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SYNTHESIS AND CRYSTAL STRUCTURE OF $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2\text{S}_4](\text{PF}_6)_2$

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Abstract The title compound was synthesized by electrochemical oxidation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2\text{S}_4$ and its X-ray crystal structure was determined. A $\mu_2\text{-S}_2$ ligand is converted to a $\mu_2\text{-}\eta^2\text{-S}_2$ ligand by the oxidation.

Keywords: Crystal structure, electrochemical oxidation

The μ -disulfido ligands in the complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2\text{S}_4$ (1) take different coordination modes.¹ One of them lies perpendicular to and the other parallel to the Fe-Fe axis (designated to $\mu_2\text{-}\eta^2\text{-S}_2$ and $\mu_2\text{-S}_2$, respectively). Many other complexes having the formula $\text{Cp}'_2\text{M}_2\text{S}_4$ (Cp' = substituted cyclopentadienyl) have been known, the structure varying with the change of metals. The diversity of the structures seems to depend on the number of valence electrons in the M_2S_4 core. Therefore the relationship between the redox behavior and the structure of such type of complexes is intriguing.

A cyclic voltammogram of 1 exhibits a quasi-reversible one-electron redox wave in CH_3CN containing $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NBF}_4$ ($E_{pa} = 0.30$, $E_{pc} = 0.19 \text{ V vs. SCE}$), which indicates the formation of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2\text{S}_4]^+$. The bulk oxidation of 1 at $+0.30 \text{ V vs. SCE}$ in CH_3CN containing NH_4PF_6 interestingly gave the title compound 2, a two-electron oxidation product.

The X-ray single crystal structure of 2 was determined: Monoclinic with the space group of $P2_1/a$; the lattice constants are $a = 9.704(1)$, $b = 17.953(3)$, $c = 8.432(1) \text{ \AA}$, $\beta = 95.40(4)^\circ$, $Z = 2$. Final R value was 0.052 for 5402 unique reflections with

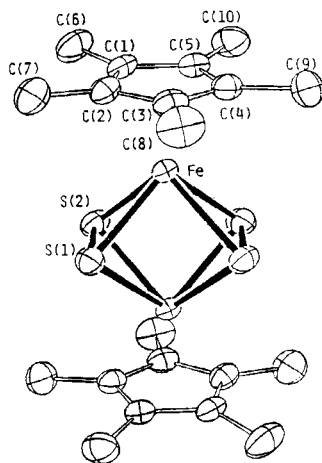


FIGURE 1. Molecular structure of 2.

$$|F_o| > 3\sigma(|F_o|).$$

The complex has a center of symmetry between Fe atoms. The configuration of Fe_2S_4 core changes remarkably by the oxidation: The $\mu_2\text{-S}_2$ ligand is converted to a $\mu_2\text{-}\eta^2\text{-S}_2$ ligand. The Fe_2S_4 core in 2 conforms to a distorted octahedron. Both of the disulfido ligands lie on the plane almost perpendicular to the Fe-Fe axis. This is the first example of $\text{Cp}'\text{M}_2\text{S}_4$ type complex with two $\mu_2\text{-}\eta^2\text{-S}_2$ ligands. All the Fe-S lengths range between 2.276(1) and 2.288(1) Å, and almost equal to Fe-S($\mu_2\text{-}\eta^2\text{-S}_2$) bond lengths in 1. The S-S bond length in 2 is 1.983(1) Å, and belongs to the shortest ones among the related disulfido complexes. The $\text{Fe}\cdots\text{Fe}$ interatomic distance is 2.857(1) Å, which suggests the absence of Fe-Fe bond.

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