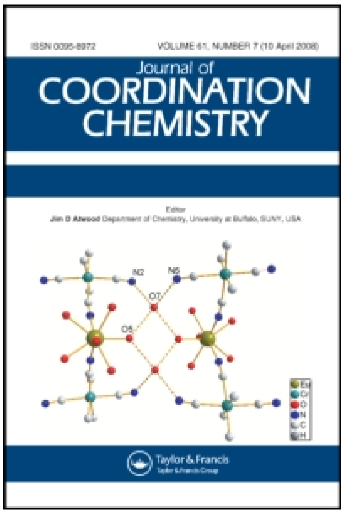

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SYNTHESIS AND CRYSTAL STRUCTURE OF $[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4](PF_6)_2$

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Abstract The title compound was synthesized by electrochemical oxidation of $(\eta^5\text{-}C_5Me_5)_2Fe_2S_4$ 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 $(\eta^5\text{-}C_5Me_5)_2Fe_2S_4$ (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 $Cp'_2M_2S_4$ (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 mol dm^{-3} Bu_4NBF_4 (E_{pa} = 0.30, E_{pc} = 0.19 V *vs.* SCE), which indicates the formation of $[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4]^+$. The bulk oxidation of 1 at +0.30 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) Å, β = 95.40(4)°, Z = 2. Final R value was 0.052 for 5402 unique reflections with

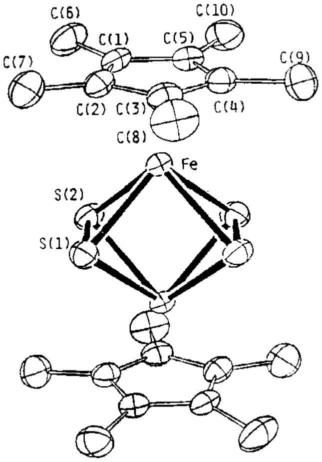

FIGURE 1. Molecular structure of **2**.

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

The complex has a center of symmetry between Fe atoms. The configuration of Fe_2S_4 core changes remarkably by the oxidation: The μ_2-S_2 ligand is converted to a μ_2-η^2-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 $Cp'M_2S_4$ type complex with two μ_2-η^2-S_2 ligands. All the Fe-S lengths range between 2.276(1) and 2.288(1) Å, and almost equal to Fe-S(μ_2-η^2-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 Fe···Fe interatomic distance is 2.857(1) Å, which suggests the absence of Fe-Fe bond.

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