Acid Degradation of 4. Complex **4**, 0.5 g (0.59 mmol) was dissolved in 50 mL of ethanol at 40 °C. To this solution was added 50 mL of 1 N aqueous HCl. A stream of N_2 was blown through the solution to remove the evolving H_2S and SO_2. Analysis of the gas phase by GC-MS revealed m/z 64 (SO_2) and 34 (H_2S). The aqueous phase was diluted and extracted with hexane to yield a colorless solid, mp 60-62 °C, identified by ^{13}C NMR spectroscopy as diphenylacetylene.

X-ray Crystallographic Structure Analysis. A crystal of **4** was obtained from acetone/dimethyl sulfoxide and was sealed in a capillary and mounted on a Nicholet R3m/V diffractometer for X-ray data collection. Since crystal decomposition occurred, probably due to loss of solvent trapped in the lattice, the data were collected at -100 °C. The intensities of monitored reflections decreased by approximately 1% during 39 h of X-ray exposure. No absorption correction was applied because of the low value of μ. The cell parameters were obtained from 20 reflections in the 2θ range 15-25°; the space group was identified as $P\bar{1}$. The positions of the nickel and sulfur atoms were obtained from automatic direct methods routine of the program SHELXTL plus. The positions of the remaining non-hydrogen atoms were determined from a difference Fourier map. All atoms were refined anisotropically. Hydrogen atoms were included in ideal positions with U fixed at 0.08 Å. Refinements gave final values of R and R_w that are given in Table I. The final difference map had no feature of any chemical significance, though it had a few residual peaks with intensity 0.63 e Å^{-3}. No evidence for secondary extinctions was found. Positional and thermal parameters are given as supplementary material. Perspective drawings of **4** are given in Figures 1 and 2. Table II lists the atomic coordinates and equivalent isotropic displacement coefficients. A summary of interatomic distances and bond angles is given in Table III.

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Supplementary Material Available: A unit cell packing diagram and tables of equivalent positions, scattering factors, positional parameters, anisotropic displacement coefficients, bond distances and bond angles, H-atom coordinates, and isotropic displacement coefficients (9 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Transition-Metal Complexes with Sulfur Ligands. 52.[1] Synthesis, X-ray Structure Characterization, and Reactions of $[Fe(CO)(\mu\text{-"}S_4\text{"})]_2$, a Novel Type of Chiral Complex with Relevance to Iron Oxidoreductases ($\text{"}S_4\text{"}^{2-}$ = 1,2-Bis((2-mercaptophenyl)thio)ethanato(2-))

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Searching for model complexes of hydrogenases and nitrogenases with chirotopic iron centers, we found that the thermal decarbonylation of $[Fe(CO)_2(\text{"}S_4\text{"})]$ (**1**) leads to $[Fe(CO)(\mu\text{-"}S_4\text{"})]_2$ (**2**) ($\text{"}S_4\text{"}^{2-}$ = 1,2-bis((2-mercaptophenyl)thio)ethanato(2-)). **2** results from the connection of two homochiral $[Fe(CO)(\text{"}S_4\text{"})]$ fragments and represents a new type of chiral complex. An analysis of theoretically possible isomers of **2** is given. One pair of enantiomers of **2** as well as **1** were characterized by X-ray structure determinations. **1**: monoclinic, $P2_1/c$, a = 1293.3 (6) pm, b = 1258.2 (6) pm, c = 1151.9 (4) pm, β = 111.88 (4)°, Z = 4, d_{calcd} = 1.60 g/cm^3, R (R_w) = 0.068 (0.054). **2**: monoclinic, $P2_1/c$, a = 1272.8 (5) pm, b = 1534.1 (23) pm, c = 1633.6 (16) pm, β = 104.76 (8)°, Z = 4, d_{calcd} = 1.69 g/cm^3, R (R_w) = 0.078 (0.065). The iron center of **1** is pseudooctahedrally coordinated by four sulfur and two carbon atoms. In **2**, the iron centers are coordinated pseudooctahedrally by five sulfur and one carbon atom and bridged via two thiolato-*S* atoms. The trans coordination of the thiolato-*S* atoms in **1** is retained in **2**. The chirotopic iron centers of **2** possess latent coordination sites and low-valent Fe centers capable of binding σ-π donors. In order to substitute or to transform the CO ligands, **2** was reacted with NO^+, NO, PMe_3, and MeLi. With $NOPF_6$, a CO/NO^+ substitution took place, yielding $[Fe_2(CO)(NO)(\mu\text{-"}S_4\text{"})_2]PF_6$ (**3**), which is isoelectronic to **2**. Treatment of **2** with NO gas or PMe_3 led to cleavage of Fe-thiolato-*S* bridges and formation of mononuclear $[Fe(NO)_2(\text{"}S_4\text{"})]$ (**4**) and $[Fe(CO)(PMe_3)(\text{"}S_4\text{"})]$ (**5**), respectively. The reaction between **2** and MeLi caused the elimination of the C_2H_4 bridge from the tetradentate $\text{"}S_4\text{"}^{2-}$ ligand under formation of $[Fe(\text{"}S_2\text{"})_2]_2^{2-}$ (**6**) ($\text{"}S_2\text{"}^{2-}$ = 1,2-benzenedithiolate), which could be isolated as a $AsPh_4^+$ salt. The mutual influence of the Fe centers in **2** and **3** was investigated by Mössbauer spectroscopy.

Introduction

Iron atoms in a coordination sphere of sulfur form the active sites of numerous oxidoreductases, e.g., nitrogenases and hydrogenases. The structures of the polynuclear centers of these enzymes as well as the molecular mechanisms of the catalyzed reactions, however, are largely unknown.[2] Model compounds for such centers are all of the structural type; i.e., they are built up from iron, sulfide, and thiolate ligands, usually possess high symmetry, and do not react with relevant substrates, e.g., CO, N_2, or H_2.[3] The metal centers in oxidoreductases, however, must be expected to be chirotopic[4] due to the protein environment, even when they catalyze only reactions of achiral substrates and form highly symmetrical building blocks like the iron centers of $[Fe_4S_4(SR)_4]$ clusters[2a] in ferredoxines. Further, such metal centers must have vacant or latently vacant sites for the coordination of substrates. In this context, we probed the formation of polynuclear complexes starting with $[Fe(CO)_2(\text{"}S_4\text{"})]$ (**1**) as chiral synthon. Our investigations yielded $[Fe(CO)(\mu\text{-"}S_4\text{"})]_2$ (**2**) ($\text{"}S_4\text{"}^{2-}$ = 1,2-bis((2-mercaptophenyl)thio)ethanato(2-)), which represents a new type of chiral complex. **2** consists of two homochiral fragments with chirotopic iron centers that have low-valent character and bind σ-π ligands.[5] Synthesis, structural

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Table I. Summary of Crystallographic Data of **1** and **2**

	1	**2**
compound	[Fe(CO)$_2$("S$_4$")]	[Fe(CO)(μ-"S$_4$")]$_2$
formula	$C_{16}H_{12}S_4O_2Fe$	$C_{30}H_{24}S_8O_2Fe_2$
M_r	420.38	784.73
cryst size, mm^3	0.40 × 0.20 × 0.10	0.30 × 0.30 × 0.20
space group	$P2_1/c$	$P2_1/c$
cell dimens		
a, pm	1293.3 (6)	1272.8 (5)
b, pm	1258.2 (6)	1534.1 (23)
c, pm	1151.9 (4)	1633.6 (16)
β, deg	111.88 (4)	104.76 (8)
molecules/unit cell	4	4
cell vol, pm^3	1739 (2) × 10^6	3085 (2) × 10^6
d_{calcd}, g/cm^3	1.60	1.69
wavelength, pm	71.073	71.073
temp of meas, K	200	200
μ, cm^{-1}	13.3	14.5
R	0.068	0.078
R_w	0.054	0.065

Table II. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (pm^2 × 10^{-1}) of the Non-Hydrogen Atoms

	x	y	z	U(eq)^a
		(a) [Fe(CO)$_2$("S$_4$")] (**1**)		
Fe(1)	8076 (1)	9245 (1)	2070 (1)	26 (1)
S(1)	9308 (2)	9408 (2)	1075 (2)	32 (1)
S(2)	9405 (2)	8324 (2)	3630 (2)	34 (1)
S(3)	7479 (2)	7703 (2)	1007 (2)	28 (1)
S(4)	6904 (2)	8979 (2)	3121 (2)	32 (1)
C(1)	8568 (8)	10465 (8)	2878 (8)	36 (4)
O(1)	8870 (5)	11252 (5)	3366 (6)	51 (3)
C(2)	7008 (7)	9953 (7)	844 (8)	33 (4)
O(2)	6344 (6)	10381 (6)	73 (7)	66 (4)
C(15)	10627 (7)	8438 (7)	3278 (8)	32 (3)
C(14)	11633 (7)	8047 (8)	4129 (8)	42 (4)
C(13)	12595 (7)	8142 (8)	3877 (10)	51 (4)
C(12)	12536 (8)	8635 (8)	2752 (10)	57 (5)
C(11)	11549 (8)	9031 (7)	1920 (10)	45 (5)
C(10)	10563 (6)	8934 (6)	2157 (8)	30 (3)
C(25)	6455 (7)	7206 (7)	1571 (8)	32 (4)
C(24)	5953 (8)	6232 (7)	1142 (9)	45 (5)
C(23)	5173 (7)	5831 (8)	1562 (9)	45 (4)
C(22)	4900 (8)	6418 (7)	2443 (9)	47 (4)
C(21)	5384 (7)	7378 (7)	2877 (9)	40 (4)
C(20)	6218 (7)	7818 (6)	2472 (8)	27 (3)
C(16)	9027 (7)	6957 (7)	3188 (8)	40 (4)
C(26)	8613 (7)	6798 (6)	1782 (8)	37 (4)
		(b) [Fe(CO)(μ-"S$_4$")]$_2$ (**2**)		
Fe(1)	764 (1)	594 (1)	7127 (1)	16 (1)
Fe(2)	3323 (1)	1378 (1)	7981 (1)	15 (1)
S(1)	2513 (2)	233 (2)	7108 (2)	18 (1)
S(2)	827 (2)	−508 (2)	8098 (2)	19 (1)
S(4)	−909 (2)	929 (2)	7334 (2)	24 (1)
S(3)	−24 (2)	−346 (2)	6089 (2)	21 (1)
S(5)	1603 (2)	1626 (2)	8126 (2)	18 (1)
S(6)	3657 (2)	575 (2)	9219 (2)	18 (1)
S(7)	4031 (2)	2556 (2)	8745 (2)	19 (1)
S(8)	5041 (2)	976 (2)	7905 (2)	25 (1)
C(1)	581 (8)	1414 (8)	6365 (6)	19 (3)
O(1)	390 (9)	1962 (6)	5851 (5)	46 (4)
C(2)	3143 (9)	1988 (7)	7054 (6)	20 (4)
O(2)	3069 (8)	2402 (7)	6453 (6)	46 (4)
C(15)	2068 (9)	−1074 (7)	8150 (7)	19 (3)
C(14)	2322 (10)	−1846 (7)	8623 (7)	28 (4)
C(13)	3232 (11)	−2279 (8)	8632 (7)	31 (4)
C(12)	3965 (10)	−1965 (8)	8190 (8)	32 (4)
C(11)	3759 (9)	−1198 (7)	7740 (7)	26 (4)
C(10)	2822 (8)	−742 (7)	7712 (6)	17 (3)
C(25)	−1432 (9)	−150 (7)	5944 (7)	22 (4)
C(24)	−2174 (10)	−566 (8)	5255 (7)	32 (4)
C(23)	−3266 (10)	−504 (8)	5169 (8)	31 (4)
C(22)	−3642 (11)	−30 (8)	5773 (8)	31 (4)
C(21)	−2914 (9)	408 (8)	6436 (7)	26 (4)
C(20)	−1804 (9)	361 (7)	6537 (7)	21 (4)
C(16)	−101 (9)	−1325 (7)	7484 (7)	22 (3)
C(26)	75 (9)	−1398 (8)	6623 (7)	25 (4)
C(35)	2471 (9)	688 (7)	9597 (6)	17 (3)
C(34)	2442 (10)	315 (8)	10382 (7)	29 (4)
C(33)	1544 (12)	455 (8)	10677 (8)	37 (5)
C(32)	677 (10)	941 (8)	10237 (7)	29 (4)
C(31)	700 (9)	1308 (7)	9458 (7)	22 (4)
C(30)	1589 (9)	1171 (7)	9158 (6)	19 (3)
C(45)	5430 (9)	2511 (7)	8803 (6)	20 (4)
C(44)	6121 (10)	3193 (7)	9242 (6)	23 (4)
C(43)	7216 (10)	3143 (8)	9347 (7)	29 (4)
C(42)	7670 (10)	2429 (8)	9030 (8)	32 (4)
C(41)	6992 (10)	1774 (7)	8612 (7)	23 (4)
C(40)	5859 (9)	1777 (8)	8449 (7)	24 (4)
C(36)	4121 (10)	2224 (7)	9840 (6)	22 (4)
C(46)	4525 (9)	1318 (8)	9999 (7)	25 (4)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

characterization, and reactions of **2** will be described here; preliminary results were published elsewhere.[1]

Experimental Section

General Methods. Unless otherwise noted, all procedures were carried out under a nitrogen atmosphere at room temperature by using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible the reactions were monitored by IR spectroscopy. Spectra were recorded on the following instruments: IR (CaF_2 cuvettes or KBr discs), Zeiss IMR 25 or Perkin-Elmer 983 (solvent bands were compensated); mass spectra, Varian MAT 212; NMR, JEOL FT-JNM-GX 270. Magnetic moments were obtained with a Johnson Matthey susceptibility balance. ^{57}Fe Mössbauer measurements were carried out with powder samples of about 100 mg in polyethylene containers of 19 mm diameter; spectra were recorded with a spectrometer consisting of a constant acceleration electronical drive and a Nuclear Data ND 2400 multichannel analyzer operating in the multiscaling mode. The γ-source used consisted of 30 mCi of ^{57}Co in rhodium at room temperature, the calibration being effected with a 25-μm iron-foil absorber. 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} has to be added. Measurements at 4.2 K were performed by using a helium cryostat, applied magnetic fields being generated by a superconducting coil capable of producing 6 T.

$NOPF_6$ was purchased from Alfa, NO gas from Messer Griesheim, MeLi from Aldrich, and $AsPh_4Cl$ from Merck. [Fe(CO)$_2$("S$_4$")] (**1**)[6] and PMe_3[7] were prepared as described in the literature.

X-ray Data Collection, Structure Determination, and Refinement for [Fe(CO)$_2$("S$_4$")] (1) and [Fe(CO)(μ-"S$_4$")]$_2$ (2). Single crystals of **1** were grown over a period of 10 days by pressure cap diffusion of a saturated CD_2Cl_2 solution in a NMR tube at 24 °C. Single crystals of **2** were directly obtained from the reaction mixture. The single crystals were sealed under N_2 in glas 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 methylene hydrogen atoms were calculated for ideal tetrahedra and rotated around the central carbon atom during refinement. The isotropic H atoms were refined with common temperature factors. Table I summarizes crystallographic data, the fractional atomic coordinates are given in Table II.

Preparation of Compounds. [Fe(CO)(μ-"S$_4$")]$_2$ (2) from [Fe(CO)$_2$("S$_4$")] (1) in DMF. A solution of **1** (1270 mg, 3.0 mmol) in 30 mL of DMF was filtered and heated to 90 °C for 48 h in the course of which the color changed from red to brown and dark brown crystals of **2** precipitated. They were separated, washed with 30 mL of acetone and dried in vacuo for 2 h. Yield: 800 mg (67%). Anal. Calcd for $C_{30}H_{24}S_8O_2Fe_2$ (mol wt 784.7): C, 45.92; H, 3.08; S, 32.69. Found: C, 45.91; H, 2.94; S, 32.65.

[Fe(CO)(μ-"S$_4$")]$_2$ (2) from [Fe(CO)$_2$("S$_4$")] (1) in THF. A solution of **1** (6800 mg, 16.3 mmol) in 50 mL of THF was filtered and heated to boiling for 6 h. The solution changed color from raspberry red to brown and brown microcrystals precipitated. They were separated, washed with 10 mL of THF, and dried in vacuo. Yield: 6200 mg (97%). Anal. Calcd for $C_{30}H_{24}S_8O_2Fe_2$ (mol wt 784.7): C, 45.92; H, 3.08; S, 32.69. Found: C, 45.43; H, 2.80; S, 33.45.

[Fe$_2$(CO)(NO)(μ-"S$_4$")$_2$]PF$_6$ (3). $NOPF_6$ (265 mg, 1.5 mmol) in solid form was added to a suspension of [Fe(CO)(μ-"S$_4$")]$_2$ (**2**) (1160 mg, 1.47 mmol) in 40 mL of CH_2Cl_2 at −15 °C. Stirring the brown reaction

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(7) Wolfsberger, W.; Schmidbaur, H. *Syn. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149.

mixture for 3 h yielded a black brown solution, which was filtered at −15 °C in order to remove unreacted **2**. After the filtrate was kept at room temperature for 48 h, black microcrystals precipitated. They were collected, washed with CH_2Cl_2, and dried in vacuo. Yield: 500 mg (37%). Anal. Calcd for $C_{29}H_{24}S_8O_2NFe_2PF_6$ (mol wt 931.7): C, 37.39; H, 2.60; N, 1.50; S, 27.53. Found: C, 37.43; H, 2.58; N, 1.09; S, 27.68.

[Fe(NO)$_2$("S$_4$")] (4). A suspension of [Fe(CO)(μ-"S$_4$")]$_2$ (**2**) (400 mg, 0.5 mmol) in 30 mL of $CHCl_3$ was treated with 50 mL (2.2 mmol) of NO gas and stirred at room temperature for 3 days. A 15-mL aliquot of EtOH was added to the resulting brown solution, and the mixture was kept at −78 °C for 3 days. The brown precipitate which formed was collected, washed with 5 mL of EtOH, and dried in vacuo for 6 h. Yield: 50 mg (12%). Anal. Calcd for $C_{30}H_{24}S_8O_2Fe_2$ (mol wt 424.7): C, 39.68; H, 2.84; N, 6.60. Found: C, 38.48; H, 2.54; N, 6.32.

(AsPh$_4$)$_2$[Fe(S$_2$C$_6$H$_4$)$_2$]$_2$ (6). A Et_2O solution of MeLi (0.9 mL, 1.4 mmol) was added to a suspension of [Fe(CO)(μ-"S$_4$")]$_2$ (**2**) (535 mg, 0.7 mmol) in 40 mL of THF. Refluxing the brown suspension for 4 h yielded a brown red solution, which was filtered and layered with a solution of $AsPh_4Cl$ (615 mg, 1.47 mmol) in 30 mL of MeOH. Black crystals, which had precipitated after 6 days, were collected, washed with MeOH and Et_2O and dried in vacuo. Yield: 430 mg (43%). Anal. Calcd for $C_{72}H_{56}S_8Fe_2As_2$ (mol wt 1439.2): C, 60.09; H, 3.92; S, 17.81. Found: C, 60.40; H, 4.24; S, 18.20.

Results and Discussion

Synthesis of [Fe(CO)(μ-"S$_4$")]$_2$ (2). Thermal decarbonylation of racemic [Fe(CO)$_2$("S$_4$")] (**1**) yields binuclear [Fe(CO)(μ-"S$_4$")]$_2$ (**2**) according to eq 1. The reaction slowly takes place

$$\underset{\mathbf{1}}{2[\mathrm{Fe(CO)_2(``S_4")}]} \xrightarrow[\text{or DMF/90 °C/3 days}]{\text{THF/66 °C/15 min}} \underset{\mathbf{2}}{[\mathrm{Fe(CO)}(\mu\text{-``S}_4\text{"})]_2} + 2\mathrm{CO} \quad (1)$$

($\text{``S}_4\text{"}^{2-}$ = 1,2-bis((2-mercaptophenyl)thio)ethanato(2−))

already at room temperature, in boiling THF or in DMF at 90 °C, it is complete within a few minutes (THF) or 2–3 days (DMF), respectively. When the reaction is carried out in boiling THF, **2** forms brown microcrystals only; in DMF at 90 °C, larger crystals grow. The crystals obtained from DMF comprised prisms being grown together and cubic single crystals. The latter proved to be suited for X-ray structure determination. They show a characteristic ν_{CO} band at 1965 cm^{-1} in the KBr IR spectrum and are almost insoluble in all common organic solvents, and the ^{1}H NMR spectrum obtained in DMF at 80 °C is of poor quality. Consequently, unambiguous structural characterization of **2** was only possible by X-ray structure analysis. Comparison of a simulated powder X-ray diffraction pattern of the single crystals with the measured powder diagram of the bulk product revealed the existence of at least one further isomer of **2**.

2 presumably forms via primary dissociation of Fe–CO bonds of **1**, yielding coordinatively unsaturated [Fe(CO)("S$_4$")] fragments, which subsequently dimerize via thiolato bridges. In order to sustain a 18-electron configuration of the Fe centers, two thiolato bridges must form in **2**. Because **1** is chiral, diastereomers of **2** have to be expected.

Analysis of Diastereomers of 2. When racemic [Fe(CO)("S$_4$")] fragments generated from **1** dimerize, 10 diastereomers can form, provided these fragments are configurationally stable (Scheme I). Otherwise, if the fragments were fluxional, yielding also structures with the thiolate donors in cis positions, the number of possible diastereomers would become even higher.

Molecular models show that the C_2H_4 bridge in **1** is conformationally rigid because of the planar $C_6H_4S_2$ entities, and in the course of dimerization *RR*, *RS*, and *SS* isomers can form.[8] In contrast to known binuclear complexes containing chiral fragments,[9] however, in the case of [Fe(CO)(μ-"S$_4$")]$_2$, each of these three combinations can theoretically yield another four isomers. Because two of them are identical, a total number of 10 isomers results.

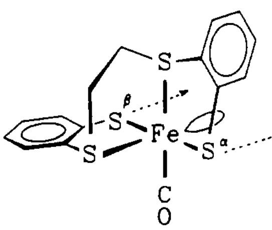

Figure 1. Difference of thiolato-*S* atoms in [Fe(CO)("S$_4$")] fragments.

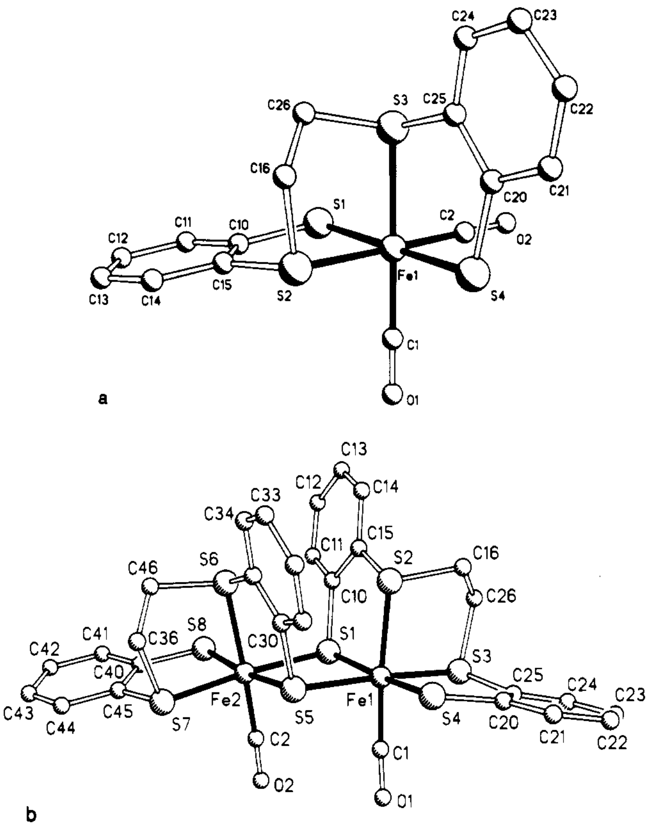

Figure 2. Molecular structures of (a) (*S*)-**1** and (b) $\alpha\alpha$-*Z*(*SS*)-**2** (H atoms omitted).

The differ in following features: (a) The CO ligands point either into the same (*Z* isomer) or into the opposite (*E* isomer) direction. (b) The bridging of the Fe centers takes place via different thiolato-*S* atoms. These S atoms differ in only one point: the thioether-*S* atom in the ortho position of the respective benzene ring stands either trans to the remaining CO ligand (α bridging) or trans to the second thiolato bridge (β bridging). This different character of the thiolato-*S* atoms is illustrated in Figure 1, where the bridging modes are indicated by α and β, respectively.

The analysis also shows that in the case of *RR* and *SS* isomers the *Z* form is possible only when $\alpha\alpha$ or $\beta\beta$ bridging occurs, and the *E* form requires $\alpha\beta$ or $\beta\alpha$ bridging. Vice versa, in the case of *RS* isomers, the *Z* form can only exist with $\alpha\beta$ or $\beta\alpha$ bridges and the *E* form only with $\alpha\alpha$ or $\beta\beta$ bridges. The centrosymmetric $\alpha\alpha$-*E*(*RS*) and $\beta\beta$-*E*(*RS*) isomers (VI and VII in Scheme I) are meso isomers of [Fe(CO)(μ-"S$_4$")]$_2$. Isomers I, II, IX, and X have C_2 symmetry; the remaining isomers possess C_1 symmetry, such that all dimers except VI and VII are chiral. The stereochemical

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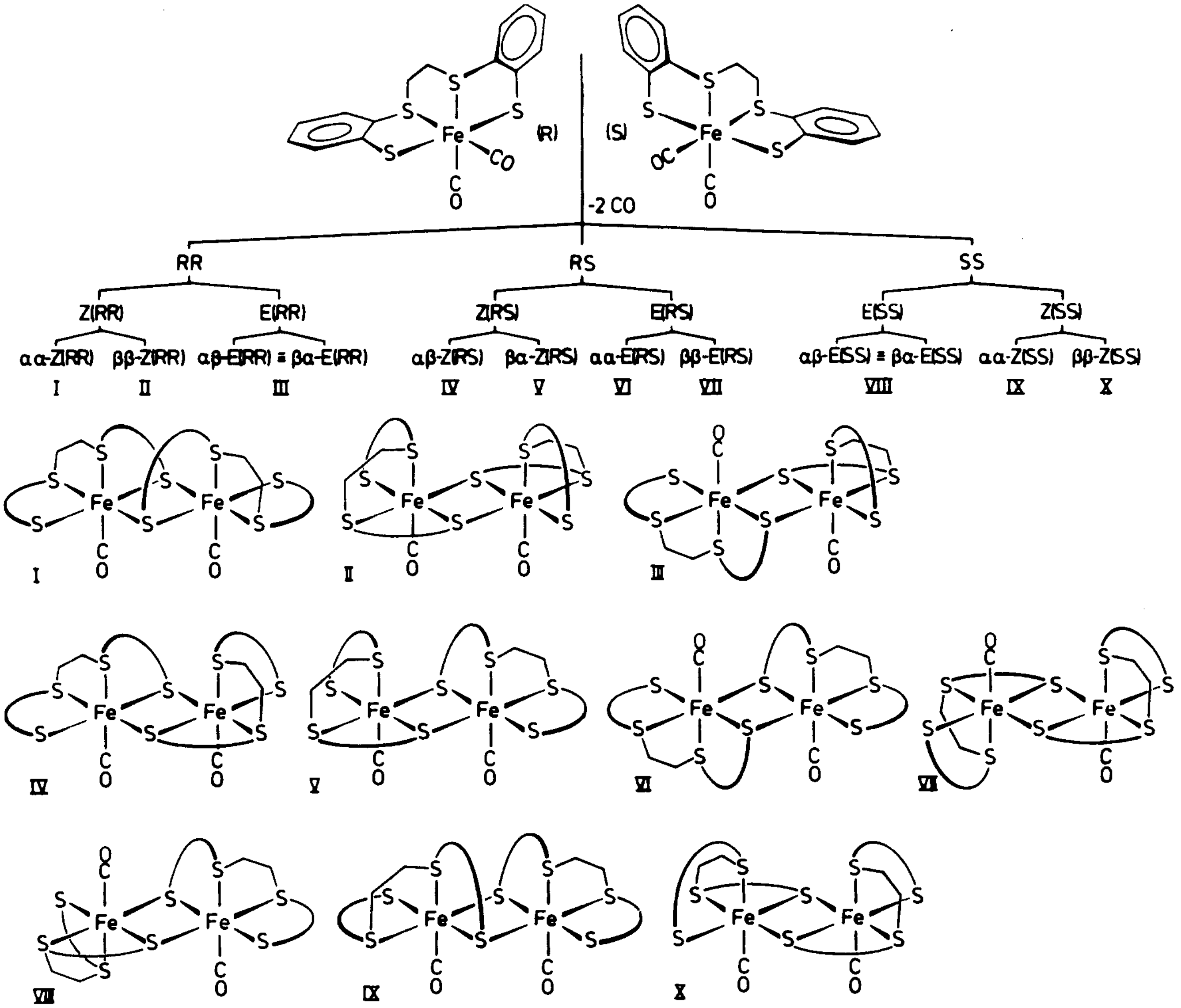
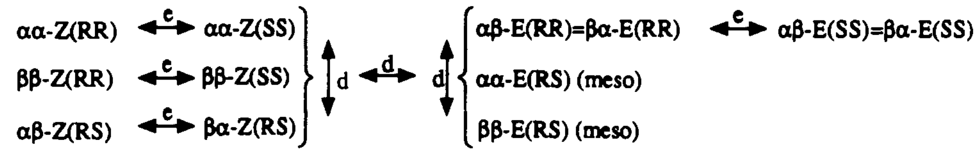
(8) R, *S* assignment was made according to: Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385. On the basis of IUPAC nomenclature the *R* and *S* isomers would be referred to as Δ and Λ isomers, respectively. But also IUPAC nomenclature allows only an insufficient stereochemical description of octahedral complexes with multidentate ligands; cf.: Deutscher Zentralausschuss für Chemie, Ed. *Internationale Regeln für die chemische Nomenklatur und Terminologie*; Verlag Chemie: Weinheim, FRG, 1976; Band 1, Gruppe 1, p 100.

(9) (a) Winter, C. H.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 219. (b) Harrowfield, J. M. B.; Wild, S. B. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 1, p 179. (c) House, D. A. *Ibid.* 1987; Vol. 2, p 23. (d) Kaufmann, G. B. *Coord. Chem. Rev.* **1974**, *12*, 105.

Scheme I. Theoretically Possible Isomers of **2** and Schematic Drawings of αα-*Z*(*RR*) (I), ββ-*Z*(*RR*) (II), αβ-*E*(*RR*) (III), αβ-*Z*(*RS*) (IV), βα-*Z*(*RS*) (V), αα-*E*(*RS*) (VI), ββ-*E*(*RS*) (VII), βα-*E*(*SS*) (VIII), αα-*Z*(*SS*) (IX), and ββ-*Z*(*SS*) (X) Isomers (⌒ = C_6H_4)



Scheme II. Stereochemical Relation between the 10 Theoretical Isomers of **2**



e = enantiomeric; d = diastereomeric

relationship between the resulting 10 isomers is summarized in Scheme II. The molecular models furthermore indicate that steric hindrance of dimerization is most likely for *Z* isomers (see Scheme I, isomers I, IV, V, and IX).

In particular, this point made it surprising that the X-ray structure determination showed the formation of enantiomeric αα-*Z*(*RR*)/αα-*Z*(*SS*) (I and IX).

X-ray Structure Determination of 1 and 2. In order to allow a comparison of educt **1** and product **2** as well as a discussion of the structural consequences when two [Fe(CO)("S_4")] fragments dimerize, the structure of **1** was also determined. Figure 2 shows the molecular structures of (*S*)-**1** and αα-*Z*(*SS*)-**2**. Selected bond lengths and angles are listed in Table III.

The iron center of **1** is pseudooctahedrally coordinated by four sulfur and two carbon atoms. The thiolato-*S* atoms of the tetradentate "S_4" ligand occupy trans positions; the carbonyl groups and thioether-*S* atoms occupy cis positions. Fe–S(thiolato) (229.2 (3)/228.9 (3) pm) and Fe–S(thioether) (228.5 (3)/227.1 (3) pm) distances are very similar and cover the range that is usually found in low-spin iron complexes of this type. Nearly identical distances are found in the closely related $[Fe(CO)_2ttd]$,[6] (ttd^{2-} = 1,4,7,10-tetrathiadecanato(2−)), $[Fe(CO)_2$("$^{bu}S_4$")$]$[10] ("$^{bu}S_4$" = 1,2-bis((3,5-di-*tert*-butyl-2-mercaptophenyl)thio)ethanato(2−)), [Fe(CO)("N_HS_4")][11] ("N_HS_4"$^{2-}$ = bis(2-((2-mercaptophenyl)thio)ethyl)aminato(2−)). Quite a similar situation exists for the bond angles of the FeC_2S_4 core. They deviate only marginally from ideal octahedral geometry.

In **2**, two six-coordinate Fe centers are connected via two thiolato-*S* bridges. The coordination geometry of each iron atom

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[10] Sellmann, D.; Freyberger, G.; Eberlein, R.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1987**, *323*, 21.

[11] Sellmann, D.; Kunstmann, H.; Knoch, F.; Moll, M. *Inorg. Chem.* **1988**, *27*, 4183.

Table III. Selected Interatomic Distances (pm) and Angles (deg)

	(a) $[Fe(CO)_2(\text{"}S_4\text{"})]$ (**1**)		
Fe(1)-S(1)	229.2 (3)	Fe(1)-S(2)	228.5 (3)
Fe(1)-S(3)	227.1 (3)	Fe(1)-S(4)	228.9 (3)
Fe(1)-C(1)	178.5 (9)	Fe(1)-C(2)	180.1 (8)
C(16)-C(26)	151.8 (12)		
S(1)-Fe(1)-S(2)	88.8 (1)	S(1)-Fe(1)-S(3)	88.1 (1)
S(2)-Fe(1)-S(3)	89.7 (1)	S(1)-Fe(1)-S(4)	176.2 (1)
S(2)-Fe(1)-S(4)	87.8 (1)	S(3)-Fe(1)-S(4)	90.0 (1)
S(1)-Fe(1)-C(1)	90.2 (4)	S(2)-Fe(1)-C(1)	90.5 (3)
S(3)-Fe(1)-C(1)	178.3 (4)	S(4)-Fe(1)-C(1)	91.6 (4)
S(1)-Fe(1)-C(2)	92.1 (4)	S(2)-Fe(1)-C(2)	178.9 (3)
S(3)-Fe(1)-C(2)	89.6 (3)	S(4)-Fe(1)-C(2)	91.3 (4)
	(b) $[Fe(CO)(\mu\text{-"}S_4\text{"})]_2$ (**2**)		
Fe(1)-Fe(2)	342.0 (1)	Fe(2)-S(1)	233.0 (3)
Fe(1)-S(1)	230.2 (3)	Fe(2)-S(5)	229.4 (3)
Fe(1)-S(2)	230.5 (3)	Fe(2)-S(6)	231.3 (3)
Fe(1)-S(4)	229.8 (3)	Fe(2)-S(7)	225.1 (3)
Fe(1)-S(3)	225.8 (3)	Fe(2)-S(8)	230.5 (3)
Fe(1)-S(5)	232.7 (3)	Fe(2)-C(2)	174.5 (10)
Fe(1)-C(1)	174.4 (11)		
Fe(2)-S(1)-Fe(1)	95.1 (1)	Fe(2)-S(5)-Fe(1)	95.4 (1)
S(2)-Fe(1)-S(1)	88.2 (1)	S(5)-Fe(2)-S(1)	84.4 (1)
S(4)-Fe(1)-S(1)	172.6 (1)	S(6)-Fe(2)-S(1)	95.0 (1)
S(4)-Fe(1)-S(2)	86.2 (1)	S(6)-Fe(2)-S(5)	88.0 (1)
S(3)-Fe(1)-S(1)	94.7 (1)	S(7)-Fe(2)-S(1)	175.4 (1)
S(3)-Fe(1)-S(2)	88.8 (1)	S(7)-Fe(2)-S(5)	93.9 (1)
S(3)-Fe(1)-S(4)	90.1 (1)	S(7)-Fe(2)-S(6)	89.1 (1)
S(5)-Fe(1)-S(1)	84.3 (1)	S(8)-Fe(2)-S(1)	92.5 (1)
S(5)-Fe(1)-S(2)	95.1 (1)	S(8)-Fe(2)-S(5)	173.5 (1)
S(5)-Fe(1)-S(4)	91.2 (1)	S(8)-Fe(2)-S(6)	86.5 (1)
S(5)-Fe(1)-S(3)	176.0 (1)	S(8)-Fe(2)-S(7)	89.6 (1)
C(1)-Fe(1)-S(2)	174.4 (4)	C(2)-Fe(2)-S(6)	177.1 (4)

[a] Estimated standard deviations are given in parentheses.

is again pseudooctahedral. The trans position of the thiolato-*S* atoms found in **1** is retained in **2**. As can be seen from Figure 2, two homochiral $[Fe(CO)(\text{"}S_4\text{"})]$ fragments are combined in **2**, and due to $\alpha\alpha$ bridging and (*SS*) combination, both CO ligands point into the same direction. **2** has approximately C_2 symmetry with the C_2 axis standing orthogonal on the center of the [Fe(1)-Fe(2)-S(1)-S(5)] four-membered ring. This ring is nearly planar, having a dihedral angle of 171°.

The Fe-S distances within the Fe_2S_2 ring show a slight alternation of ca. 3.1 pm (average), which may be due to the bridging situation, but altogether the Fe-S-Fe (thiolato bridge), Fe-S(thiolato terminal), and Fe-S(thioether trans to CO) distances are remarkably similar and vary only from 229.4 (3) to 233.0 (3) pm. Only the Fe-S(thioether) distances of 225.5 (3) pm (average) in the trans position to the Fe-S-Fe bridges fall out of this range. Possibly, π-donation from the thioether-*S* atoms to the Fe centers may be responsible for this effect, in order to avoid an electron deficiency at the Fe centers, which is caused by the bridging situation. Thus despite of the very different bonding situations and trans ligands, the individual Fe-S distances are remarkably similar. This may be explained by the high electron density at the sulfur donors and their π-donation capacity.

When respective Fe-S distances of **1** and **2** are compared a slight elongation (3.5 pm (average)) of the Fe-S bonds trans to the remaining CO ligands is noted. Also a slight shortening (3.1 pm (average)) of the Fe-S bonds trans to the Fe-S(thiolato) bridge caused by substitution of CO in **1** by a thiolato-*S* bridge in **2** can be seen. These differences may be valued as indication for the electronic origin of the $\alpha\alpha$-bridging mode in **2**.

2 is diamagnetic, and the Fe centers each are formally 18-electron configurated. Not unexpectedly, there is no indication of direct interaction between the two iron centers whose distance is 342.0 (1) pm. In complexes with Fe-Fe bonds usually much shorter distances in the range of 250–270 pm are observed, e.g., in $[Fe(CO)_3(\mu\text{-}SEt)_2]_2$ (253.7 pm)[12] or $[Fe(NO)_2(\mu\text{-}SEt)]_2$ (272.0 pm).[13] C-C and C-S distances of **1** and **2**, respectively, show no anomalities. As typical for chelate complexes, the core angles slightly deviate from ideal octahedral values.

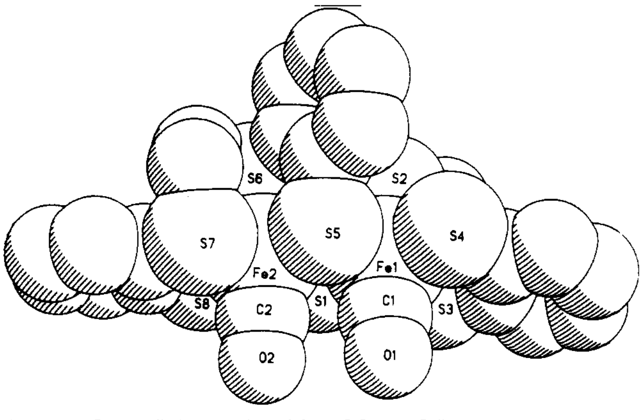

Figure 3. Space-filling model of $[Fe(CO)(\mu\text{-"}S_4\text{"})]_2$ (**2**).

The homochiral $[Fe(CO)(\text{"}S_4\text{"})]$ fragments in **2** are exclusively bridged by thiolato-*S* atoms whose corresponding thioether-*S* atom in the ortho position of the respective benzene ring stands trans to the CO ligand (α bridging). Therefore, we assume that electronic and not steric reasons are responsible for the regioselectivity of the dimerization. These electronic reasons might be rooted in the different electronical character of the thiolato-*S* atoms in the $[Fe(CO)(\text{"}S_4\text{"})]$ fragments (cf. Figure 1).

A remarkable feature of **2** is the very unequal spatial filling of the iron coordination sphere. The "upper moiety" (Figures 2b and 3) of the molecule is sterically overcrowded by the bulky "S_4"-ligands, whereas the "lower moiety" is occupied by the small CO ligands only. In this respect, the structure of **2** reminds one of a section of a metal protein where the folding of the peptide chain generates a specific environment of the vacant coordination sites.

Reactions of 2. Provided the CO ligands can be removed, **2** offers, in principle, the possibility to study enantiofacial reactions[14] of chiral molecules with a bicentric chirotopic metal site. Reactions of this sort are of fundamental significance in elucidating the origin of enantioselectivity, which is in general not well understood.[15] In order to investigate possibilities for removing the CO ligands, we reacted **2** with NO^+, NO, PMe_3, and MeLi and observed a variety of reactions including CO/NO^+ substitution, cleavage of **2** into mononuclear complexes, and elimination of the C_2H_4 bridge from the "S_4" ligands. With $NOPF_6$, under evolution of CO, the mononitrosyl complex **3** forms, which is isoelectronic with **2** (eq 2).

$$\underset{\mathbf{2}}{[Fe(CO)(\mu\text{-"}S_4\text{"})]_2} + NOPF_6 \xrightarrow[48\ h/-CO]{CH_2Cl_2/-15\ °C} \underset{\mathbf{3}}{[Fe_2(CO)(NO)(\text{"}S_4\text{"})_2]PF_6} \quad (2)$$

When the reaction is monitored by IR spectroscopy, the formation of **3** is indicated by a ν_{CO} band at 1990 cm^{-1} and a ν_{NO} band at 1855 cm^{-1}. In KBr the ν_{CO} absorption of **3** is slightly shifted to 1984 cm^{-1} and the ν_{NO} splits into two bands at 1852 and 1840 cm^{-1}. **3** was further characterized by elemental analysis, FD mass spectrometry, and Mössbauer spectroscopy. When we tried to substitute both CO ligands of **2** by applying 2 equiv of $NOPF_6$, again only **3** was obtained.

The formation of **3** is suggested to occur via thionitrosylation of thiolato-*S* atoms, yielding $[Fe_2(CO)_2(\mu\text{-"}S_4\text{"})_2(NO)]^+$ intermediates as primary products. Loss of CO and subsequent NO

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(13) Thomas, J. T.; Robertson, J. H.; Cox, E. G. *Acta Crystallogr.* **1958**, *11*, 599.

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(15) (a) Halpern, J. In *Asymmetric Synthesis*; Morrison, J. D., ed.; Academic Press: New York, 1985; Vol. 5, p 41. (b) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598.

Table IV. Selected Spectroscopic Data for **1**–**3**[a]

compd (color)	KBr IR, cm^{-1}	δ, ppm		FD MS, *m/e*
		^1H NMR	^{13}C NMR	
[Fe(CO)$_2$("S$_4$")] (**1**) (raspberry)	2036 ν_{CO} 1992 ν_{CO}	7.8–7.5 m[b] } (C_6H_4) 7.4–7.1 m 3.5 d } (C_2H_4) 2.6 d	209.2 (CO)[b] 157.0, 131.4 } (C_6H_4) 131.1, 130.6 130.3, 124.1 43.2 (C_2H_4)	420 [M^+]
[Fe(CO)(μ-"S$_4$")]$_2$ (**2**) (brown)	1965 ν_{CO}	8.4–6.8 m[c] (C_6H_4) 0.8–2.5 m (C_2H_4)	*d*	784 [M^+]
[Fe$_2$(CO)(NO)(μ-"S$_4$")$_2$]PF$_6$ (**3**) (black)	1984 ν_{CO} 1850 ν_{NO} 1840 ν_{NO} (sh) 841 ν_{PF}	*d*	*d*	786 [M^+ – PF_6]

[a] Key: d, doublet; m, multiplet; FD, field desorption. [b] In $CDCl_3$. [c] In DMF-d_7. [d] Could not be obtained.

shift to the iron center as proposed previously for related complexes[16,17] finally leads to **3**. In order to test whether mononuclear intermediates also occur, e.g., [Fe(CO)(NO)("S$_4$")]$^+$, we tried to synthesize such complexes according to eq 3 but neither [Fe-

$$\underset{\mathbf{1}}{[Fe(CO)_2(\text{"}S_4\text{"})]} + NOPF_6 \xrightarrow[-CO]{-60\ ^\circ C/CH_2Cl_2} [Fe(CO)(NO)(\text{"}S_4\text{"})]PF_6 + \text{other products} \quad (3)$$

(CO)(NO)("S$_4$")]PF$_6$ nor **3** could be isolated. Upon addition of NOPF$_6$ to the red-brown solution of **1**, a dark violet reaction mixture formed. IR spectroscopy of the mixture revealed a new ν_{CO} band at 2077 cm^{-1} together with the ν_{CO} absorptions of **1** at 2051 and 2006 cm^{-1}, and only a very weak and broad ν_{NO} band at 1796 cm^{-1} could be detected. The new species with the ν_{CO} band at 2077 cm^{-1} could not be isolated. During work up at ambient temperatures, the color of the reaction mixture turned back to red brown, and except for the educt **1**, no other complex could be identified.

When in **2** the 2-electron donor CO is substituted by the 3-electron donor NO, complexes with 19-electron configuration must result. Such complexes are, in general, highly reactive and undergo subsequent reactions, and they could be isolated only in a very few cases.[17,18] Mononuclear complexes formed when **2** was reacted with NO according to eq 4. The dicarbonyl complex **1**

$$\mathbf{2} + 2NO \xrightarrow[3\ \text{days}]{CH_2Cl_2/\text{room temp}} \underset{\mathbf{1}}{[Fe(CO)_2(\text{"}S_4\text{"})]} + \underset{\mathbf{4}}{[Fe(NO)_2(\text{"}S_4\text{"})]} + \text{other products} \quad (4)$$

and the dinitrosyl complex [Fe(NO)$_2$("S$_4$")] (**4**) were identified in the reaction solution by their characteristic ν_{CO} and ν_{NO} bands, respectively (Figure 4). Evidently, the cleavage of **2** into mononuclear species must be accompanied by CO-transfer reactions between the Fe centers. **4** was previously obtained by reacting **1** with an excess of NO gas.[17] It is the only product when **2** is reacted with an excess of NO. **2** was also cleaved into mononuclear species in the reaction according to eq 5. In contrast to the mild

$$\mathbf{2} + PMe_3\ (\text{excess}) \xrightarrow[24\ h]{THF/66\ ^\circ C} \underset{\mathbf{5}}{[Fe(CO)(PMe_3)(\text{"}S_4\text{"})]} + \text{other products} \quad (5)$$

reaction conditions of eq 4, higher temperatures were required. **5** was previously obtained from **1** and PMe$_3$;[6] it was spectroscopically characterized.

Finally, we wanted to probe whether the CO ligands of **2** undergo nucleophilic additions or substitutions with MeLi. Nucleophilic addition of lithium organyls to CO ligands in this type of Fe–S complexes was previously observed with [Fe(CO)$_2$(CH$_3$SC$_6$H$_4$S)$_2$].[19] Considering the strong nucleophilicity (and Lewis basicity) of MeLi, we were surprised to observe no reaction according to eq 6 in the temperature range from –50 °C up to

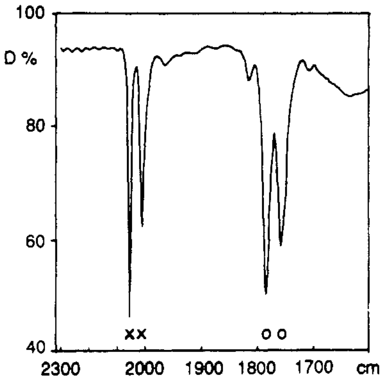

Figure 4. Solution IR spectrum of the reaction between [Fe(CO)(μ-"S$_4$")]$_2$ and NO according to eq 4 (XX = **1**, OO = **4**).

$$\mathbf{2} + 2MeLi \xrightarrow[-CO/-C_2H_4]{THF/66\ ^\circ C/4\ h} \underset{\mathbf{6}}{[Fe(\text{"}S_2\text{"})_2]_2^{2-}} + \text{other products} \quad (6)$$

+40 °C. Only when the THF solution was boiled, the suspended **2** slowly dissolved and a dark red solution formed which, however, showed no ν_{CO} bands in the IR spectrum. From this solution the benzenedithiolate complex (AsPh$_4$)$_2$[Fe(S$_2$C$_6$H$_4$)$_2$]$_2$ ((AsPh$_4$)$_2$[**6**]) could be precipitated by addition of AsPh$_4$Cl. The structure of this complex was confirmed by an X-ray structure determination. It will not be further discussed here because the structure of the analogous NEt$_4$$^+$ salt has been recently published elsewhere.[20] In the anion, two planar [Fe(S$_2$C$_6$H$_4$)$_2$]$^-$ moieties are connected via thiolato bridges, yielding a binuclear species with five-coordinate iron centers. Distances and angles of (AsPh$_4$)$_2$[**6**] correspond also with the corresponding toluenedithiolate Fe^{III} complex.[21] Obviously, the formation of [Fe(S$_2$C$_6$H$_4$)$_2$]$_2$$^{2-}$ (**6**) from **2** comprises several transformations, including the oxidation of the Fe centers and the cleavage of "S$_4$" ligands into benzenedithiolato units. In Table IV, selected spectroscopic data of **1**–**3** are summarized.

Mössbauer Investigations of [Fe$_2$(CO)(NO)(μ-"S$_4$")$_2$]PF$_6$ (3), [Fe(CO)(μ-"S$_4$")]$_2$ (2), and Related Compounds. The large Fe–Fe distance of **2** excludes a direct metal-metal bond, but the Fe centers could influence one another via the thiolato bridges, and in order to investigate such effects Mössbauer spectra of **2** and **3** were recorded. Figure 5 displays the spectra of **2** and **3** and Table V lists the relevant data for **2**, **3**, and a few related com-

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[18] (a) Yu, J. S.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1982**, *21*, 3106. (b) Aoyagi, K.; Mukaida, M.; Kakihana, H.; Shimuzu, K. *J. Chem. Soc. Dalton Trans.* **1985**, 1733. (c) Callahan, R. W.; Meyer, T. J. *Inorg. Chem.* **1977**, *16*, 574.

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[21] Sawyer, D. T.; Srivatsa, G. S.; Bodini, M. E.; Schaefer, W. P.; Wing, R. M.; *J. Am. Chem. Soc.* **1986**, *108*, 936.

Table V. Mössbauer Fitting Parameters of **2**, **3**, and Related Compounds

	[Fe(CO)(μ-"S$_4$")]$_2$ (**2**)	[Fe$_2$(CO)(NO)(μ-"S$_4$")$_2$]PF$_6$ (**3**)		[Fe(CO)$_2$("S$_4$")] (**1**)	[Fe(CO)(PMe)$_3$("S$_4$")] (**5**)	[Fe(CO)-("S$_5$")]
ref.	*a*	*a*	*a*	19	19	19
doublet	A	A′	B′			
T, K	4.2	4.2	4.2	295	295	295
δ, mm s^{-1}	0.246 (1)	0.232 (1)	0.146 (1)	0.011	0.083	0.130
ΔE_Q,^{b} mm s^{-1}	+0.486 (1)	+0.620 (2)	+1.465 (2)	0.518	0.305	0.240
Γ,^{c} mm s^{-1}	0.315 (2)	0.302 (5)	0.303 (4)			
% area		49	51			
η^d	≈1	≈0	≈0			

^{a}This work. ^{b}The sign of the ΔE_Q values was determined from the Mössbauer measurements at H = 4 T. ^{c}Half-width. ^{d}Asymmetry parameter.

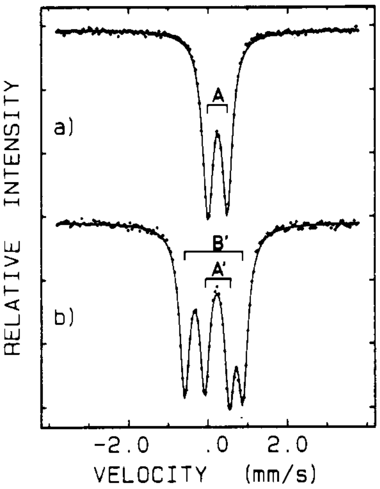

Figure 5. Zero-field Mössbauer spectra of **2** (a) and **3** (b) at 4.2 K. The full lines are least-squares fits with Lorentzian line shapes.

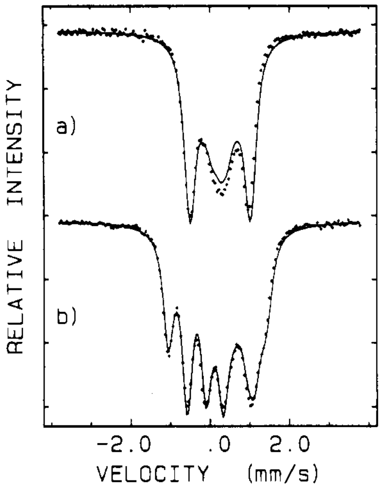

Figure 6. Magnetically perturbed (H = 4 T, parallel γ-ray) Mössbauer spectra of **2** (a) and **3** (b) at 4.2 K.

plexes. A second aim was to get additional information about the structure of **3**.

2 and **3** show isomer shifts that are typical of low-spin Fe$^{\mathrm{II}}$ centers in a coordination sphere dominated by sulfur donors.[22] Similar shifts as well as quadrupole splittings were previously observed for related complexes, e.g., [Fe(CO)$_2$("S$_4$")] (**1**) [Fe(CO)(PMe)$_3$("S$_4$")] (**5**) and [Fe(CO)("S$_5$")].[19]

The Mössbauer spectrum of **3** (Figure 5b) shows two equally intensive doublets with different isomer shifts and quadrupole splittings confirming the presence of two distinct Fe centers. In contrast, the spectrum of **2** displays only one doublet (doublet A, Figure 5a), proving the identity of the iron centers. The Fe–CO center of **3** is expected to show a similar isomer shift and quadrupole splitting, whereas the respective values for the Fe–NO center should be more different. Accordingly, we assign doublet A′ (δ = 0.232 mm s^{-1}; ΔE_Q = 0.620 mm s^{-1}) to the Fe–CO and doublet B′ (δ = 0.146 mm s^{-1}; ΔE_Q = 1.465 mm s^{-1}) to the Fe–NO center.

In order to corroborate this assignment, Mössbauer spectra of **2** and **3** were also measured in an external magnetic field of H = 4 T parallel to the γ-ray direction. Spectra of both compounds were simulated for an effective field of H = 4 T at the nucleus parallel to the γ-ray direction according to Collins and Travis[23] and by use of the measured parameters of doublets A, A′, and B′ listed in Table V. Figure 6 displays the good agreement between measured and calculated spectra confirming the assignments. The lower isomer shift of the Fe–NO center in comparison to the Fe–CO center of **3** agrees with the assumption that NO$^+$ is a stronger π-acceptor ligand than CO. This leads to a stronger withdrawing of d electrons (and higher s-electron density) at the Fe–NO nucleus.

It is noted that despite the larger ΔE_Q's of **3** the asymmetry parameters η are smaller in **3** than in **2**. This might indicate that the differences of bond lengths in the Fe$_2$S$_6$ core in the plane of **3** are diminished by the electron-withdrawing NO$^+$ ligand such that the iron centers in **3** surprisingly obtain a more symmetric environment. The ν_{CO} band of **3** (1985 cm^{-1}/KBr) is shifted to higher energies compared with the frequencies of [Fe(CO)(μ-"S$_4$")]$_2$ (**2**) (ν_{CO} = 1965 cm^{-1}) or related compounds, e.g., [Fe(CO)("S$_5$")] (ν_{CO} = 1960 cm^{-1}) or [Fe(CO)(PMe$_3$)("S$_4$")] (**5**) (ν_{CO} = 1943 cm^{-1}),[19] indicating an decreased electron density at the Fe–CO center. Summarizing the Mössbauer results, we can state that the Fe centers in **2** and **3**, respectively, interact, but the degree of interaction is low. When one CO ligand in **2** is substituted by NO$^+$, isomer shifts and quadrupole splitting of the remaining Fe–CO center change, but only slightly (0.232 (1)/0.620 (2) mm s^{-1} in **3** vs 0.246 (1)/0.486 (1) mm s^{-1} in **2**). These Mössbauer results are consistent with the IR spectroscopic observations.

Summary and Conclusion

Binuclear iron carbonyl and iron carbonyl nitrosyl complexes with sulfur-dominated coordination spheres were synthesized. The isolation of **2** shows an access to binuclear complexes containing two potentially vacant coordination sites with low-valent metal centers that bind soft substrates, e.g., CO. In this regard, complex **2** differs from the well-known "Werner-type" complexes with polydentate amine ligands. Despite sterical hindrance, dimerization of racemic [Fe(CO)$_2$("S$_4$")] (**1**) results in formation of the *αα-Z*(*RR*)/*αα-Z*(*SS*) enantiomers of **2**. This indicates that the dimerization of [Fe(CO)("S$_4$")] fragments is dominated by the different *electronic* character of their thiolato-*S* atoms and not by steric control.

2 is chiral, consists of homochiral [Fe(CO)("S$_4$")] fragments connected via thiolato-*S* atoms, and contains chirotopic iron centers. The structure of **2** in which the iron centers are wrapped up with the multidentate sulfur ligands such that only two coordination sites, one at each iron center, are accessible reminds one of a section in a metal protein where peptide chains with cysteine and methionine residues generate specific and chiral coordination geometries at the metal. Complexes such as **2** also

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offer the possibility to study bicentric metal-centered reactions between chiral complexes and chiral or prochiral substrates in order to achieve asymmetric syntheses.

Formation of $[Fe_2(CO)(NO)(\mu\text{-}``S_4")_2]PF_6$ (**3**) from **2** and $NOPF_6$ proves the accessibility of coordination sites at the iron centers in **2**. Surprisingly, only one of the two CO ligands in **2** can be substituted by NO^+. This indicates an interaction of the iron centers via thiolato bridges such that the CO/NO^+ substitution at one iron center reduces the electron density at the second iron center in the molecule, preventing the substitution of the second CO ligand. Interaction between the iron centers is also revealed by IR and Mössbauer spectra of **2** and **3**.

The iron centers of **2** are 18-electron configurated. Substitution of the 2-electron donor CO by the 3-electron donor NO leads to metal centers exceeding the noble gas configuration. As a consequence, the Fe–S(thiolato) bridges are cleaved, and mononuclear 18-electron configurated $[Fe(NO)_2(``S_4")]$ (**4**) forms in which the "$S_4$" ligand acts as tridentate ligand only. Drastic conditions are required for the reactions of **2** with $PMe_3$ and MeLi, respectively. They lead also to cleavage of **2** into mononuclear entities and formation of $[Fe(CO)(PMe_3)(``S_4")]$ (**5**) in the case of PMe_3. With MeLi, the final reaction product is the binuclear anion $[Fe(``S_2")_2]_2^{2-}$ (**6**). The results show that mononuclear iron carbonyl complexes with multidentate thioether thiolato ligands can be used as synthons for the synthesis of binuclear and possibly even polynuclear complexes. The binuclear complexes described here have model character for several iron oxidoreductases with respect to their structure, e.g., coordination sphere of sulfur and chirotopicity of metal centers, as well as to their reactivity shown by the coordination of "soft" σ–π ligands CO and NO to the iron centers.

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Supplementary Material Available: Listings of crystallographic data and data collection procedures, anisotropic thermal parameters, complete bond distances and bond angles, and fractional coordinates of atoms and isotropic thermal parameters (15 pages); listings of F_o and F_c values (24 pages). Ordering information is given on any current masthead page. Further details of the X-ray crystal structure analysis have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG, and can be obtained by quoting the deposition number (CSD-320152 (**2**), CSD-320153 (**1**)), the authors' names, and the reference.

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Iron(II) Complexes of 2,2'-Biimidazole and 2,2'-Bibenzimidazole as Models of the Photosynthetic Mononuclear Non-Heme Ferrous Sites. Synthesis, Molecular and Crystal Structure, and Mössbauer and Magnetic Studies

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A series of seven high-spin ferrous complexes of 2,2'-biimidazole and 2,2'-bibenzimidazole ligands have been prepared and studied with IR and Mössbauer spectroscopy and variable-temperature magnetic susceptibility. The crystal and molecular structures of $[Fe(bbzimH_2)_3](ClO_4)_2\cdot H_2O$ (**1**) and $[Fe(bbzimH_2)_3]Cl_2\cdot MeOH\cdot 4.33H_2O$ (**2**) have been determined. **1** crystallizes in the monoclinic system, space group $P2_1/c$, with $Z = 4$ and $a = 13.564$ (3) Å, $b = 19.122$ (3) Å, $c = 18.328$ (5) Å, and $\beta = 109.82$ (2)°. **2** crystallizes in the hexagonal system, space group $R\bar{3}$, with $Z = 6$ and $a = 15.509$ (3) Å and $c = 37.989$ (7) Å. The structure of **1** consists of the mononuclear cations $[Fe(bbzimH_2)_3]^{2+}$ separated by ClO_4^- anions and molecules of water of crystallization. The structure of **2** includes $[Fe(bbzimH_2)_3]^{2+}$ cations with two chloride anions and one water molecule statistically disordered over three sites. Steric hindrance considerations indicate that the $bbzimH_2$ ligands of $Fe(bbzimH_2)_2]Cl_2$ (**4**) and $Fe(bbzimH_2)_2](HCO_2)_2$ (**7**) are cis to each other as confirmed by the Mössbauer spectroscopy results. A trans arrangement of the $bimH_2$ ligands of $Fe(bimH_2)_2Cl_2$ (**3**) and $Fe(bimH_2)_2(HCO_2)_2$ (**6**), although implying some steric hindrance, is favored by the Mössbauer results. The Mössbauer spectroscopy and variable-temperature magnetic susceptibility results obtained provide evidence that the seven complexes described herein are mononuclear high-spin iron(II) species experiencing zero-field splitting of the iron(II) ground state. The distortion of the coordination sphere is predominantly axial for **2–4**, **6** and **7** and rhombic for **1** and **5** ($Fe(bimH_2)_2(CH_3CO_2)_2$). Complex **5** shows two iron(II) sites possibly corresponding to a mixture of cis and trans arrangements. This complex shows the closest similarity to the bacterial reaction centers and photosystem 2 ferrous sites. The large variability in the Mössbauer properties in this rather similar set of complexes indicates that in addition to the nature of the ligands the distortion of the Fe(II) coordination sphere is a factor that has to be taken into account in designing proper spectral analogues of the photosynthetic iron(II) complex.

Introduction

The reaction centers of photosynthetic bacteria[2] and the photosystem 2 of oxygenic photosynthetic organisms[3] have been shown to include a ferrous ion between the primary and the secondary quinone electron acceptors. The X-ray molecular structure determination of the reaction center of ***Rhodopseudomonas viridis***[4] and ***R. sphaeroides***[5] indicates that the ferrous ion is in a distorted-octahedral ligand environment including four nitrogen atoms pertaining to the imidazole moiety of histidine residues and two oxygen atoms from a glutamic acid residue of the surrounding protein. A similar iron coordination has been evidenced for native soybean lipoxygenase-1.[6] This enzyme pertains to the family of mononuclear non-heme-iron-containing dioxygenases that catalyze

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