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Transition metal complexes with sulfur ligands CIII☆. $[(\mu\text{-}S_2)\{Fe(\mu\text{-}`S_4')\}_2]$, a novel [2Fe–2S] cluster with octahedral low-spin $[Fe^{II}S_6]$ centers ($`S_4'^{2-} = 1,2\text{-bis-}$(2-mercaptophenylthio)ethane(2−))

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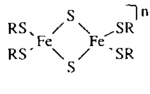
Abstract

The novel [FeS] cluster $[(\mu\text{-}S_2)\{Fe(\mu\text{-}`S_4')\}_2]$ (**1**) spontaneously forms under standard conditions when $Fe^{2+}$ ions are reacted with elemental sulfur and the tetradentate thioether thiolato ligand $`S_4'^{2-}$. **1** was characterized by X-ray structure analysis, spectroscopic methods, and by its reactions. **1** contains pseudooctahedral low-spin Fe^{II} centers which are exclusively coordinated by sulfur donors. The structure of **1** is composed of two homochiral $[Fe(`S_4')]$ fragments which are linked to each other in a specific way via two thiolato donors and an $S_2$ bridge. The $[FeS_2Fe]$ unit is a chromophore. In spite of having no vacant sites, **1** reacts with CO yielding $[\{Fe(CO)(\mu\text{-}`S_4')\}_2]$ under standard conditions. Although **1** has no S^{2-} ligands, it reacts according to the methylene blue reaction proving that this reaction, in contrast to current views, can not be considered a specific test for S^{2-} ligands in metal sulfur proteins. This and other properties of **1**, including its redox activity, are discussed with respect to the structures of as yet uncharacterized [FeS] proteins.

Keywords: Crystal structures; Iron complexes; Sulfur ligand complexes; Cluster complexes

1. Introduction

Enzymes with [FeS] centers are ubiquitous in nature and include electron transferases and oxidoreductases, e.g. ferredoxins and nitrogenases [2]. Until now, the structures of these [FeS] centers have been elucidated only in few enzymes, mainly ferredoxins. They were found to contain [FeS] clusters of the [2Fe–2S], [3Fe–4S] and [4Fe–4S] types, I–III [3], in which the iron atoms are always tetrahedrally coordinated by thiolate and sulfide S donors.



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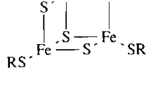

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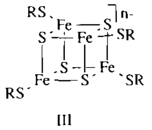
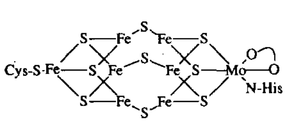


III

[FeS] centers differing from these conventional [FeS] clusters were recently suggested for the X-ray structural models of the FeMo cofactors and P clusters in FeMo nitrogenases (IV and V) [4].



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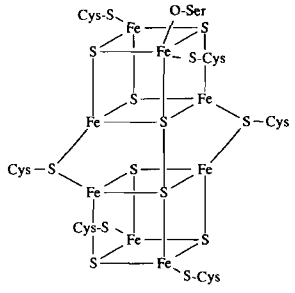

V

The FeMo cofactor contains three-coordinate iron centers, which are trigonally planar, surrounded by S donors. In addition to the conventional tetrahedrally coordinated iron centers, the P cluster exhibits a five-coordinate iron atom and an S_2 bridge, a building unit which had not been found in [4Fe–4S] clusters before. However, iron atoms which are octahedrally coordinated by sulfur donors exclusively have not yet been observed

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☆For Part CII see Ref. [1].

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in these enzymes. This is surprising, because besides four the major coordination number of Fe^{II} and Fe^{III} complexes is six [5]. Searching for complexes with new types of [FeS] centers we have now found $[(\mu\text{-}S_2)\{Fe(\mu\text{-}'S_4')\}_2]$ (**1**). It reveals an S_2 bridge, low-spin Fe^{II} centers, which are pseudooctahedrally coordinated by sulfur donors, and many other unusual properties. Preliminary results have been reported elsewhere [6].

2. Experimental

2.1. General

Unless otherwise noted all reactions were carried out under N_2 using standard Schlenk techniques. Solvents were dried and distilled under nitrogen before use. Spectra were recorded with the following instruments: Perkin-Elmer IR spectrophotometer 983, Perkin-Elmer IR spectrophotometer 1600 FT (KBr pellets), Jeol JNM-GX 270 FT NMR spectrometer, Shimadzu UV–Vis–NIR recording spectrophotometer UV-3101 PC, Varian MAT 212 mass spectrometer.

Mössbauer spectra (100 mg sample of **1** in 19 mm polyethylene containers) were recorded with constant acceleration, multi-scaling mode data recording, and ^{57}Co in rhodium (30 mCi) as γ-radiation source; isomeric shifts refer to metallic iron at room temperature. Magnetic measurements were carried out with a Johnson Matthey susceptibility balance at 295 K; cyclovoltammetric measurements with a PAR model 264 A polarographic analyzer/stripping voltammeter (Ag/AgCl reference electrode, glassy carbon working and Pt counter electrode; 10^{-5} M solutions in CH_2Cl_2 containing 10^{-3} M $(NBu_4)PF_6$ as supporting electrolyte were flushed with N_2 for 30 min before measurement).

The starting materials $[Fe(PBu_3)_2('S_4')]$ [7], $[Fe(CO)_2('S_4')]$ [8] and $'S_4'\text{-}H_2$ [9] were prepared as described in the literature.

2.2. Syntheses and reactions

2.2.1. $[(\mu\text{-}S_2)\{Fe(\mu\text{-}'S_4')\}_2]$

2.2.1.1. From $FeCl_2\cdot 4H_2O$, $'S_4'\text{-}Na_2$ and S_8

$NaOCH_3$ (725 mg, 13.4 mmol) was added to a solution of $'S_4'\text{-}H_2$ (2060 mg, 6.68 mmol) in 75 ml of THF. A white suspension resulted, to which $FeCl_2\cdot 4H_2O$ (1320 mg, 6.68 mmol) was added whereupon the color immediately changed to red–brown. After stirring for 15 min, elemental sulfur (220 mg, 6.70 mmol) was added, and the color changed from red–brown to black–green. The resulting black–green precipitate was separated after 1 day, washed with 20 ml of THF and 10 ml of CS_2, dried in vacuo for 1 day, and recrystallized twice from boiling CH_2Cl_2 yielding microcrystalline black–green **1**. Yield 2150 mg (81%). *Anal.* Calc. for $C_{28}H_{24}Fe_2S_{10}$ (792.85): C, 42.42; H, 3.05; S, 40.44. Found: C, 42.28; H, 2.93; S, 40.42%. ^1H NMR, δ (ppm): 2.6 (m), 2.9 (m, C_2H_4, 8H; in CD_2Cl_2), 6.8–7.8 (m, C_6H_4, 8H; in $[D_7]$-DMF).

2.2.1.2. From $[Fe(CO)_2('S_4')]$ and S_8

Elemental sulfur (65 mg, 2.0 mmol) was added to a red solution of $[Fe(CO)_2('S_4')]$ (840 mg, 2.0 mmol) in 50 ml of THF. The solution was heated to the boiling point of THF in the course of which it became a suspension, whose color slowly changed from brown to black–green. After 24 h the mixture was cooled to room temperature, the solid black–green precipitate was separated, washed with 25 ml of THF and 10 ml of CS_2, dried in vacuo for 1 day, and identified as **1**. Yield 570 mg (72%).

2.2.1.3. From $[Fe(PBu_3)_2('S_4')]$ and S_8

Elemental sulfur (195 mg, 6.0 mmol) was added to a solution of $[Fe(PBu_3)_2('S_4')]$ (1540 mg, 2.0 mmol) in 50 ml of THF. The mixture was stirred yielding a dark green suspension in the course of 24 h. Dark green **1** was separated after 2 days and treated as above. Yield 585 mg (74%).

2.2.2. Methylene blue reaction of 1

13 ml of a 1% aqueous solution of $Zn(ac)_2$ and 0.5 ml of a 12% aqueous solution of NaOH were added to **1** (8.0 mg, 0.01 mmol). The white suspension was heated to 100 °C for 15 min and then cooled to room temperature. 2.5 ml of 4.27 M solution of *N,N-p*-phenylenediamine in 5.5 N HCl were added whereupon the white precipitate disappeared. 0.5 ml of a 0.023 M solution of $FeCl_3$ in 12 N aqueous HCl was added, and the mixture was stirred for another 30 min under exclusion of light. The resulting methylene blue was identified by its absorptions at 746 and 670 nm in the UV–Vis spectrum.

2.2.3. Reaction of 1 with CO

A black–green suspension of **1** (795 mg, 1.0 mmol) in 100 ml of CH_2Cl_2 was stirred for 1 week under CO. Additional CO was bubbled through the suspension for 2 h per day. The resulting brown precipitate of $[\{Fe(CO)(\mu\text{-}'S_4')\}_2]$ was filtered off, washed with 20 ml of THF and 50 ml of CH_2Cl_2, and dried in vacuo. Yield 640 mg (82%). *Anal.* Calc. for $C_{30}H_{24}Fe_2O_2S_8$ (784.74): C, 45.92; H, 3.08; S, 32.69. Found: C, 46.02; H, 3.16; S, 32.48%. IR (cm^{-1}): 1965 vs, br, $\nu(CO)$.

2.2.4. Reduction of 1 with Na

Sodium (10 mg, 0.40 mmol) was added to a green suspension of **1** (93 mg, 0.12 mmol) in 50 ml of liquid NH_3 whereupon the color changed to brown. NH_3 was evaporated, the yellow–brown residue was dissolved in 20 ml of MeOH, and the resulting solution was filtered. Solid NMe_4Cl (110 mg, 1.0 mmol) was added to the dark red filtrate and microcrystalline red $(NMe_4)_2[\{Fe(S_2C_6H_5)_2\}_2]$ precipitated. It was separated, washed with MeOH and dried in vacuo. Yield 87 mg (89%). *Anal.* Calc. for $C_{32}H_{40}Fe_2N_2S_8$ (820.91): C, 46.82; H, 4.91; N, 3.41. Found: C, 46.77; H, 4.96; N, 3.21%.

2.3. X-ray structure analysis of 1

Suitable single crystals of **1** were grown from saturated DMF solutions at −20 °C, sealed without drying in glass capillaries, and mounted on the diffractometer. The structure was solved by direct methods (SHELXTL-PLUS); non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms with a common isotropic thermal parameter. Aromatic hydrogen atoms were placed at calculated positions and refined as rigid groups; methylene hydrogen atoms were placed at ideal tetrahedral positions and allowed to rotate around their central carbon atom during refinement.

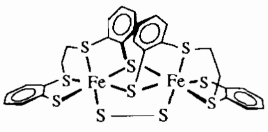
Tables 1 and 2 contain selected crystallographic data, fractional atomic coordinates and equivalent isotropic thermal parameters.

3. Results and discussion

3.1. Syntheses

$[(\mu\text{-}S_2)\{Fe(\mu\text{-}`S_4')\}_2]$ (**1**) spontaneously formed under standard conditions in yields of up to 80% when $Fe^{2+}$ ions were reacted with elemental sulfur and the tetradentate thioether thiolate ligand $`S_4'^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane(2−) [9] according to Eq. (1).

$$2\,FeCl_2\cdot 4\,H_2O + 2\,`S_4'\text{-}Na_2 + 0.25\,S_8 \xrightarrow[-4\,NaCl,\,-8\,H_2O]{THF,\ 1\ day}$$



1

(1)

Black–green **1** is diamagnetic and soluble in CH_2Cl_2, DMF and DMSO. IR and NMR spectra of **1** only exhibit the typical bands and signals of complexes with $[Fe(`S_4')]$ cores and thus allowed no conclusion to be made about the structure. In the FD mass spectrum, however, the molecular ion at $m/e = 792$ could be observed.

1 is also produced from the phosphine complex $[Fe(PBu_3)_2(`S_4')]$ [7] and elemental sulfur at ambient temperature (Eq. (2a)); the analogous reaction of the carbonyl complex $[Fe(CO)_2(`S_4')]$ [8], however, needed heating in boiling THF for 2 days (Eq. (2b)).

$$2[Fe(PBu_3)_2(`S_4')] + 0.75S_8 \xrightarrow[-4SPBu_3]{THF,\ r.t.,\ 1\ day} [(\mu\text{-}S_2)\{Fe(\mu\text{-}`S_4')\}_2] \quad (2a)$$

$$2[Fe(CO)_2(`S_4')] + 0.25S_8 \xrightarrow[-4CO]{THF,\ 65\ ^\circ C,\ 2\ days} [(\mu\text{-}S_2)\{Fe(\mu\text{-}`S_4')\}_2] \quad (2b)$$

3.2. X-ray structure analysis

The molecular structure of **1** was determined by X-ray structure analysis. Fig. 1 shows the molecular structure of **1** and Table 3 lists selected distances and angles. See also Supplementary material.

1 contains two iron centers which are pseudo-octahedrally coordinated by six sulfur donors. It is composed of two $[Fe(`S_4')]$ units whose iron atoms are linked to each other via two thiolate bridges of the $`S_4'$ ligands and the S_2 unit. The Fe–S(thiolate) and

Table 1
Selected crystallographic data of $[(\mu\text{-}S_2)\{Fe(\mu\text{-}`S_4')\}_2]$

Compound	$[(\mu\text{-}S_2)\{Fe(\mu\text{-}`S_4')\}_2]$	Temperature (K)	200
Formula	$C_{28}H_{24}Fe_2S_{10}$	Diffractometer	Nicolet R3m/V
M_r (g/mol)	792.8	Radiation (pm)	Mo Kα (71.073)
Crystal dimension (mm)	0.30×0.20×0.10	Scan technique	ω-scan
Crystal system	triclinic	2θ Range (°)	3–54
Space group	$P\bar{1}$	Scan speed (°/min)	3.0–15
a (pm)	1093.8(4)	Measured reflexions	6260
b (pm)	1113.2(4)	Independent reflexions	6025
c (pm)	1384.1(10)	Observed reflexions	3287
α (°)	111.36(5)	σ Criterion	$F > 6.0\sigma(F)$
β (°)	97.60(5)	Refined parameters	362
γ (°)	100.71(3)	R; R_w (%)	8.4; 6.6
Cell volume (pm³)	$1504(2)\times10^6$	Weighting scheme	$1/\sigma^2$
Z	2	Absorption correction	none
D_c (g/cm³)	1.75	μ (cm⁻¹)	16.5

Table 2
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($pm^2 \times 10^{-1}$) of $[(\mu\text{-}S_2)\{Fe(\mu\text{-'}S_4\text{'})\}_2]$

Atom	x	y	z	U_{eq} [a]
Fe(1)	2128(2)	7438(2)	4(1)	21(1)
Fe(2)	3395(2)	5910(2)	−2004(1)	20(1)
S(1)	1391(3)	5678(3)	−1606(2)	21(1)
S(2)	756(3)	8489(3)	−571(2)	23(1)
S(3)	645(3)	6721(3)	793(2)	25(1)
S(4)	2935(3)	9322(3)	1523(2)	29(1)
S(5)	3730(3)	8058(3)	−805(2)	22(1)
S(6)	2877(3)	6583(3)	−3335(2)	23(1)
S(7)	5437(3)	6224(3)	−2172(2)	27(1)
S(8)	2970(3)	3771(3)	−3296(2)	27(1)
S(9)	3314(3)	6332(3)	506(2)	32(1)
S(10)	3915(3)	5270(3)	−767(3)	34(2)
C(15)	81(11)	7454(11)	−1925(9)	25(5)
C(14)	−673(11)	7879(12)	−2562(9)	27(5)
C(13)	−1132(12)	7091(13)	−3614(10)	36(6)
C(11)	−105(11)	5455(12)	−3410(9)	26(5)
C(12)	−878(11)	5859(12)	−4074(9)	34(6)
C(10)	390(10)	6227(12)	−2386(8)	23(5)
C(25)	926(11)	8032(12)	2083(9)	25(5)
C(24)	146(12)	7878(12)	2778(9)	28(5)
C(23)	425(12)	8805(12)	3801(9)	32(6)
C(22)	1491(12)	9868(12)	4130(10)	32(6)
C(21)	2249(12)	10013(11)	3437(9)	30(5)
C(20)	1980(11)	9097(11)	2391(8)	23(5)
C(16)	−610(11)	8182(11)	−3(9)	27(5)
C(26)	−811(11)	6863(11)	119(9)	28(5)
C(35)	2984(11)	8326(11)	−2667(9)	26(5)
C(34)	2669(13)	9045(13)	−3301(10)	41(7)
C(33)	2709(14)	10374(14)	−2771(12)	49(8)
C(32)	3042(13)	10993(13)	−1670(12)	43(7)
C(31)	3310(11)	10289(11)	−1071(9)	27(5)
C(30)	3262(10)	8914(11)	−1596(9)	20(5)
C(45)	5592(11)	4597(11)	−2937(9)	24(5)
C(44)	6826(11)	4427(11)	−2986(9)	24(5)
C(43)	6939(12)	3146(13)	−3562(10)	34(6)
C(42)	5905(13)	2105(12)	−4005(10)	32(6)
C(41)	4674(13)	2272(12)	−3967(9)	34(6)
C(40)	4515(10)	3555(12)	−3395(9)	22(5)
C(36)	4274(12)	6536(12)	−3923(9)	32(6)
C(46)	5517(12)	7045(12)	−3100(10)	35(6)

[a] Equivalent isotropic U as one third of the trace of the orthogonalized U_{ij} tensor.

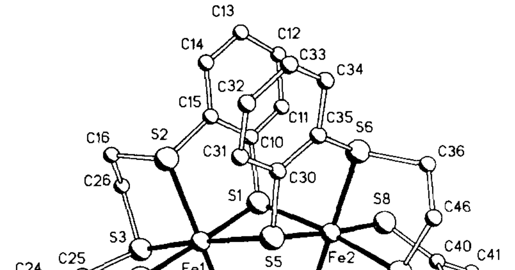


Fig. 1. Molecular structure of $[(\mu\text{-}S_2)\{Fe(\mu\text{-'}S_4\text{'})\}_2]$ (H atoms omitted).

Table 3
Selected distances (pm) and angles (°) of $[(\mu\text{-}S_2)\{Fe(\mu\text{-'}S_4\text{'})\}_2]$

Fe(1)–S(1)	228.3(3)	Fe(2)–S(1)	232.1(4)
Fe(1)–S(2)	229.5(4)	Fe(2)–S(5)	228.6(3)
Fe(1)–S(3)	225.5(4)	Fe(2)–S(6)	227.3(5)
Fe(1)–S(4)	228.2(3)	Fe(2)–S(7)	225.2(4)
Fe(1)–S(5)	233.1(4)	Fe(2)–S(8)	231.3(4)
Fe(1)–S(9)	215.9(5)	Fe(2)–S(10)	213.1(5)
S(9)–S(10)	200.3(5)	Fe(1)–Fe(2)	331.5
Fe(1)–S(1)–Fe(2)	92.1(1)	Fe(1)–S(5)–Fe(2)	91.8(1)
S(1)–Fe(1)–S(5)	83.2(1)	S(1)–Fe(2)–S(5)	83.3(1)
S(2)–Fe(1)–S(9)	176.2(1)	S(6)–Fe(2)–S(10)	178.8(2)

Fe–S(thioether) distances (225.2(4)–233.1(4) pm) exhibit no anomalies and are typical for diamagnetic low-spin [Fe('S_4')] complexes [8,10]. The S–S distance of the S_2 bridge (200.3(5) pm) lies almost exactly in the middle of the values observed for the distances in the neutral S_2 molecule (188.7 pm) [11] and S_2^{2-} ions (215.3(6) pm), e.g. in FeS_2 [12]. S–S distances of ~200 pm were also found in other μ-S_2 complexes [13]. The S_2 units in these complexes can alternatively be discussed as neutral S_2 molecules with elongated S–S bonds or as anionic S_2^{2-} ligands with shortened S–S bonds. In any case, we believe, a distance of ~200 pm is indicative for partial double bond character between the S atoms. The Fe–Fe distance of 331.5 pm excludes a direct Fe–Fe bond. The very short Fe–S distances of 215.9(5) and 213.1(5) pm in the [FeS_2Fe] unit are remarkable. They indicate multiple bonding character of these Fe–S bonds, because they are even shorter than the Fe–S bonds in the high-valent and coordinatively unsaturated complex $[Fe(PMe_3)(S_2C_6H_4)_2]$ (d(Fe–S) = 218.5(3) pm) [14] for which a partial double bond character of the Fe–S bonds has to be assumed for electronic reasons. Likewise short Fe–S distances like in **1** were only found in the related $[(\mu\text{-}S_2)(\mu\text{-}SEt)_2\{FeCp\}_2]$ (212.9(5) pm) [13c].

The [Fe('S_4')] units of **1** are homochiral and this necessarily means that **1** is also chiral [15]. **1** has approximately C_2 symmetry. The C_2 axis perpendicularly goes through the centers of the four-membered [Fe1S1Fe2S5] ring and the S_2 bridge. Dimerization of [M(L)('S_4')] fragments can theoretically lead to ten different stereoisomers [16,17]. They can be classified as E and Z isomers, and, in addition, as α or β isomers according to which of the distinctive thiolate donors in the chiral [M(L)('S_4')] fragments functions as bridging donor [16]. The coligand of the [Fe('S_4')] units in **1** is the S_2 bridge. This excludes a priori the formation of E isomers and limits the number of possible stereoisomers to six. According to the above mentioned classification **1** is a Z stereoisomer with α,α-thiolate linkage. α linkage means in this context that those thiolate S donors of the 'S_4' ligands function as bridges whose *ortho* thioether S atoms at the same benzene ring stand *trans* to the coligand L [17].

Thus, the formation of **1** also supports our previous assumption that electronic factors control the regioselective dimerization of chiral [M(L)('S_4')] fragments and favor the linkage of homochiral units, even in those cases where the dimerization yields sterically unfavorable molecules [17]. The sterically extremely variable demand of the iron coordination sphere is illustrated by the space-filling model of **1** in Fig. 2. The 'top' of the molecule is overloaded, whereas the 'bottom' is nearly empty.

3.3. Spectra of [(μ-S_2){Fe(μ-'S_4')}$_2$]

3.3.1. UV–Vis–NIR spectrum

Due to its intense black–green color **1** differs in a characteristic way from related complexes like the red–brown [{Fe(CO)(μ-'S_4')}$_2$] [16]. The intense color, in addition to the S–S distance of the S_2 bridge, indicates a particular bonding situation in the [FeS_2Fe] unit of **1**. This assumption was supported by the electronic spectrum of **1** (Fig. 3).

The UV–Vis–NIR spectrum of **1** shows two overlapping absorptions at 640 nm ($\epsilon = 1950$ M^{-1} cm^{-1}) and 760 nm ($\epsilon = 2100$ M^{-1} cm^{-1}) and an unusual band at especially long wavelengths at 1050 nm ($\epsilon = 1650$ M^{-1} cm^{-1}) in the NIR region. By comparison with the electronic spectrum of [{Fe(CO)(μ-'S_4')}$_2$] showing no absorptions in the range between 600 and 1250 nm, these bands can be attributed to the [FeS_2Fe] unit and assigned to π–π^* transitions in its bonding system. The bonding in the [FeS_2Fe] unit can be plausibly described by a 4c–6e π system. It consists of occupied Fe–d orbitals and the π and π^* orbitals of the μ-S_2 ligand and comprises one empty and three occupied localized molecular orbitals.

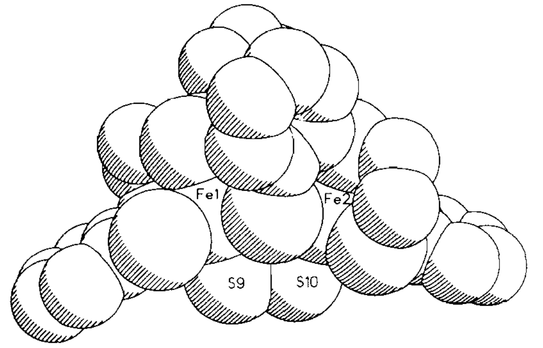


Fig. 2. Space-filling model of [(μ-S_2){Fe(μ-'S_4')}$_2$] (H atoms omitted).

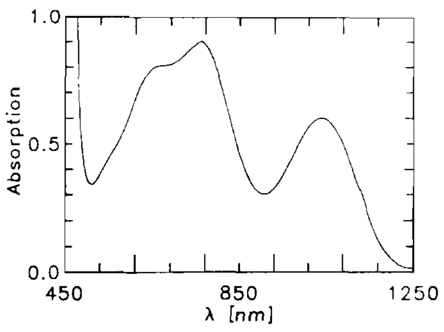


Fig. 3. UV–Vis–NIR spectrum of [(μ-S_2){Fe(μ-'S_4')}$_2$] in CH_2Cl_2; λ_{max} (nm) (ϵ(M^{-1} cm^{-1})): 640 (1950), 760 (2100), 1050 (1650).

This model easily accounts for the elongation of the S_2 bridge in comparison to free S_2 molecules, and the short Fe–S distances in the [FeS_2Fe] unit. It also explains that the [FeS_2Fe] units is a chromophore, and, according to Fig. 4, the NIR band can be assigned to a $\pi_3 \rightarrow \pi_4$ transition. The absorptions at shorter wavelengths, which cause the black–green color of **1**, are accordingly assigned to $\pi_2 \rightarrow \pi_4$ and $\pi_1 \rightarrow \pi_4$ transitions.

Similar bonding schemes were previously discussed for the [M–NH=NH–M] chromophores in dinuclear diazene complexes such as [(μ-N_2H_2){Mn(Cp)(CO)$_2$}$_2$] [18], [(μ-N_2H_2){Cr(CO)$_5$}$_2$] [19], [(μ-N_2H_2){Ru(PPh_3)('S_4')}$_2$] [20] and [(μ-N_2H_2){Fe('N_HS_4')}$_2$] [21]. Even more closely related to **1** is the S_2 complex [(μ-S_2){Ru(PPh_3)('S_4')}$_2$] [22,23]. It also contains an [MS_2M] chromophore which, being centrosymmetrical, differs from the C_2 symmetrical chromophore found in **1** only with respect to symmetry. When discussing the bonding in [(μ-S_2){Ru(PPh_3)('S_4')}$_2$] [23], we noted that the colors of [(μ-S_2)(μ-SEt)$_2${FeCp}$_2$] [13c] and [(μ-S_2){Ru(NH_3)$_5$}$_2$]$^{4+}$ [24a,b] might also be due to π–π^* transitions in 4c–6e π systems, which in these complexes, however, have to be assigned to the HOMO → LUMO transitions $\pi_3 \rightarrow \pi_4$, in accordance with Isied and coworkers who were the first to propose treating the [MS_2M] units in such complexes as 4c–6e π systems [24c].

Intense colors and in particular NIR bands are often observed in mixed-valence complexes and then assigned to intervalence-charge-transfer (ICT) transitions [25]. Such ICT transitions were discussed elsewhere for [(μ-S_2){Ru(NH_3)$_5$}$_2$]$^{4+}$ [26] and in the first paper on [(μ-S_2){Ru(PPh_3)('S_4')}$_2$] [22], because these complexes showed a slight residual paramagnetism. Due to that it was argued that the μ-S_2 complexes possibly contain Ru^{II} and Ru^{III} centers being bridged by S_2^- radical anions, quite analogous to the Ru centers bridged by pyrazine in the Creutz–Taube ion [(μ-pyrazine){Ru(NH_3)$_5$}$_2$]$^{5+}$. Later, however, when [(μ-S_2){Ru(PPh_3)('S_4')}$_2$] [23] had been sufficiently purified the complex turned out to be diamagnetic, and thus this reasoning was dropped. As shown for [(μ-S_2){Ru(PPh_3)('S_4')}$_2$] [23] and corroborated by this discussion such assumptions are not necessary. Consistent with

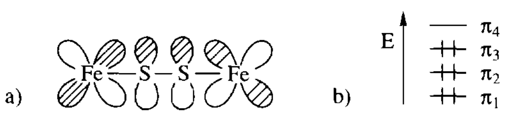


Fig. 4. Bonding scheme of the 4c–6e π system of the [FeS_2Fe] unit in **1**: (a) Lowest occupied molecular orbital, (b) energy levels.

the 4c–6e π-bonding model, it is fully sufficient to consider the two iron centers of **1** as Fe^{II} centers and the S_2 bridge as a neutral entity.

3.3.2. Mössbauer spectra

This conclusion is confirmed by the Mössbauer spectra of **1** which were recorded at 270.7, 85.6 and 4.2 K. Fig. 5(a) shows the Mössbauer spectrum of **1** at 4.2 K and Table 4 contains the relevant parameters.

The Mössbauer spectrum of **1** shows a single doublet proving the identity of both the iron centers. The isomeric shift of 0.367(1) mm s^{-1} at 4.2 K is typical for sulfur coordinated low-spin Fe^{II} centers [10b,28]. The low-spin Fe^{II} character of the iron centers is further corroborated by the quadrupole splitting which is independent of temperature, and finally by the excellent agreement of measured and fitted curves of the magnetically disturbed spectrum (Fig. 5(b)) [29].

Having two Fe^{II} centers, **1** differs from the usual [2Fe–2S] clusters $[Fe_2(\mu\text{-}S)_2(SR)_4]^{n-}$, which can occur in Fe^{III}/Fe^{III} and Fe^{III}/Fe^{II} but not in Fe^{II}/Fe^{II} oxidation states [2]. The similarity of the magnetic properties of **1** and of the H clusters of Fe/Fe hydrogenases is also notable, which, in the reduced form of the protein, are diamagnetic in external magnetic fields up to 6.0 T [30].

3.4. Redox chemistry of $[(\mu\text{-}S_2)\{Fe(\mu\text{-}'S_4')\}_2]$

Though having only two iron centers, **1** shows a surprisingly extensive redox chemistry in the cyclovoltammogram (Fig. 6). Three anodic and two cathodic waves can be observed, of which the first cathodic wave is reversible. Corresponding potentials are listed in Table 5.

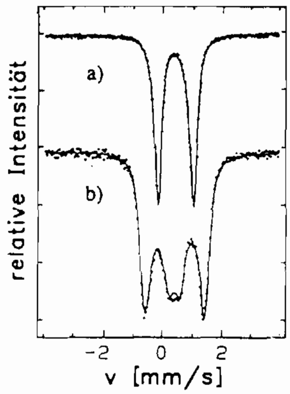


Fig. 5. Mössbauer spectra of $[(\mu\text{-}S_2)\{Fe(\mu\text{-}'S_4')\}_2]$ at (a) 4.2 K and (b) 4.2 K with a magnetic field (4.0 T) parallel to γ-radiation.

Table 4
Isomeric shift (δ), quadrupole splitting (ΔE_Q) and linewidth (Γ) of $[(\mu\text{-}S_2)\{Fe(\mu\text{-}'S_4')\}_2]$

T (K)	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ (mm s^{-1})
270.7	0.274(1)	1.124(1)	0.290(3)
85.6	0.347(1)	1.152(1)	0.290(3)
4.2	0.367(1)	1.161(1)	0.306(1)

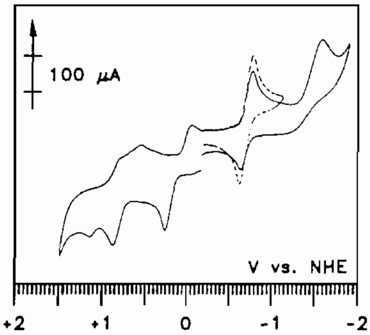


Fig. 6. Cyclovoltammogram of $[(\mu\text{-}S_2)\{Fe(\mu\text{-}'S_4')\}_2]$ in CH_2Cl_2, $v = 100$ mV s^{-1}.

Table 5
Redox potentials $E_f{}^a$ (V) of $[(\mu\text{-}S_2)\{Fe(\mu\text{-}'S_4')\}_2]$ in CH_2Cl_2

	E_f(red.) (V)	E_f(ox.) (V)
Reduction		
$1^0/1^{1-}$	−0.78 (r)^b	−0.64 (r)
$1^{1-}/1^{2-}$	−1.62 (i)^c	
Oxidation		
$1^0/1^{1+}$		+0.30 (i)
$1^{1+}/1^{2+}$		+0.96 (i)
$1^{2+}/1^{3+}$		+1.26 (i)

^{a}All potentials versus NHE.
^{b}Reversible.
^{c}Irreversible.

Thus, with respect to redox behavior, **1** completely differs from [2Fe–2S] clusters of the $[Fe_2(\mu\text{-}S)_2(SR)_4]^{n-}$ type, which can take up or release only one electron [2]. **1** much more resembles $[(\mu\text{-}S_2)\{Ru(PPh_3)('S_4')\}_2]$ [22,23], which also contains six-coordinate metal centers that are strongly coupled via a S_2 bridge and contain sulfur rich coordination spheres. Thus, it may be assumed that the redox chemistry of **1** is based on the high electron density at the iron centers resulting from six electron rich sulfur donors per iron center, and on the fact that these are coupled via two thiolate donors and especially strong via the S_2 bridge.

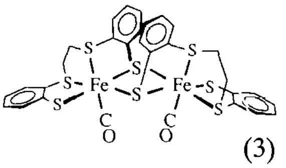
3.5. Reactions of $[(\mu\text{-}S_2)\{Fe(\mu\text{-}'S_4')\}_2]$

A typical method to detect and determine S^{2-} ligands in cluster compounds of types I–III is the methylene blue reaction [31]. The native proteins are treated with solutions of alkaline zinc acetate, acidic *N*,*N*-*p*-phenylenediamine, and Fe^{3+} ions. The colorimetrically detectable concentration of resulting methylene blue allows the number of S^{2-} ions in the active centers of the proteins to be determined. However, there are several problems, which were recently published elsewhere, when the exact number of S^{2-} ligands is to be elucidated [32], and we were interested whether **1** being formally a [2Fe–2S] cluster would give a methylene blue reaction in spite of having no S^{2-} ligands.

The test reaction which was carried out corresponding to the procedure described for enzymes yielded methylene blue. This result shows that the methylene blue reaction is not specific for S^{2-} ligands, but comprises also S_2 ligands. Hence, when structures of metal sulfur centers of enzymes which have not been characterized by X-ray structure analysis are discussed, it should be taken into account that part of the 'inorganic' sulfur could be present in the form of S_2 ligands. The structure which was recently proposed for the P clusters of FeMo nitrogenases [4] has to be seen in this context.

1 exhibits coordinatively saturated iron centers or, in other words, no vacant sites of coordination. Nevertheless we investigated whether **1** would coordinate CO under standard conditions. Rather contrary to our expectations, it did so and yielded, according to Eq. (3), $[\{Fe(CO)(\mu\text{-'S}_4\text{'})\}_2]$ [16] which was characterized by comparison with authentic samples.

$$[(\mu\text{-S}_2)\{Fe(\mu\text{-'S}_4\text{'})\}_2] + \text{exc.CO} \xrightarrow[-0.25\ S_8]{CH_2Cl_2,7d}$$



(3)

The formation of $[\{Fe(CO)(\mu\text{-'S}_4\text{'})\}_2]$ proves that the coordinatively saturated iron centers of **1**, which is highly stable, are still reactive enough to cleave off the S_2 bridge and bind CO. A more detailed mechanism of this substitution reaction is not known as yet, but due to the fact that **1** can easily be reduced, it could be discussed that excess CO first reduces **1** to give a species with 19 valence electron iron centers. Such species are known to be highly labile towards substitution [33].

The reaction of **1** with CO is also of interest with respect to hydrogenases which likewise bind CO. As mentioned in the discussion of the Mössbauer spectra, the H clusters of hydrogenases are diamagnetic in the reduced form of the protein, and, according to EXAFS measurements, they show Fe–Fe distances of 3.3 Å being nearly identical with those of **1** [30]. The H clusters are the most probable binding sites for CO. Although hydrogenases contain more iron centers than **1**, possibly 8 to 16 [34], the similarities of structural, spectroscopic and reactive properties between the H clusters and **1** are remarkable and worth noting.

The cyclovoltammogram of **1** (Fig. 6) shows two reduction waves, the first of them being reversible. Therefore we tried to reduce **1** chemically and to isolate the resulting complexes. So far, these experiments have been largely unsuccessful. Electrolytical reduction of **1** in CH_2Cl_2 yielded a brown powder. It could not be reoxidized by air, neither in the solid state nor in solution, and it was not characterized more closely. Reduction of **1** by cobaltocene yielded insoluble products which could not be purified or recrystallized. Reaction of **1** with sodium in liquid ammonia gave the benzenedithiolato Fe^{III} complex $[\{Fe(S_2C_6H_4)_2\}_2]^{2-}$ which was isolated and characterized as $(NMe_4)_2[\{Fe(S_2C_6H_4)_2\}_2]$ according to Eq. (4).

$$[(\mu\text{-S}_2)\{Fe(\mu\text{-'S}_4\text{'})\}_2] \xrightarrow[\text{(ii) + NMe}_4\text{Cl/MeOH}]{\text{(i) + 3.3Na, NH}_3,\ -33\ ^\circ\text{C}} (NMe_4)_2[\{Fe(S_2C_6H_4)_2\}_2] + \text{other products} \quad (4)$$

The formation of the $[\{Fe(S_2C_6H_4)_2\}_2]^{2-}$ ion can be explained when **1** experiences a single electron reduction by sodium at first and subsequently cleaves off not only the S_2 bridge, but also the C_2H_4 bridges of the 'S_4' ligands, probably as ethylene. Such C_2H_4 eliminations were previously also observed with other [M('S_4')] complexes always leading to an increase in the metal oxidation state by two units [35].

Conclusions

The novel [FeS] cluster $[(\mu\text{-S}_2)\{Fe(\mu\text{-'S}_4\text{'})\}_2]$ (**1**) was obtained by 'spontaneous self-assembly' from Fe^{2+} ions, elemental sulfur and the tetradentate thioether thiolate ligand 'S_4'$^{2-}$. It also formed in substitution reactions of labile $[Fe(L)_2(\text{'S}_4\text{'})]$ complexes with elemental sulfur. **1** differs in a characteristic way from [FeS] clusters found in enzymes by containing pseudooctahedral low-spin Fe^{II} centers, and it also differs from the metal–organic clusters $[Cp_2Fe_2(\mu\text{-S}_2)(\mu\text{-SR})_2]$ and $[Cp_2Fe_2(\eta^1\text{-}\mu\text{-S}_2)(\eta^2\text{-}\mu\text{-S}_2)]$ by its sulfur-only coordination of the iron centers.

Chiral **1** is composed of two homochiral [Fe('S_4')] fragments which are linked via specific thiolate donors of the 'S_4' ligands. This indicates that the enantio- and regioselective dimerization of chiral [Fe('S_4')] fragments is controlled by electronic factors. The low-spin Fe^{II} character of the metal centers in **1** is supported by its diamagnetism and was further corroborated by its Mössbauer spectra. In contrast to the ferredoxin type clusters $[Fe_2(\mu\text{-S})_2(SR)_4]^{n-}$ which only occur in two different oxidation states, five redox steps can cyclovoltammetrically be detected for **1**. In spite of containing no S^{2-} ligands **1** responded positively to the methylene blue reaction. This demonstrates that, in contrast to current views, the methylene blue reaction is not well suited to specifically detect S^{2-} ligands and to exactly determine their number in metal sulfur proteins. With respect to Fe–Fe distances, magnetism and reactivity, **1** shows a remarkable similarity to the as yet structurally uncharacterized H clusters of Fe/Fe hydrogenases. In spite of having no vacant sites of coordination **1** reacts, for example, with CO. When reacted with strongly reducing agents such as sodium, **1** gives, under loss of the S_2 bridge and C_2H_4 bridges of the 'S_4' ligands, the Fe^{III} complex $[\{Fe(S_2C_6H_4)_2\}_2]^{2-}$.

Due to its structure and properties, **1** is of relevance only when structures of, as yet, insufficiently characterized iron sulfur proteins are discussed. This was shown in particular by comparison of **1** with the properties of the so-called H clusters of Fe/Fe hydrogenases.

Supplementary material

Further details of the X-ray crystal structure analysis of $[(\mu\text{-}S_2)\{Fe(\mu\text{-}'S_4')\}_2]$ have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen 2, and can be obtained by quoting Deposition No. CSD 320253, the authors' names, and the reference.

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