matographically, as would be expected from an outer-sphere reaction (eq 4b). The (ethanethiolato)chromium(III) complex was purified by cation-exchange chromatography. It exhibited an absorption band at 280 nm, characteristic of a Cr-S MLCT band.[26-29] The chromium to sulfur ratio was determined by ICP/MS to be 1.1:1, consistent with the formula $(H_2O)_5CrSC_2H_5^{2+}$.

The kinetic results for Cr^{2+} were confirmed by an independent method without the use of $ABTS^{2-}$. Flash photolysis of EtSSEt at 266 nm with a Nd-YAG laser generated ethanethiyl radicals in the presence of Cr^{2+}. Product buildup at 280 nm, an absorption maximum for the (ethanethiolato)chromium(III) complex, gave $k_4 = 3.9 \times 10^8$ L mol^{-1} s^{-1}, in satisfactory agreement with the probe method.

The Fe^{2+} reaction with $C_2H_5S^\bullet$ is inferred to proceed by an inner-sphere mechanism, since its rate constant (1.2×10^6 L mol^{-1} s^{-1}) is comparable to that for the reaction of Br_2^- with Fe^{2+} (3.6×10^6 L mol^{-1} s^{-1}), which is known to be an inner-sphere process.[30] The relatively slow substitution rate for Fe^{3+} (ca. 10-10^2 L mol^{-1} s^{-1}) means it can be considered inert on the time scale of the oxidation by ethanethiyl radicals. However, the initial product of the reaction, presumably $(H_2O)_5FeSC_2H_5^{2+}$, was not observed, probably due to low extinction coefficients. Ethanethiol was detected as a final product gas chromatographically.

An outer-sphere mechanism for $V(H_2O)_6^{2+}$ is consistent with the slow ligand substitution of this ion. Attack of $RS^\bullet$ at a trigonal face may provide the site of electron transfer.[31,32] Ethanethiol was detected gas chromatographically.

The flash photolytic method described here may be applied to the study of the biologically significant cysteinyl and glutathionyl radicals without pulse radiolysis. It is particularly suited to the study of thiyl radicals with metal complexes and should prove useful in many inorganic and bioinorganic studies.

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Registry No. $ABTS^{2-}$, 1180-72-9; TMPD, 100-22-1; $EtS^\bullet$, 14836-22-7; EtSSEt, 110-81-6; $Cr(H_2O)_6^{2+}$, 20574-26-9; $V(H_2O)_6^{2+}$, 15696-18-1; $Fe(H_2O)_6^{2+}$, 15365-81-8; $(H_2O)_5CrSC_2H_5^{2+}$, 138541-77-2; $MeCo([14]aneN_4)(H_2O)^{2+}$, 51240-12-1; $EtCo([14]aneN_4)(H_2O)^{2+}$, 111323-55-8; H_2, 1333-74-0; ethanethiol, 75-08-1; cysteine, 52-90-4; glutathione, 70-18-8; cysteine radical, 35772-84-0; glutathione radical, 40055-99-0.

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Synthesis and Structure of Mixed-Ligand Iron-Sulfur Cubane-like Clusters $[(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5]^n$ (n = 0 and 1+)

A number of transition metal clusters have been synthesized and structurally characterized[1,2] which possess M_4S_4 cubic cores with four supporting ligands on each metal. Most, however, carry the same supporting ligands on all metals, and clusters possessing different supporting ligands on a homometallic M_4S_4 core are rare.[3] Recently we reported the synthesis of the mixed-ligand iron-sulfur cubane cluster $(\eta\text{-}C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (**1**) by the reaction of $(\eta\text{-}C_5Me_5)_2Fe_2(CO)_4$, S_8, and PhC≡CPh.[4,5] From the same reaction mixture, we have recently succeeded in the isolation of another mixed-ligand iron-sulfur cluster, $(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$ (**2**), which was less stable than **1**. A cluster similar to **2** but carrying the same supporting ligands, $Cp_4Fe_4S_5$, has been reported by Kubas et al.[7] We now report the structural change which accompanies a onè-electon oxidation of this cluster.

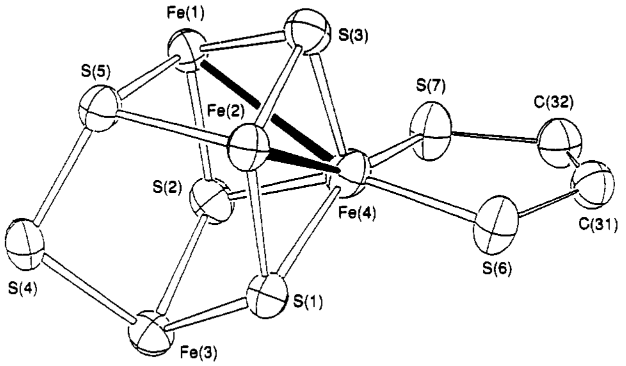
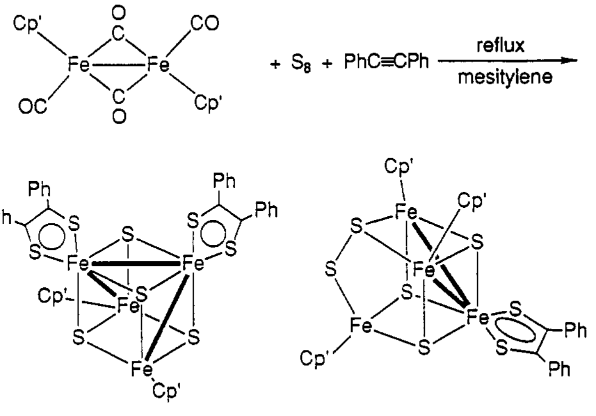


Figure 1. ORTEP drawing of the Fe_4S_5 core of $(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$ (**2**) with a dithiolene chelate ring. Thermal ellipsoids are plotted at the 50% probability level. Selected distances (Å): Fe(1)···Fe(2), 3.300 (1); Fe(1)···Fe(3), 3.769 (1); Fe(1)-Fe(4), 2.716 (1); Fe(2)···Fe(3), 3.760 (2); Fe(2)-Fe(4), 2.725 (1), Fe(3)···Fe(4), 3.307 (2).

The reaction between $(\eta\text{-}C_5Me_5)_2Fe_2(CO)_4$, S_8, and PhC≡CPh in a 1:0.5:1 ratio in refluxing mesitylene for 12 h[8] gave a brown reaction mixture containing **1** and **2** (eq 1). After removal of mesitylene in vacuo, the residue was chromatographed on silica gel which had been deactivated by prior treatment with acetone, since **2** was not stable on commercially available silica gel. By use of the deactivated silica gel, **2** was obtained as dark green crystals in 24% yield[9] together with **1** (41% yield). The single



(1)

1 2

Cp'=η-C5Me5

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(8) In the previous paper, we used the ratio of 1:0.5:2 for these compounds and carried out the reaction in refluxing xylene for 120 h. No significant difference has been found in the products.

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Inorg. Chem. **1992**, *31*, 723-724

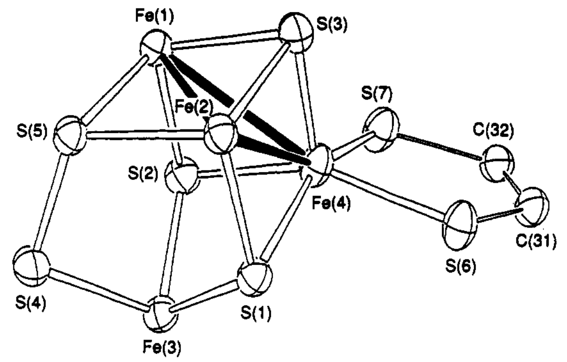

Figure 2. ORTEP drawing of the Fe_4S_5 core of $[(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5]^+$ (3) with a dithiolene chelate ring. Thermal ellipsoids are plotted at the 30% probability level. Selected distances (Å): Fe(1)–Fe(2), 2.736 (2); Fe(1)⋯Fe(3), 3.760 (2); Fe(1)–Fe(4), 2.783 (1); Fe(2)⋯Fe(3), 3.765 (2); Fe(2)–Fe(4), 2.767 (2), Fe(3)⋯Fe(4), 3.047 (2).

crystals used for the X-ray structural analysis were grown by means of layering hexane on a solution of 2 in THF.[10]

The structure of the Fe_4S_5 core of 2 with the dithiolene chelate ring is shown in Figure 1. Three (η-C_5Me_5) ligands coordinate to Fe(1), Fe(2), and Fe(3), while one dithiolene ligand coordinates to Fe(4). The Fe_4S_5 core of 2 consists of four Fe atoms, three μ_3-S ligands, and one μ_3-S_2 ligand. The μ_3-S_2 ligand is located on the opposite side of the core from the dithiolene ligand. It was found that the interatomic separations Fe(1)–Fe(4) (2.716 (1) Å) and Fe(2)–Fe(4) (2.725 (1) Å) were significantly smaller than the other four Fe–Fe distances (3.300 (1)–3.769 (1) Å). The former values are in the range expected for an Fe–Fe single bond. The plane of the dithiolene–Fe(4) chelate ring is nearly coplanar with that containing two Fe–Fe bonds. This phenomenon is also observed in both 1[4] and the monocation salt of 2, $[(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5](PF_6)$ (3) (vide infra). Three Fe atoms are arranged in a V-shaped configuration with the Fe atom having the dithiolene ligand, on Fe(4), at the apex. The coordination mode of μ_3-S_2 to the three iron atoms of 2 and 3 (see Figure 2) is different from that found in $[Cp_4Fe_4S_5]^+$[11] and $[Cp_4Fe_4S_5]^{2+}$.[12] In the former complexes, one of the S_2 sulfur atoms is bonded to two iron atoms, and the other is bonded to the third iron atom. In the latter complexes, the S_2 ligand is bonded to an iron atom in a "side-on" manner, with each of its sulfur atoms bonded to one other iron atom.

The ^1H NMR spectrum of 2 shows characteristically broad signals at δ 7.5 and 6.8 (Ph), 2.8 (two η-C_5Me_5's), and −0.5 ppm (one η-C_5Me_5). These line broadenings and shifts of signals are consistent with the paramagnetic nature of 2 as predicted from the skeletal electron counting[13] (2 has 19 skeletal electrons).

The cyclic voltammogram of 2 exhibits four reversible one-electron redox waves at +1.19, +0.58, −0.14, and −0.90 V vs SCE in CH_2Cl_2 solution containing 0.1 M n-Bu_4NBF_4 as supporting electrolyte. The resting potential was around −0.20 V vs SCE. These results indicate the existence of five discrete species $[(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5]^n$ for which n = 3+, 2+, 1+, 0, and 1−.

The reaction of 2 with 1 equiv of $[Cp_2Fe](PF_6)$ in CH_2Cl_2 afforded the monocation salt 3 in 77% yield.[14] The ORTEP drawing of the Fe_4S_5 core of 3[15] with the dithiolene chelate ring is shown in Figure 2. In the Fe_4S_5 core of 3, there are three Fe–Fe bonds, which combine three iron atoms (Fe(1), Fe(2), and Fe(4)). The remaining three Fe⋯Fe distances are longer than 3.0 Å, suggesting the absence of Fe–Fe bonds. The structural change of the Fe_4S_5 core of 2 which accompanies one-electron oxidation, in particular the increase in the total Fe–Fe bond order resulting from bond formation between Fe(1) and Fe(2), strongly suggests that the electron was removed from a metal-based antibonding orbital.

Supplementary Material Available: Tables of crystal data, atomic positional and thermal parameters, and bond distances and bond angles and ORTEP diagrams for 2 and 3 (32 pages); listings of observed and calculated structure factors for 2 and 3 (84 pages). Ordering information is given on any current masthead page.

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(9) Anal. Calcd for $C_{44}H_{55}Fe_4S_7$: C, 51.22; H, 5.37. Found: C, 51.27; H, 5.34. MS (FAB, m-nitrobenzylalcohol matrix, Xe): m/z 1031 (M^+). ^1H NMR (200 MHz, $CDCl_3$): δ 7.5 (6 H, br, $W_{1/2}$ = 9 Hz, Ph), 6.8 (4 H, br, $W_{1/2}$ = 10 Hz, Ph), 2.8 (30 H, br, $W_{1/2}$ = 21 Hz, Me), −0.5 (15 H, br, $W_{1/2}$ = 46 Hz, Me).

(10) Crystal data for 2·THF: $C_{48}H_{63}Fe_4OS_7$, F_w = 1103.9, monoclinic, space group $P2_1/c$, a = 17.302 (3) Å, b = 17.639 (2) Å, c = 17.099 (3) Å, β = 102.99 (3)°, V = 5085 (1) $Å^3$, Z = 4, D_c = 1.44, D_m = 1.44 g cm^{-3}, μ (Mo Kα) = 14.56 cm^{-1}. Diffraction data were collected with the ω–2θ scan mode, at 21 °C. The structure was solved by the standard heavy atom method. Block-diagonal least-squares refinement led to convergence with a final R value of 0.058 for 8164 reflections $[|F_o| > 3\sigma(F_o)]$ out of 15293 measured (3 ° < 2θ < 60°).

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(14) Anal. Calcd for $C_{50}H_{67}F_6Fe_4O_2PS_7$ (3·2$(CH_3)_2CO$): C, 46.45; H, 5.22. Found: C, 46.27; H, 5.01. MS (FAB, m-nitrobenzylalcohol matrix, Xe): m/z 1031 (M^+). ^1H NMR (200 MHz, $CDCl_3$): δ 7.8–7.5, 7.2–6.7 (10 H, m, Ph), 3.6 (30 H, br, $W_{1/2}$ = 52 Hz, Me), −1.7 (15 H, br, $W_{1/2}$ = 67 Hz, Me).

(15) Crystal data for 3·2$(CH_3)_2CO$: $C_{50}H_{67}F_6Fe_4O_2PS_7$, F_w = 1292.9, triclinic, space group $P\bar{1}$. a = 14.112 (4) Å, b = 17.712 (3) Å, c = 13.325 (4) Å, α = 108.08 (2)°, β = 114.74 (3)°, γ = 84.00 (2)°, V = 2874 (1) $Å^3$, Z = 2, D_c = 1.49, D_m = 1.49 g cm^{-3}, μ (Mo Kα) = 13.44 cm^{-1}. Diffraction data were collected with the ω–2θ scan method, at 21 °C. The structure was solved by direct methods. Block-diagonal least-squares refinement led to convergence with a final R value of 0.066 for 9747 reflections $[|F_o| > 6\sigma(F_o)]$ out of 16771 measured (3° < 2θ < 60°).

Synthesis of Cationic Ruthenium Thiobenzaldehyde Complexes through β-Hydride Abstraction[1]

The heteroaldehydes RHC═E (E = S, Se, Te) are classical examples of the instability of π bonds involving heavier elements.[2] Their pronounced tendency to oligomerize can be suppressed either by introducing sterically demanding groups R[3] or by coordinating to a transition metal.[4-8] Complexes of thioaldehydes are particularly interesting since they offer the opportunity to selectively tailor the reactivity of the C═S function.[5] Two fairly general syntheses of heteroaldehyde complexes have been developed in

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