Bridging CH_2 Addition to the Disulfur Ligands of an Iron–Sulfur Cluster Compound. X-ray Structure of $[Fe_4(\mu_3\text{-}S)_2((\mu_3\text{-}S_2)\text{-}CH_2\text{-}(\mu_3\text{-}S_2))(C_5H_4Me)_4]^{2+}(FeCl_4)^{2-}$

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The nucleophilic sulfur atoms of the disulfur ligands in $Fe_4S_6(C_5H_4R)_4$ (**1**) (R = H, Me) react easily with the alkyl halides CH_2X_2 (X = Cl, I) or CH_3I, to give the cluster compounds $[Fe_4(\mu_3\text{-}S)_2((\mu_3\text{-}S_2)\text{-}CH_2\text{-}(\mu_3\text{-}S_2))(C_5H_4R)_4]^{2+}(FeCl_4)^{2-}$ (R = H, **2a**$[FeCl_4]$; R = Me, **2b**$[FeCl_4]$), $[Fe_4(\mu_3\text{-}S)_2((\mu_3\text{-}SSCH_3)_2)(C_5H_5)_4](PF_6)_2$ (**3**$[PF_6]_2$), and $[Fe_4(\mu_3\text{-}S)_2((\mu_3\text{-}SSCH_3)(\mu_3\text{-}S_2)(C_5H_5)_4](I)$ (**4**[I]). The structure of **2b**$[FeCl_4]$, determined by X-ray diffraction, shows that a CH_2 bridge is present between the sulfur atoms of each of the disulfido ligands. In this way a new, μ_6-bonded ligand $SSCH_2SS$ is produced. **2b**$[FeCl_4]$ crystallizes in the monoclinic system, space group *Cc*, with cell dimensions $a = 15.847(2)$ Å, $b = 13.050(2)$ Å, $c = 16.395(2)$ Å, $\beta = 107.15°$, $V = 3166.1$ Å^3, and $Z = 4$. Refinement of 392 parameters on 5859 observed reflections gave an R value of 0.047 ($R_w = 0.048$). The structure of the new iron–sulfur cluster compound **2** differs from the parent compound **1** in that only the S–S bond distances increase from 2.04 to 2.19 Å. The Fe–Fe and Fe–S bond distances remain unchanged. The ^1H NMR spectrum of **2** recorded in CD_3CN indicates that the iron–sulfur core is rigid with nonfluxional disulfur units. In solution, **1** reacts immediately with CH_3I to form the monomethylated product $\mathbf{4}^+$. Stirring **1** in pure MeI for 48 h affords the dimethylated product $\mathbf{3}^{2+}$. This indicates the diminished nucleophilic character of $\mathbf{4}^+$ as compared to **1**.

Introduction

The electron-rich disulfur ligands in $Fe_4S_2(S_2)_2(C_5H_4R)_4$ (R = H, **1a**; R = Me, **1b**) are able to bind sulfur dioxide or a molybdenum moiety, yielding adducts like **1a**$\cdot 2SO_2$ and **1a**$\cdot Mo(CO)_4$.[1-3] Reaction of **1a** with Ag^+ in CH_3CN gives the paramagnetic trication $[(\mathbf{1a})_2Ag]^{3+}$, in which the silver atom is tetrahedrally coordinated by one sulfur of each disulfur ligand.[4]

Recent attempts to obtain pure samples of **1b** from mixtures of this compound with the related iron–sulfur cluster compounds $Fe_4S_4(C_5H_4Me)_4$ and $Fe_4S_3(S_2)(C_5H_4Me)_4$ showed that CH_2Cl_2 is reactive toward **1b**.[5]

The electron-rich two-coordinated sulfur atoms in the disulfido ligands of $Fe_4S_6(C_5H_4R)_4$ (**1**) are easily alkylated. Alkylation of sulfido or disulfido ligands in iron–sulfur cluster compounds has not been observed previously. Alkylation of sulfido ligands by organic halides has been observed for certain molybdenum and platinum complexes.[6]

In this paper we report the electrophilic addition of an alkyl group to the disulfido ligands of $Fe_4S_6Cp_4$, in which compounds such as $[Fe_4(\mu_3\text{-}S)_2((\mu_3\text{-}S_2)\text{-}CH_2\text{-}(\mu_3\text{-}S_2))(C_5H_4R)_4]^{2+}(X^-)_2$ are formed.

Results and Discussion

Synthesis and Structure. When **1** dissolved in pure CH_2Cl_2 was allowed to stand for 3 days or was allowed to react with CH_2I_2 in chloroform, the black compound **2**$[FeCl_4]$ or **2**$[I]_2$, respectively, was precipitated. The paramagnetic $FeCl_4^{2-}$ ion or the I^- ion was easily exchanged by reaction with excess KPF_6 in aqueous solutions. Recrystallization of **2b**$[FeCl_4]$ from DMF gave black crystals suitable for an X-ray structure determination (Table I).

Table I. Crystallographic Data for $[Fe_4(\mu_3\text{-}S)_2((\mu_3\text{-}S_2)\text{-}CH_2\text{-}(\mu_3\text{-}S_2))(C_5H_4CH_3)_4](FeCl_4)$

chem formula	$C_{25}H_{30}Cl_4Fe_5S_6$	space group	*Cc* (No. 9)
fw	943.9	*T*, K	293
a, Å	15.847(2)	λ, Å	0.710 73
b, Å	13.050(2)	ρ_{calcd}, g/cm^3	1.79
c, Å	16.395(2)	μ(Mo Kα), cm^{-1}	29.82
β, deg	107.15(3)	R^a	0.047
V, Å^3	3166.1	$R_w{}^b$	0.048
Z	4		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

1a reacts also with CH_3I in chloroform solution. The alkylation reaction proceeds quite fast, and after a few minutes the monomethyl product **4**[I] is formed. **4**$[PF_6]$ was isolated by ion exchange. The introduction of a second alkyl group on $\mathbf{4}^+$ is a much slower process, most likely because of the positive charge on this ion, and **3**$[I]_2$ is formed after 48 h of stirring in pure MeI.

$$\mathbf{2}^{2+}:\ [Fe_4(\mu_3\text{-}S)_2((\mu_3\text{-}S_2)\text{-}CH_2\text{-}(\mu_3\text{-}S_2))(C_5H_4R)_4]^{2+}$$

$$\mathbf{2a}^{2+},\ R = H;\ \mathbf{2b}^{2+},\ R = Me$$

$$\mathbf{3}^{2+}:\ [Fe_4(\mu_3\text{-}S)_2((\mu_3\text{-}SSCH_3)_2)(C_5H_5)_4]^{2+}$$

$$\mathbf{4}^{+}:\ [Fe_4(\mu_3\text{-}S)_2((\mu_3\text{-}SSCH_3)(\mu_3\text{-}S_2)(C_5H_5)_4]^{+}$$

Due to the considerable nucleophilicity of the disulfido ligands in **1**, they are subject to facile electrophilic attack by alkyl reagents. Indeed, CH_2I_2 reacted much faster than CH_2Cl_2, where I^- is the best leaving group among the halides.

The structure of **2b**$[FeCl_4]$ (Figure 1) shows that the iron–sulfur core of the parent cluster is completely preserved and that a CH_2 group is linked to a sulfur atom of each of the disulfur ligands. In this way, a completely new ligand is formed, $SSCH_2SS$, which is bonded to the four iron atoms in a μ_6-mode. The end-on sulfur atoms coordinate to two irons, and the other

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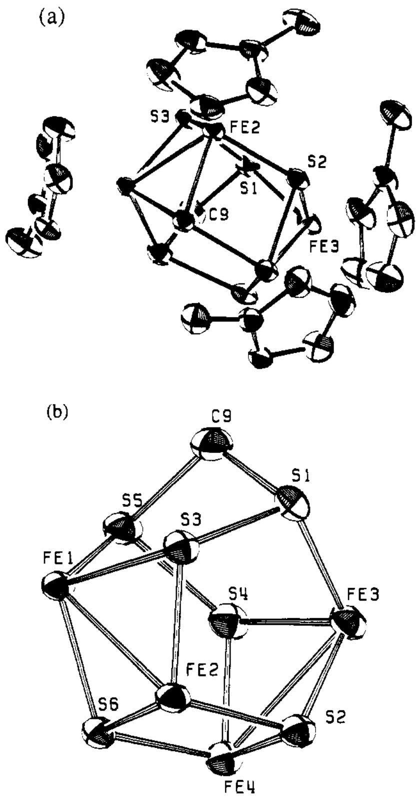

Figure 1. ORTEP views of the crystal structure of **2b**[$FeCl_4$]: (a) with C_5H_4Me rings; (b) without C_5H_4Me rings.

sulfur atoms, to one iron atom. Compared to that of the parent compound, the coordination of the iron atoms does not change. The two S–S bond lengths in the $SSCH_2SS$ ligand are both 2.19 Å, which is considerably longer than the distance that is normally found for a disulfur ligand where S–S bond lengths extend from 1.98 to 2.07 Å.[3,5,7]

The carbon–sulfur distances, 1.796 and 1.812 Å, and the tetrahedral S–C–S angle, 108.6°, are in the ranges normally found for these bonds. The twelve Fe–S distances show values similar to those found in analogous iron–disulfur clusters.[5,7] Eight out of the twelve Fe–S bond lengths are close to 2.19 Å. Two iron atoms, Fe(2) and Fe(4), are involved in two shorter as well as two somewhat longer Fe–S distances: from those iron to the sulfide (2.14 Å) and to the $SSCH_2SS$ ligand (2.24 Å). Compared to those in $Fe_4S_6Cp_4$, the iron–sulfur Fe–S distances differ at most by 0.05 Å and the Fe–Fe bond lengths remain the same.

In conclusion, the major effect of the CH_2 bridge insertion is the 0.15-Å lengthening of the S–S bond.

The origin of the $FeCl_4^{2-}$ ion must be a partial decomposition of the Fe_4S_6 cluster. Evidence for the presence of Fe(II) in $FeCl_4^{2-}$ comes from the Fe–Cl distances (average 2.31 Å) and the infrared stretching frequency at ν = 286 cm^{-1} normally found for this anion.[8,9]

^1H NMR Spectra. The presence of a CH_2 bridge is shown by a single peak at 5.36 ppm for $\mathbf{2a}^{2+}$ and at 5.32 ppm for $\mathbf{2b}^{2+}$. For the compounds **3**[PF_6]$_2$ and **4**[PF_6], the presence of the methyl groups is seen by the resonance signals at δ = 2.82 and 2.67 ppm, respectively (Table IV). Neither the methylene-bridge signal nor that for the two methyl groups was split, so a C_2 symmetry axis must be present in $\mathbf{2}^{2+}$ and in $\mathbf{3}^{2+}$, as in the parent compound **1**. The pattern found for the Cp-ring protons also indicates the presence of this C_2 symmetry. For the monoalkylated compound $\mathbf{4}^{+}$, only four resonance signals for the Cp-ring protons were observed, indicating the absence of a C_2 symmetry axis.

Table II. Atomic Positional Parameters (with Esd's) for **2b**[$FeCl_4$]

atom	*x*	*y*	*z*
Fe(1)	–0.05478(8)	0.10465(7)	–0.02190(7)
Fe(2)	0.04633(9)	0.27188(7)	0.01485(8)
Fe(3)	–0.07614(9)	0.29793(8)	0.18503(8)
Fe(4)	–0.15782(9)	0.35616(7)	0.02663(8)
S(1)	0.0030(1)	0.1562(1)	0.1965(1)
S(2)	–0.0131(1)	0.3714(1)	0.0961(1)
S(3)	0.0609(1)	0.1360(1)	0.0906(1)
S(4)	–0.1955(1)	0.2315(1)	0.0932(1)
S(5)	–0.1493(1)	0.0862(1)	0.0544(1)
S(6)	–0.0979(1)	0.2633(1)	–0.0580(1)
C(9)	–0.0796(5)	0.0564(6)	0.1615(5)
C(11)	–0.1011(5)	–0.0462(5)	–0.0712(5)
C(12)	–0.0071(6)	–0.0421(5)	–0.0450(5)
C(13)	0.0205(5)	0.0329(6)	–0.0940(5)
C(14)	–0.0566(6)	0.0777(6)	–0.1482(5)
C(15)	–0.1317(5)	0.0311(6)	–0.1346(5)
C(16)	–0.1566(6)	–0.1226(7)	–0.0411(7)
C(21)	0.1750(5)	0.3395(6)	0.0533(5)
C(22)	0.1775(6)	0.2512(6)	0.0040(6)
C(23)	0.1207(6)	0.2647(7)	–0.0773(6)
C(24)	0.0786(6)	0.3615(8)	–0.0807(6)
C(25)	0.1126(6)	0.4073(6)	–0.0016(6)
C(26)	0.2282(7)	0.3603(9)	0.1428(6)
C(31)	0.0048(6)	0.3587(6)	0.3023(5)
C(32)	–0.0548(7)	0.4347(7)	0.2561(5)
C(33)	–0.1436(7)	0.4022(10)	0.2424(6)
C(34)	–0.1414(7)	0.3110(11)	0.2818(6)
C(35)	–0.0508(6)	0.2799(7)	0.3184(5)
C(36)	0.1050(6)	0.3635(8)	0.3329(6)
C(41)	–0.2370(6)	0.4308(6)	–0.0905(6)
C(42)	–0.2918(5)	0.3971(6)	–0.0421(5)
C(43)	–0.2638(7)	0.4480(7)	0.0382(6)
C(44)	–0.1905(7)	0.5103(7)	0.0392(7)
C(45)	–0.1715(7)	0.4975(6)	–0.0406(7)
C(46)	–0.2458(7)	0.3998(7)	–0.1799(6)
Fe(5)	0.56712(9)	0.21491(8)	0.16373(7)
Cl(1)	0.4328(2)	0.2008(2)	0.1984(2)
Cl(2)	0.5399(2)	0.1854(2)	0.0207(2)
Cl(3)	0.6104(2)	0.3834(2)	0.2029(2)
Cl(4)	0.6791(2)	0.1076(2)	0.2404(2)

Table III. Selected Bond Lengths (Å) (with Esd's) for **2b**[$FeCl_4$]

Fe(1)–Fe(2)	2.650(2)	Fe(4)–S(2)	2.204(3)
Fe(3)–Fe(4)	2.643(2)	Fe(4)–S(4)	2.134(3)
Fe(1)–S(3)	2.197(2)	Fe(4)–S(6)	2.239(3)
Fe(1)–S(5)	2.201(3)	S(1)–S(3)	2.193(3)
Fe(1)–S(6)	2.203(2)	S(4)–S(5)	2.186(3)
Fe(2)–S(2)	2.242(3)	S(1)–C(9)	1.796(8)
Fe(2)–S(3)	2.138(2)	S(5)–C(9)	1.812(7)
Fe(2)–S(6)	2.203(2)	Fe(5)–Cl(1)	2.320(3)
Fe(3)–S(1)	2.196(2)	Fe(5)–Cl(2)	2.290(3)
Fe(3)–S(2)	2.201(3)	Fe(5)–Cl(3)	2.332(2)
Fe(3)–S(4)	2.189(2)	Fe(5)–Cl(4)	2.294(3)

The C_5H_4Me compound **2b**[PF_6]$_2$ shows eight resonances for the ring protons and two resonances with equal intensity for the C_5H_4Me protons. This indicates that the iron–sulfur core is rigid with nonfluxional disulfur units, as previously concluded for the parent compound **1b**.[5]

Cyclic Voltammetry. In DMF, $\mathbf{2b}^{2+}$ undergoes a reversible oxidation at 0.28 V (*vs* $Fc^{0/+}$) (ΔE_p = 65 mV; i_b/i_f = 1.0), two reversible reductions at –0.70 and –1.04 V (*vs* $Fc^{0/+}$) (both ΔE_p = 60 mV; i_b/i_f = 1.0), and, further, an irreversible reduction at $E_{p,c}$ = –1.9 V (i_b/i_f = 0.0) (Table V). $\mathbf{2a}^{2+}$ shows a redox pattern analogous to that of $\mathbf{2b}^{2+}$, but at about 30–70 mV higher potentials. Introduction of methyl groups on the Cp ring more often causes a small negative shift in the redox potentials.[5] Notable is the negative shift of 0.5 V for the redox potentials of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ as compared to those of **1**. $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ show an enhanced redox stability, while $\mathbf{1}^{2+}$ is only stable on the cyclic voltammetric time scale.[10]

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Table IV. Proton NMR Data for Iron–Sulfur Clusters

		chem shift,[a] ppm		
cluster	solvent	ring protons	CpMe protons	S–R′
1a[b]	$CDCl_3$	4.82 (10), 4.33 (10)		
1b[b]	$CDCl_3$	4.82 (2), 4.63 (2), 4.59 (2), 4.17 (2), 4.01 (4), 3.95 (2), 3.65 (2)	2.20 (6) 1.90 (6)	
2a$[PF_6]_2$	CD_3CN	5.64 (10), 5.01 (10)		5.36 (2)
2b$[PF_6]_2$	CD_3CN	5.90 (2), 5.43 (2), 5.09 (4), 4.90 (2), 4.54 (4), 4.47 (2)	2.28 (6) 1.85 (6)	5.32 (2)
3$[PF_6]_2$	CD_3CN	5.62 (10), 4.93 (10)		2.82 (6)
4$[PF_6]$	CD_3CN	5.31 (5), 5.19 (5), 4.66 (5), 4.60 (5)		2.67 (3)

[a] TMS was used as reference; the number of protons is given in parentheses. [b] Data from ref 5.

Table V. Electrochemical Data for Iron–Sulfur Cluster Compounds[a]

	redox transitions		
cluster series	2+/3+	2+/1+	1+/0
2a	0.31	−0.65	−0.98
2b	0.28	−0.70	−1.04
3	0.24	−0.68	−0.99
1a[b]	0.85[c]	−0.14	−0.46
1b[b]	0.86[c]	−0.24	−0.57

[a] In DMF; potentials in volts *vs* the Fc/Fc$^+$ redox couple. [b] In CH_2Cl_2; from ref 5. [c] Peak potential.

For the compounds with $FeCl_4^{2-}$ as the counterion, an oxidation wave was found at −0.41 V (*vs* $Fc^{0/+}$), the same potential as that observed for $(Bu_4N)_2FeCl_4$.

This study shows that the reactivity of the disulfido ligands in $Fe_4S_6(C_5H_4R)_4$ toward alkyl halides opens the possibility to prepare various new disulfido ligands such as $-SSCH_2SS-$ and $-SS(CH_3)$. With α,ω-dihalides or $\alpha,\alpha,\omega,\omega$-tetrahalides, various clusters may be connected to each other. The rich redox chemistry of these multicluster compounds makes them candidates for the design of miniature electronic components.

Experimental Section

Materials. **1a** and **1b** were prepared as described previously.[1,5]

Syntheses of 2a[FeCl$_4$] and 2b[FeCl$_4$]. A 0.25-g (0.37-mmol) sample of **1** was dissolved in dichloromethane. After the solution was left under nitrogen for 3 days, a black precipitate formed. This was filtered off, washed with CH_2Cl_2, and recrystallized from DMF. Yield: 90 mg (0.08 mmol). Anal. Calcd for 2a[FeCl$_4$], $C_{21}H_{22}Cl_4Fe_5S_6$: C, 28.41; H, 2.50; S, 21.67. Found: C, 28.57; H, 2.66; S, 21.59. Calcd for 2b[FeCl$_4$], $C_{25}H_{30}Cl_4Fe_5S_6$: C, 31.81; H, 3.20; S, 20.38. Found: C, 31.57; H, 3.23; S, 20.38.

Synthesis of 2[PF$_6$]$_2$. This compound was synthesized from **2**[FeCl$_4$] by a metathesis reaction with KPF_6 in water. **2**[FeCl$_4$] was slurried in water to which an excess of KPF_6 was added. The mixture was stirred thoroughly for some minutes and filtered, and the precipitate was washed successively with small amounts of water, ethanol, and diethyl ether. Recrystallization occurred from acetone–hexane (20:1 v/v) mixtures.

Synthesis of 3[PF$_6$]$_2$. A 250-mg (0.37-mmol) sample of **1a** was stirred in 5 mL of methyl iodide. After 48 h, the reaction was complete. The black precipitate was filtered off and washed with chloroform (yield of 3[I]$_2$ 90%). The product was taken up in water, the solution was filtered, and to the filtrate was added an excess of KPF_6 dissolved in water. The formed precipitate was filtered off and washed with water, ethanol, and diethyl ether. Recrystallization occurred from acetone–hexane mixtures. Yield: 200 mg (0.2 mmol).

Synthesis of 4[PF$_6$]. A 250-mg (0.37-mmol) sample of **1a** was dissolved in $CHCl_3$, and an excess of MeI (1 mL) was added. After 10 min, diethyl ether was added to the solution and a brown-black precipitate formed. This was filtered off and washed with $CHCl_3$ and diethyl ether, delivering 4[I] (yield 80%). This product was dissolved in water, and an excess of KPF_6 in water was added, forming a precipitate. The black product was filtered off and washed with small amounts of water, ethanol, and diethyl ether. Recrystallization occurred from an acetonitrile–diethyl ether mixture. Yield: 125 mg (0.15 mmol).

Physical Measurements. ^1H NMR spectra were recorded on a Bruker AC 100 spectrometer. Electrochemical measurements were made as described earlier[5,7] using a PAR Model 175 universal programmer and a PAR Model 173 potentiostat.

X-ray Structure Determination of 2b[FeCl$_4$]. Black crystals were grown from a DMF solution. A crystal of dimensions 0.23 × 0.20 × 0.32 mm was selected. The unit cell dimensions were determined from 25 reflections with $10° < \theta < 12°$. Intensity data were collected from 18 484 reflections (complete sphere up to $\theta = 23°$). The structure was determined using vector search methods (ORIENT) on a Fe–Fe vector of 2.7 Å as a model, automatically followed by positioning (TRACOR) and further expansion of the structure (DIRDIF). Least-squares refinement in two blocks (SHELX) converged to $R = 0.047$ ($R_w = 0.048$) for 392 variables and 5859 reflections with $F_o > 6.0\sigma(F_o)$. Standard experimental and computational details and references to ORIENT, TRACOR, DIRDIF, and SHELX (Sheldrick) are given in ref 10. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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Supplementary Material Available: Table A, listing hydrogen atomic parameters, anisotropic temperature factors, bond lengths, and bond angles (6 pages). Ordering information is given on any current masthead page.

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