Structural Change accompanying Electrochemical Oxidation of $[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4]$ to $[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4](PF_6)_2$

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Electrochemical oxidation of $[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4]$ in MeCN containing NH_4PF_6 affords $[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4](PF_6)_2$ in which a bidentate $\mu\text{-}S_2$ ligand in the parent complex is converted to a doubly bidentate $\mu\text{-}S_2$ ligand; the structure of the resulting Fe_2S_4 core can be described as a distorted octahedron, as shown by an *X*-ray crystal structure determination.

Neutral complexes of the type $[(cp)_2M_2S_4]$ (cp = cyclopentadienyl or substituted cyclopentadienyl) have been synthesised for M = V, Cr, Mo, W, Fe, Ru, and Co.[1—4] These complexes, whose structures depend on the nature of the transition metals, exemplify an important system for understanding the relationship between electron count and structure and the nature of complexes with disulphur ligands. However, the relationship between the redox behaviour of $[(cp)_2M_2S_4]$ and their structures has not been investigated. This prompted us to investigate the electrochemical behaviour of $[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4]$ (**1**) in which two μ-disulphur ligands adopt different co-ordination modes:[5] one lies perpendicular to and the other parallel to the Fe–Fe axis.

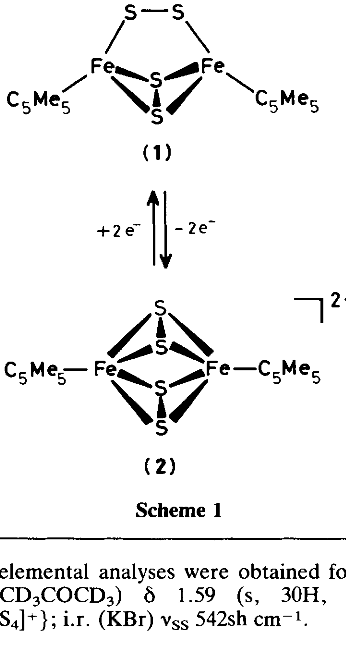
Cyclic voltammetric (c.v.) and thin-layer coulometric experiments on (**1**) in MeCN containing 0.1 mol dm^{-3} $Bu^n_4NBF_4$ show that (**1**) undergoes quasi-reversible one-electron oxidation [E_{pa} +0.30, E_{pc} +0.19 V *vs.* saturated calomel electrode (S.C.E.); equation (1)]. The bulk oxidation

$$[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4]^+ + e^- \rightleftharpoons [(\eta^5\text{-}C_5Me_5)_2Fe_2S_4] \quad (1)$$

$$2[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4]^+ \rightleftharpoons [(\eta^5\text{-}C_5Me_5)_2Fe_2S_4] + [(\eta^5\text{-}C_5Me_5)_2Fe_2S_4]^{2+} \quad (2)$$

of (**1**) was carried out at +0.30 V *vs.* S.C.E. in MeCN containing 0.1 mol dm^{-3} NH_4PF_6. To our surprise, the dark green diamagnetic dication salt $[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4](PF_6)_2$ (**2**) rather than the monocation salt was isolated in 72% yield after removal of solvent and washing with water.† Thus, the bulk electrolysis of (**1**) gave the two-electron oxidation product, whereas c.v. experiments showed the formation of $[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4]^+$. This indicates that the relatively slow disproportionation reaction (2) occurs. Reaction (2) does not proceed appreciably on the c.v. time scale. This fact is further supported by spectroelectrochemical studies of (**1**) and (**2**) using an optically transparent thin-layer electrode. Furthermore, e.s.r. measurements at 77 K demonstrated the formation of paramagnetic species for a solid solution (MeCN–MeOH) containing equimolar amounts of (**1**) and (**2**). The ^1H n.m.r. spectrum of a mixture of (**1**) and (**2**) showed a new broad signal at δ *ca.* −11.9 ascribable to the paramagnetic monocation.

The structure of (**2**) was determined by *X*-ray structure



Scheme 1

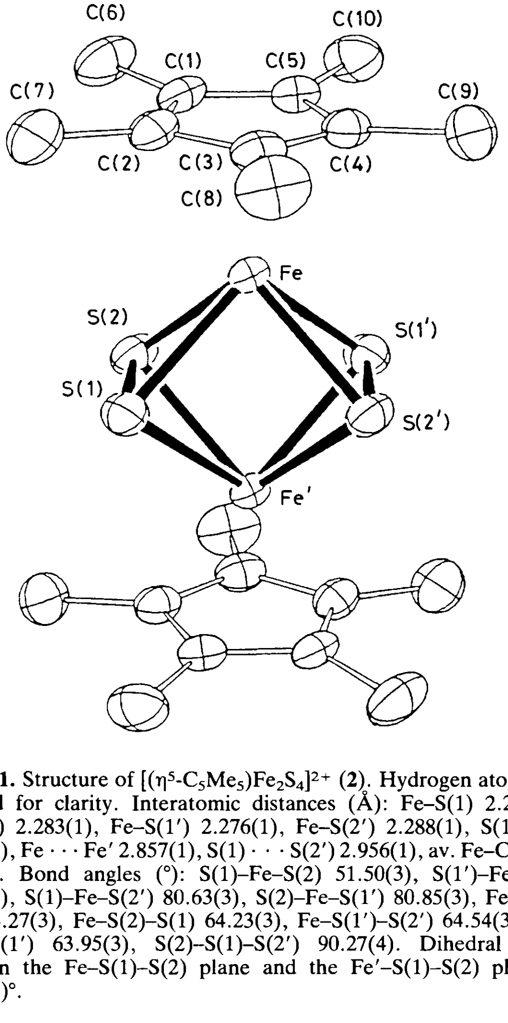


Figure 1. Structure of $[(\eta^5\text{-}C_5Me_5)Fe_2S_4]^{2+}$ (**2**). Hydrogen atoms are omitted for clarity. Interatomic distances (Å): Fe–S(1) 2.282(1), Fe–S(2) 2.283(1), Fe–S(1′) 2.276(1), Fe–S(2′) 2.288(1), S(1)–S(2) 1.983(1), Fe ··· Fe′ 2.857(1), S(1) ··· S(2′) 2.956(1), av. Fe–C(1—5) 2.10(3). Bond angles (°): S(1)–Fe–S(2) 51.50(3), S(1′)–Fe–S(2′) 51.51(3), S(1)–Fe–S(2′) 80.63(3), S(2)–Fe–S(1′) 80.85(3), Fe–S(1)–S(2) 64.27(3), Fe–S(2)–S(1) 64.23(3), Fe–S(1′)–S(2′) 64.54(3), Fe–S(2′)–S(1′) 63.95(3), S(2)–S(1)–S(2′) 90.27(4). Dihedral angle between the Fe–S(1)–S(2) plane and the Fe′–S(1)–S(2) plane is 88.06(3)°.

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† Satisfactory elemental analyses were obtained for (**2**); ^1H n.m.r. (200 MHz; CD_3COCD_3) δ 1.59 (s, 30H, Me); *m/z* 510 $\{[(C_5Me_5)_2Fe_2S_4]^+\}$; i.r. (KBr) ν_{SS} 542sh cm^{-1}.

analysis.‡ The complex has a centre of symmetry between the Fe atoms (Figure 1). A dramatic configurational change of the Fe_2S_4 core occurs upon oxidation (Scheme 1). The geometry of the Fe_2S_4 core in (**2**) is a distorted octahedron. Both the disulphur ligands lie in a plane almost perpendicular to the Fe–Fe axis. This is the first example of a $[(cp)_2M_2S_4]$ type complex with two doubly bidentate μ-S_2 ligands. The S–S bond length [1.983(1) Å] in (**2**) is the shortest for a disulphur ligand in $[(cp)_2M_2S_4]$ type complexes.§ The Fe $\cdots$ Fe′ interatomic distance is significantly shorter (0.67 Å) than that in (**1**), but its length, 2.857(1) Å, still suggests the absence of an Fe–Fe bond. It should be noted that (**2**) is isoelectronic with $[(\eta^5\text{-}C_5Me_5)_2Mn_2S_4]$ whose structure has not been determined.[1]

The chemical oxidation of (**1**) has been examined. When a suspension of (**1**) was stirred in hexane open to the air, a brown precipitate was formed. Two major products, the reddish brown (**3**) and the greenish brown (**4**), were separated chromatographically from this precipitate. Species (**3**) was tentatively assigned the structure $[(\eta^5\text{-}C_5Me_5)_2Fe_2(S_2)(SO_2)]$.¶ When (**3**) was allowed to react with air, complex (**4**), which has not yet been characterised, was formed.

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‡ *Crystal data*: $C_{20}H_{30}F_{12}Fe_2P_2S_4$, M = 800.34, monoclinic, space group $P2_1/a$, a = 9.704(1), b = 17.935(3), c = 8.423(1) Å, β = 95.40(4)°, U = 1459.5(4) Å^3, Z = 2, D_c = 1.82, D_m = 1.82 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 15.0 cm^{-1}. Diffraction data were collected in the ω–2θ scan mode, at 23 °C. The structure was solved by the heavy-atom method. Block-diagonal least-squares refinement converged at an R value of 0.052 for 5402 unique reflections $[|F_o| > 3\sigma(|F_o|)]$ out of 9609 measured ($3° < 2\theta < 80°$). Atomic co-ordinates, bond lengths and angles, thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The shortest reported bond length for doubly bidentate μ-S_2 is 1.956(2) Å in $[(\eta^5\text{-}C_5H_4Me)_2V_2S_5]$.[6]

¶ *Spectroscopic data* for (**3**): m/z 510 (M^+); i.r. (KBr) ν_{SO} 1225s, 1212s, and 1008s cm^{-1}; ν_{SS} 592s and 525w cm^{-1}; ^{1}H n.m.r. (90 MHz; $CDCl_3$) δ 1.64 (s, 30H, Me).

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