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# Synthesis, Structure, and Properties of a Binuclear Iron−Thiolate Complex with a *trans*-Disulfur Bridge: A Structural Isomer of the [$Fe_2S_2$] Core of 2-Fe Ferredoxins

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The biological [Fe−S] centers which have been structurally characterized fall into three major classes: [2Fe−2S], [3Fe−4S], and [4Fe−4S].[1] In each of these clusters, the iron atoms are linked together by $\mu_2$- or $\mu_3$-$S^{2-}$ bridging atoms. The remaining sites of the tetrahedrally coordinated [$FeS_4$] units are generally supplied by cysteinyl ligands. The structure and properties of the active site of many [Fe−S] enzymes remain unknown. There are strong indications that there are [Fe−S] centers (for example, the H-clusters of Fe hydrogenase and the P-clusters of nitrogenase) that are significantly different from the "classical" iron−sulfur structures described above.[2]

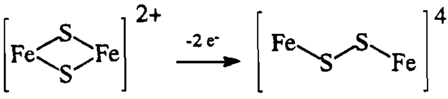
We report the synthesis, structure, and electronic properties of $[R_4N]_2[Fe_2(\mu\text{-}S_2)(P(o\text{-}C_6H_4S)_3)_2]$ (**1**). Notably, this compound contains a *trans*, end-on disulfur [Fe−S−S−Fe] bridging unit and thus is a structural isomer of the familar $[Fe(\mu_2\text{-}S)_2Fe]$ core which is found in [2Fe−2S] ferredoxins.

Compound **1** is formed through two synthetic pathways: (1) a self-assembly pathway starting with Fe(II) and $S^{2-}$ (eq 1); (2) a ligand replacement reaction starting with $[Fe_2S_2Cl_4]^{2-}$ which contains the $[Fe(\mu_2\text{-}S)_2Fe]$ core[3] (eq 2).

$$2FeCl_2{\cdot}4H_2O + 2P(o\text{-}C_6H_4SLi)_3 + 2NaSH + 2LiOMe + 2Pr_4NBr \rightarrow [Pr_4N]_2[Fe_2(\mu\text{-}S_2)(P(o\text{-}C_6H_4S)_3)_2] \quad \text{39\% yield} \tag{1}$$

$$[Et_4N]_2[Fe_2S_2Cl_4] + 2P(o\text{-}C_6H_4SLi)_3 \rightarrow [Et_4N]_2[Fe_2(\mu\text{-}S_2)(P(o\text{-}C_6H_4S)_3)_2] \quad \text{43\% yield} \tag{2}$$

In reaction 2, the $[Fe_2S_2]^{2+}$ core in the reactant is transformed to an $[FeS-SFe]^{4+}$ core.



The mechanism by which two electrons are lost is not understood at this time. However, the low yield of the product (43%) suggests that a reduced iron−sulfur species is also produced but not isolated.

The X-ray structural analysis (Figure 1) of **1**[7] reveals a centrosymmetric dimer in which the iron centers are in a trigonal bipyramidal arrangement with the thiolate atoms in the equatorial plane and the phosphine and [S−S] bridge unit in the axial position. The Fe−thiolate and Fe−phosphine distances are 2.30 Å (average) and 2.212(2) Å, respectively, while the Fe−$S_2$ distance is 2.191(3) Å. DeVries and Davison have previously shown that $[P(o\text{-}C_6H_4S)_3]^{3-}$ coordinates to Tc(III) to form a trigonal bipyramidal complex, $\{Tc[P(o\text{-}C_6H_4S)_3](CNR)\}$.[5] We have shown that the $[P(o\text{-}C_6H_4S)_3]^{3-}$ ligand forms dimeric [Ni(II)−Ni(II)] and [Ni(II)−Ni(III)] products, having square planar and square pyramidal geometries, respectively.[8]

The distance of the [S−S] bond in **1** is 2.046(4) Å, which can be compared to that in free $S_2$ (1.887 Å)[9] and $H_2S_2$ (2.055 Å).[10] Dimeric iron complexes with disulfur bridges have already been reported.[11] Significantly, all of these compounds posses a *cis*, end-on bridging coordination of the [Fe−S−S−Fe] unit in which the iron atoms are also linked to one or more other bridging ligands.[12] Of particular note is the recent report of $[\{Fe(2,2'\text{-(ethylenedithio)bis(benzenethiolate)})\}_2(\mu\text{-}S_2)]$ in which two bridging thiolates support the *cis*, end-on $S_2$ group.[11a] There are several examples of non-iron disulfur complexes which have the planar, *trans*, end-on bridging coordination. These include $[(CN)_5Co(S_2)Co(CN)_5]^{6-}$,[13] $[(NH_3)_5Ru(S_2)Ru(NH_3)_5]^{4-}$,[14] $[CpRu(PR_3)_2]_2(\mu\text{-}S_2)^{2+}$,[15] [$\mu$-$S_2$\{Ru(PPh$_3$)(1,2-bis((2-mercaptophenyl)-

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[3] Synthesis of $[Et_4N]_2[Fe_2(\mu\text{-}S_2)(P(o\text{-}C_6H_4S)_3)]$ (**1**) by reaction 2 $\{P(o\text{-}C_6H_4SH)_3$ = tris(2-mercaptophenyl)phosphine\} (all procedures were done under a dinitrogen atmosphere): An $CH_3CN$ solution (50 mL) of $P(o\text{-}C_6H_4SLi)_3$[4,5] (0.50 mmol) was added via cannula to an $CH_3CN$ (50 mL) solution of $[Et_4N]_2[Fe_2S_2Cl_4]$[6] (0.14 g; 0.25 mmol). The green reaction mixture was filtered through Celite and concentrated. Upon standing, the solution deposited black crystals of **1** (0.125 g; 43% yield). The product can be recrystallized from hot acetonitrile. $^1H$ NMR ($d^6$-DMSO): thiolate, −9.78 $\delta$ (6H), 5.29 (6H), 5.63 (6H), 7.70 (6H); cation, 1.12 (24H), 3.09 (16H). Electronic spectrum (DMF) [$\lambda_{nm}$ ($\epsilon_M$)]: 360 nm (21 875 $M^{-1}$ $cm^{-1}$), 420 (16 667), 520 (7750), 640 (5625), 980 (8125), 1140 (6275), 1260 (3750).

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[7] Crystal data for $[Pr_4N]_2[Fe_2(\mu\text{-}S_2)(P(o\text{-}C_6H_4S)_3)]{\cdot}4CH_3CN$: triclinic, $P\bar{1}$ (No. 2), $a$ = 13.946(6) Å, $b$ = 14.539(5) Å, $c$ = 10.131(4) Å, $\alpha$ = 98.05(2)°, $\beta$ = 109.64(2)°, $\gamma$ = 102.24(2)°, $V$ = 1840(3) Å$^3$, $Z$ = 1. A total of 3400 unique reflections with $I > 3\sigma(I)$ were refined to $R$ = 0.059 and $R_w$ = 0.071. $[Et_4N]_2[Fe_2(\mu\text{-}S_2)(P(o\text{-}C_6H_4S)_3)]$ displayed a similar structure.

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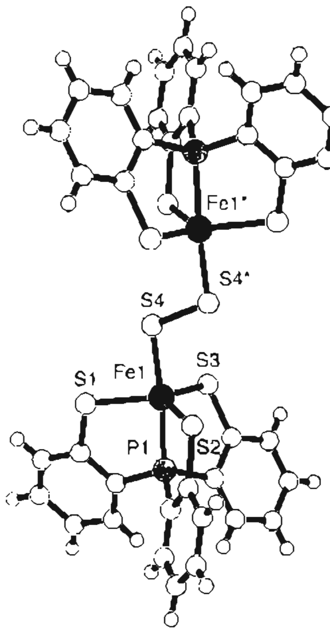

**Figure 1.** Structural diagram of $[Fe_2(\mu\text{-}S_2)(P(o\text{-}C_6H_4S)_3)_2]^{2-}$ (anion of **1**). Selected bond distances (Å) and angles (deg): Fe−S1 = 2.284(3); Fe−S2 = 2.272(2); Fe−S3 = 2.351(3); Fe−S4 = 2.191(3); Fe−P1 = 2.212(2); S−S′ = 2.046(4); Fe−Fe′ = 5.455(3); P1−Fe1−S4 = 175.7(1); P1−Fe1−S1 = 84.35(9); S1−Fe1−S2 = 122.27(9); S1−Fe1−S3 = 114.6(1); S1−Fe−S4 = 91.61(9); S2−Fe1−S3 = 119.97(9); Fe1−S4−S4′ = 110.8(1).

thio)ethane)}$_2$].[16] $[CpMn(CO)_2]_2(\mu\text{-}S_2)$,[17] and $K_2Re_3S_6$.[18] The bond distance of the $[S_2]$ unit in **1** is in the range (1.97−2.09 Å) of the S−S distances found for these examples of *trans*, end-on $S_2$ units.[12−18]

The UV−vis−near-IR spectrum of compound **1** is shown in Figure 2.[3] The deep green complex shows intense absorptions in the visible and the near-IR that are in the same range as other $S_2$-bridged systems: [{Fe(2,2′-(ethylenedithio)bis(benzenethiolate))}$_2(\mu\text{-}S_2)$],[11a] [{Ru(PPh$_3$)(1,2-bis((2-mercaptophenyl)thio)ethane}$_2(\mu\text{-}S_2)$],[16] and $[CpRu(PR_3)_2(\mu\text{-}S_2)][SbF_6]_2$.[15] The independence of these absorptions on the metal and the other ligands suggests that these bands involve the $[M_2S_2]$ core. Sellmann[11a,16] has assigned the characteristic absorptions in the visible and near-IR regions of the spectrum as $\pi-\pi^*$ transitions of the 4-center−6-electron $[M_2S_2]$ chromophore.

The Mössbauer spectra recorded at 4.2 K in applied magnetic fields of 450 G and 5 T show that **1** is diamagnetic and both irons in **1** are identical. The isomer shift of 0.35 mm/s and the quadrupole splitting of 2.04 mm/s indicate that the irons are consistent with low-spin Fe(II) or antiferromagnetically coupled Fe(III). The shifts in the resonances in the $^1H$ NMR of **1** rules out a low-spin Fe(II).[3] The lack of a suitable monomeric analog prevents a more definitive interpretation of the Mössbauer spectrum. However, an $[Fe^{III}(S_2^{2-})Fe^{III}]$ redox state would seem to be the most reasonable for **1** rather than the formalism of $[Fe^{II}(S_2^{0})Fe^{II}]$.[11a]

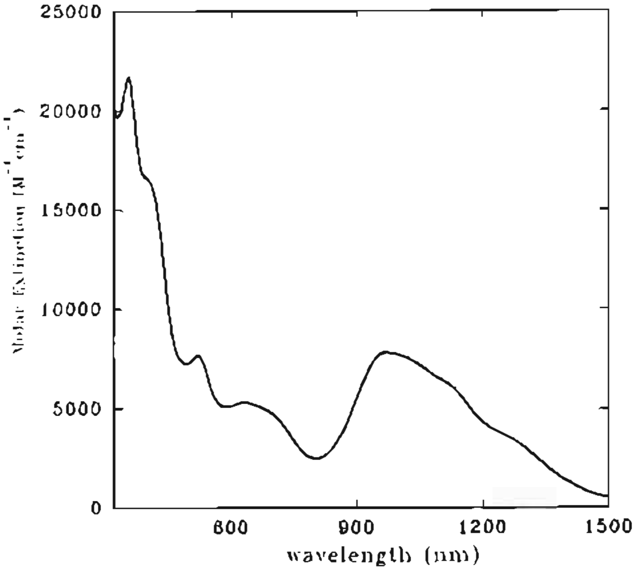

**Figure 2.** Electronic spectrum of **1**.[3]

Electrochemical studies show that $[Et_4N]_2[Fe_2(\mu\text{-}S_2)(P(o\text{-}C_6H_4S)_3)_2]$ undergoes two one-electron quasi-reversible reductions at −1.0 and −1.60 V (vs SCE) to produce complexes containing an $[Fe^{II}Fe^{III}]$ center and an $[Fe^{II}Fe^{II}]$ center, respectively. The complex also undergoes irreversible oxidations at −0.44, −0.12, and +0.26 V, possibly attributable to disulfide oxidations.

While the nature of the electronic transitions is not totally clear, the structural and spectroscopic data indicate that the [FeSSFe] core contains two Fe(III) atoms linked together by disulfide. The near-IR transition would be the signature of an $[Fe-S-S-Fe]^{4+}$ unit in a biological system. It is possible that the existence of such a biological species has been over looked since the near-IR region of the spectrum of biological molecules is not routinely measured. The indication of a $S_2$ group in the P-clusters of nitrogenase provides further impetus for the study $Fe_xS_2$ complexes.[2c]

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**Supplementary Material Available:** Tables of crystallographic parameters, atomic coordinates, thermal parameters, and bond distances and angles for **1** (7 pages). Ordering information is given on any current masthead page.

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