(CN)_2)_3]^{n-}$ (n = 2, 3), showing room-temperature ΔE_Q's of 1.65 mm/s for the Fe(III) compound[60] and of 1.53 mm/s for the Fe(IV) species,[36] respectively.

The large ΔE_Q of **2** is comparable to ΔE_Q of $[Fe(S_2C_2Ph_2)_2(PPh_3)]$ (2.78 mm/s at 77 K)[61] and can be attributed to a more asymmetric ligand environment of iron in a square-pyramidal than in a pseudooctahedral coordination sphere. In conclusion, the Mössbauer results corroborate the presence of Fe(IV) centers in the neutral mono- and bis-adducts [Fe("S_2")$_2$(PMe_3)] (**2**) and [Fe("S_2")$_2$(PMe_3)$_2$] (**1**).

Electrochemical Results

The syntheses of **1** and **4** proved the stability of the [Fe("S_2")$_2$(PMe_3)$_2$] unit in different oxidation states. A characteristic feature of dithiolene complexes is their versatile electrochemistry: In general, two reversible one-electron redox steps are observed for $[M(S_2C_2R_2)_2]^n$ complexes (n = 0, −1, −2);[4,13] in special cases four and even five redox states were reported.[4,28,62] The redox flexibility of these species is commonly attributed to the noninnocence of dithiolene ligands, leading to extensive delocalization and stabilization of charge.

X-ray and Mössbauer results indicate that in **1**, **2**, and **4** the aromatic C_6 rings of the 1,2-benzenedithiolate ligands are not involved in charge delocalization. This implies that the stabilization of different Fe oxidation states is due to the thiolate donors and not to the fact that the sulfur atoms are connected via unsaturated C–C bonds. Thus it was also of interest to test the electrochemical behavior of **1**, **2**, and **4**. Cyclic voltammograms (CVs) were recorded in acetone in the range from +1.2 to −1.9 V vs NHE (Figure 7). **1** and **4** display identical CVs with two reversible redox waves (Table VI) and three irreversible oxidation peaks at +0.70, +0.50, and +0.37 V. **2** shows analogous cathodic behavior with two reversible redox waves at −0.28 and −1.02 V, but the anodic electrochemistry is more simple: Only one oxidation wave at +0.68 V is observed which is quasi-reversible.

The reversible redox waves of **1**, **2**, and **4** at about −0.3 and −1.0 V are assigned to Fe(IV/III) and Fe(III/II) couples, respectively. The irreversible peaks of **1** and **4** at +0.50 V were independently proved to be due to oxidation of free PMe_3. The anodic peaks at about +0.70 V, being irreversible for **1** and **4** and quasi-reversible for **2**, are therefore possibly due to the [Fe("S_2")$_2$(PMe_3)] → [Fe("S_2")$_2$(PMe_3)]$^+$ oxidation of the monophosphine adduct, which forms when **1** or **4** loses one PMe_3. This indicates that even an Fe(V) species may be accessible in this system. The irreversible peak for **1** and **4** at +0.37 V is suggested to be caused by oxidation of [Fe("S_2")$_2$(PMe_3)$_2$] but could not be assigned definitely. Selected electrochemical parameters are listed in Table VI.

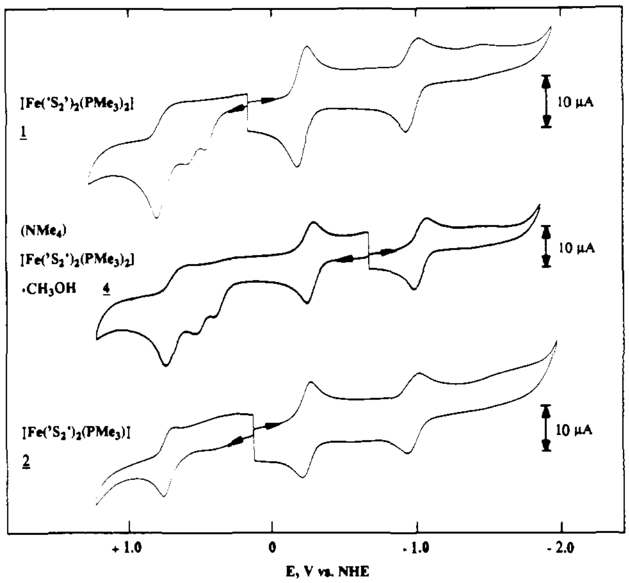

Figure 7. Cyclic voltammograms of **1**, **4**, and **2**, 1 × 10^{-4} M, 0.10 M NBu_4ClO_4, acetone. Scan rate = 0.100 V s^{-1}.

Empirical relationships between redox potentials and chemical reactivity of dithiolenes were stated by Davison and Holm.[63] These relationships are also applicable to the Fe("S_2")$_2$ phosphine complexes. First, reduced species in redox couples with potentials more negative than ca. +0.2 V[64] are oxidized by air. This was found for [Fe("S_2")$_2$(PMe_3)$_2$]$^-$ which is oxidized by air to the neutral Fe(IV) complex. Second, reduction of oxidized species in couples with potentials more negative than ca. −0.8 V[64] is not possible by normal chemical methods due to irreversible destruction of the complex. This too proved to be true for the [Fe("S_2")$_2$(PMe_3)$_2$] system: Salts of [Fe("S_2")$_2$(PMe_3)$_2$]$^{2-}$ could not yet be obtained in substance, in the system Fe(II)/"S_2"/PMe_3 only neutral [Fe("S_2")(PMe_3)$_3$] was isolated.[7]

The CV results demonstrate that 1,2-benzenedithiolate iron complexes exhibit similar electrochemical properties as comparable dithiolene systems.[4,5,13] The number of PMe_3 donors barely influences the redox potentials of the [Fe("S_2")$_2$(PMe_3)$_n$] species (n = 1, 2). Regarding the innocence of the "S_2" ligands derived from X-ray and Mössbauer investigations, it must be concluded that the electronic flexibility of **1**, **2**, and **4** along with the stabilization of the Fe oxidation states from +II to +IV is restricted to the FeS_4 unit.

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Table VII. Average Fe–S Bond Lengths, Oxidation States, Coordination, Electron, and S Donor Numbers, and Average Fe–S Bond Order of Low Spin Fe("S_2") and Related Complexes

complex	*d*Fe–S_{av}, pm	ox state (Fe)	coordination no.	electron no.	no of S donors	av Fe–S bond order	ref
[Fe("S_2")$_2$(PMe_3)], **2**	218.5 (3)	+IV	5	14	4	1.5	this work
[Fe("S_2")(PMe_3)$_3$], **5**	220.5 (3)	+II	5	16	2	1.5	7
($AsPh_4$)$_2$[Fe("S_2")$_2$], **6**	222.6 (3)	+II	4	14	4	1.5	7
($AsPh_4$)$_2$[Fe("S_2")$_2$]$_2$, **7**	222.9 (4)^c	+III	5	15	4^c	1.375	47
(NBu_4)$_2$[μ-N_2H_4{Fe("S_2")$_2$}$_2$], **8**	223.0 (5)	+III	5	15	4	1.375	10
[Fe("S_2")$_2$(PMe_3)$_2$], **1**	224.4 (3)	+IV	6	16	4	1.25	this work
(NMe)$_4$[Fe("S_2")$_2$(PMe_3)$_2$]·CH_3OH, **4**	226.0 (2)	+III	6	17	4	1.125	this work
[Fe("S_5")(CO)],^{a} **9**	228.2 (1)	+II	6	18	5	1.0	68
[Fe("S_4")(CO)$_2$],^{b} **10**	228.4 (3)	+II	6	18	4	1.0	66
[Fe("S_4")(CO)]$_2$,^{b} **11**	229.8 (3)	+II	6	18	5^d	1.0	65, 66

^{a}"S_5"$^{2-}$ = dianion of 2,2′-bis((2-mercaptophenyl)thio)diethyl sulfide, pentadentate thioether–thiolate ligand. ^{b}"S_4"$^{2-}$ = dianion of 1,2-bis((2-mercaptophenyl)thio)ethane, tetradentate thioether–thiolate ligand. ^{c}Only the planar S_4 unit regarded. ^{d}Thiolato–sulfur-bridged dimer.

Iron–Sulfur Bonding in "S_2" Complexes

The results presented in this paper give rise to numerous questions.

(a) Structural as well as spectroscopic data indicate that **1** and **2** contain Fe(IV) centers. Apparently, the potential dithiolene character of 1,2-benzenedithiolate is not responsible for the stabilization of the +IV iron oxidation state. By what effects is it stabilized instead?

(b) The observation of very different average Fe–S bond lengths ranging from 218.5 (3) pm in **2** via 224.4 (3) pm in **1** and 226.0 (2) pm in **4** up to 229.8 (3) pm in related [Fe("S_4")(CO)]$_2$[65,66] gives rise to the question whether any correlation exists between distances and, for example, oxidation states or coordination numbers.

(c) How can one explain the strange trapezoid distortion of the FeS_4 plane in **1** where each "S_2"$^{2-}$ ligand forms one long and one short Fe–S bond?

(d) Why is **2** mononuclear when dithiolate/dithiolene systems increasingly tend to dimerize going from d^8 via d^7 and d^6 to d^5 configurations?[11] Dimerization then should be expected even more for d^4 systems.

(e) Highly unexpected in this context is also the structure of [Fe("S_2")$_2$]$^{2-}$.[7] Why is it square-planar and mononuclear? On the one hand, a planar d^6 dithiolene system should dimerize;[11] on the other hand, monomeric tetracoordinate Fe(II)–thiolato complexes are usually tetrahedral, for example, [Fe(SPh)$_4$]$^{2-}$.[67]

In order to find answers we have analyzed the Fe–S distances in low-spin Fe("S_2") and related complexes which were arranged according to increasing bond lengths in Table VII. It can clearly be seen, that the Fe–S bond lengths in these compounds are not a function of the Fe oxidation state. The Fe^{II}("S_2") complexes [Fe("S_2")(PMe_3)$_3$] (**5**) and ($AsPh_4$)$_2$[Fe("S_2")$_2$] (**6**) have short average Fe–S distances of 220.5 (3) and 222.6 (3) pm, respectively; in the Fe(III)/"S_2" system the Fe–S bond lengths range from 223 to 226 pm, slightly longer, and the Fe(IV)/"S_2" system exhibits long (224.4 (3) pm) as well as very short (218.5 (3) pm) Fe–S distances. Additionally—and contrasting with the Fe^{II}("S_2") complexes—the Fe^{II}("S_4") and Fe^{II}("S_5") compounds ("S_5"$^{2-}$ = dianion of 2,2′-bis((2-mercaptophenyl)thio)diethyl sulfide) exhibit distinctly longer average Fe–S bond lengths ranging from 228 to 230 pm.

Also when the different coordination numbers ranging from four to six are taken into account, no common trend is observable. The six-coordinate complexes show decreasing average Fe–S bond lengths when going to higher oxidation states, but the pentacoordinate species have the largest Fe–S distances in Fe(III) and smaller ones in Fe(II) as well as Fe(IV) complexes.

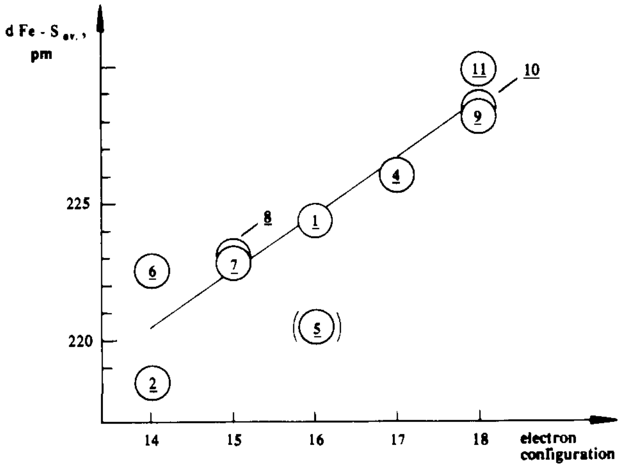

Figure 8. Fe–S distances in low-spin ("S_2") and related complexes as a function of the electron configuration.

Because no correlation could be detected between oxidation states or coordination numbers and distances, we investigated the potential influence of the formal electron configurations with respect to the 18-electron rule on the Fe–S bond lengths. With only S → Fe σ-bonding taken into account, the iron centers of the complexes have electron configurations ranging from 14 to 18. When the complexes are arranged according to increasing electron numbers, a clear correlation with the bond distances results. It is approximately linear as shown in Figure 8. Low electron numbers correlate with short Fe–S distances, and the 18-electron-configurated species have the largest Fe–S bonds. The exception is [Fe("S_2")(PMe_3)$_3$] (**5**) having only two sulfur donors, but, as we will point out below, even this complex can be fitted to the series.

The correlation between Fe–S bond lengths and formal electron count can be rationalized when π-donation from thiolate sulfur donors to iron is considered. Lone pair sulfur p electrons form π-bonds with empty iron orbitals to such an extent that the iron center achieves an 18-electron configuration. For example, the 14-electron Fe center in **2** needs two lone pairs or π-bonds, respectively. When the two π-bonds are averaged over all four Fe–S bonds, an Fe–S bond order of 1.5 is obtained. Analogously all other average bond orders in Table VII are received.

Also the Fe–S bond distances of [Fe("S_2")(PMe_3)$_3$] (**5**) and [Fe("S_2")$_2$(PMe_3)$_2$] (**1**) now can be understood. In the 16-electron configurated [Fe("S_2")(PMe_3)$_3$] (**5**), the two "additional" π-electrons can distribute only over two Fe–S bonds leading to an average Fe–S bond order of 1.5. Therefore, the short Fe–S distances (av 220.5 (3) pm) of **5** have to be compared to the Fe–S bond lengths of 14-electron-configurated [Fe("S_2")$_2$(PMe_3)] (**2**) and ($AsPh_4$)$_2$[Fe("S_2")$_2$] (**6**) with Fe–S bond orders of 1.5 each and are in good agreement with the values obtained from the correlation in Figure 8.

Even the strong trapezoid distortion of the FeS_4 plane in [Fe("S_2")$_2$(PMe_3)$_2$] (**1**) can be regarded under the aspect of

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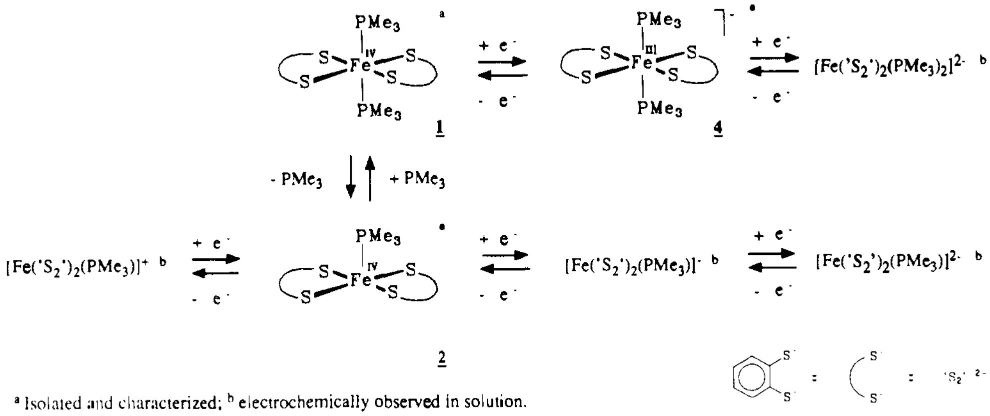
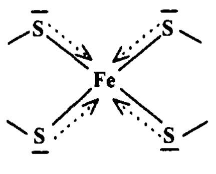
Scheme II



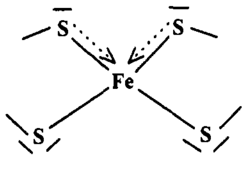
^{a} Isolated and characterized; ^{b} electrochemically observed in solution.

π-donation: 16-electron-configurated **1** is coordinated by four sulfur donors leading to an average Fe–S bond order of 1.25. **1**, however, exhibits two long and two short Fe–S distances of 229–230 and 219 pm, respectively. Figure 8 shows that distances of ~220 pm correspond to 14-electron systems, and bond lengths of ~230 pm correspond to 18-electron systems; in the case of a four sulfur donor set this is equivalent with Fe–S bond orders of 1.5 and 1.0, respectively. Thus it must be concluded that **1** represents the unique case in which π-bonding is not delocalized over all four Fe–S thiolate bonds available as illustrated in V but is restricted to two Fe–S bonds as shown in VI. Therefore, the strong distortions from octahedral symmetry are ultimately due to electronic effects.

Sulfur → metal π-donation was previously invoked to explain the stability of $[Cr(\text{“}S_2\text{”})(CO)_3]^{2-}$,[6] $[Ru(SC_6Me_4H)_4(CO)]$,[69] and $[MoCp(NO)(SC_6H_5)_2]$[70] but is also the reason for destabilizing interactions in $[FeCp(CO)_2SR]$.[71]



V



VI

In the Fe/“S_2” system, sulfur π-donation ultimately answers the questions raised above. It stabilizes high valency of metal centers and vacant coordination sites as well as low coordination numbers. When required, thiolate sulfur ligands donate π-electrons to the metal such that it can achieve a noble gas electron configuration.

Biological Relevance

Compounds modelling structural and functional properties of Fe–S oxidoreductases should have sulfur coordinate iron centers which allow them to carry out enzymatically relevant reactions, for example, substrate coordination/decoordination and/or reduction/oxidation. Accessibility of vacant coordination sites is a precondition to the coordination of substrates.

In this context **1**, **2**, and **4** can be regarded as model complexes for such centers. The high-valent metal sulfur center in coordinatively unsaturated $[Fe(\text{“}S_2\text{”})_2(PMe_3)]$ (**2**) possesses a vacant coordination site and can bind a PMe_3 “substrate” reversibly, and the resulting $[Fe(\text{“}S_2\text{”})_2(PMe_3)_2]$ (**1**) is able to take up electrons reversibly. **2** is redox active also without prior addition of PMe_3, and evidence was obtained that it may even be oxidized to the Fe(V) species $[Fe(\text{“}S_2\text{”})_2(PMe_3)]^+$. Coordination/decoordination and redox behavior of **1**, **2**, and **4** are summarized in Scheme II.

Summary

Neutral mono- and bis-PMe_3 adducts of iron bisbenzenedithiolate **1** and **2** were proved by X-ray structure analyses and Mössbauer spectroscopy to contain high-valent Fe(IV) centers coordinated by dianionic “S_2” ligands. Comparison of **1** and **2** to anionic 4 and $[Fe(\text{“}S_2\text{”})_2]^{2-}$ reveals that bond distances within the “S_2” ligands do not change indicating that “S_2” behaves as an innocent dithiolate, regardless of the oxidation state of the iron center to which it coordinates. Cyclovoltammetry proves the electrochemical versatility of these systems, showing reversible two-step one-electron redox interconversions of the neutral into the dianionic species. A linear relationship between Fe–S distances and formal electron count in low-spin Fe(“S_2”) complexes was discovered. It allowed a rationalization of the Fe–S bond lengths on the assumption of sulfur π-donation and simultaneously proved the importance of sulfur p electrons for stabilization of high-valent metal centers and vacant coordination sites as well as low coordination numbers in these systems. The biological relevance of the new complexes with respect to their redox and coordination/decoordination behavior was illustrated.

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Supplementary Material Available: Figures of ^1H NMR spectra of **1** and **2**, stacking plot of **2**, and listings of anisotropic thermal parameters and fractional coordinates of atoms and complete listings of bond distances and bond angles (22 pages); listings of F_o and F_c values (45 pages). Ordering information is given on any current masthead page. Further details of the X-ray crystal structure analyses have been deposited and can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, by citing the deposition Nos. CSD 320138 ($[Fe(\text{“}S_2\text{”})_2(PMe_3)_2]$, **1**), CSD 320139 ($[Fe(\text{“}S_2\text{”})_2(PMe_3)]$, **2**), CSD 320140 ($(NMe_4)[Fe(\text{“}S_2\text{”})_2(PMe_3)_2]\cdot CH_3OH$, **4**), the authors, and the reference.

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