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Redox behaviour of ferrocene derivatives VII [☆]. Chalcogen-bridged tri- and tetra-nuclear ferrocenes

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Abstract

The electrochemical behaviour of the trinuclear and tetranuclear chalcogen-bridged ferrocenes Fc–E–(fc)–E–Fc and Fc–E–(fc)–E–E–(fc)–E–Fc (Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$– (ferrocenyl); fc = –$(\eta^5\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4)$– (1,1'-ferrocenediyl); E = S, Se or Te) has been studied in dichloromethane solution. In the trinuclear complexes, the expected reversible one-electron oxidation of each ferrocene unit takes place through two nearly overlapping one-electron steps followed by a one-electron process at higher potential. It is assumed that the first two-electron step corresponds to almost simultaneous electron removals from the terminal, non-interacting ferrocenyl units, whereas the second process is centred on the central ferrocene. In the tetranuclear species, the oxidation occurs through a single two-electron process, again centred on the terminal ferrocenyl units, followed by two separate one-electron steps centred on the inner dichalcogen-bridged diferrocene unit.

Keywords: Iron; Ferrocenes; Electrochemistry

1. Introduction

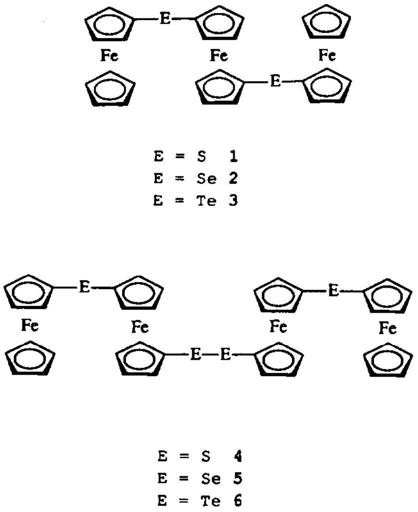
A great deal of research has concerned the well known ability of single ferrocenes to lose reversibly one electron. In contrast, the number of electrochemical investigations on oligo- and poly-ferrocenes decreases rapidly with increasing number of linked ferrocene units present. We report here on the electrochemistry of the chalcogen-bridged tri- and tetra-nuclear ferrocenes illustrated in Scheme 1 [2].

2. Results and discussion

2.1. *Electrochemistry of the trinuclear complexes* 1–3

Fig. 1(a) and 1(b) show the electrochemical response exhibited by **1** in dichloromethane solution. It undergoes two closely spaced anodic steps followed by another oxidation process at higher potential. All the electron transfers exhibit directly associated responses in the reverse scan.

Controlled-potential coulometry at $E_w = +0.6$ V shows that two electrons per molecule are consumed and the original lemon-yellow solution turns brown. On



Scheme 1.

[☆] For Part VI, see Ref. [1].

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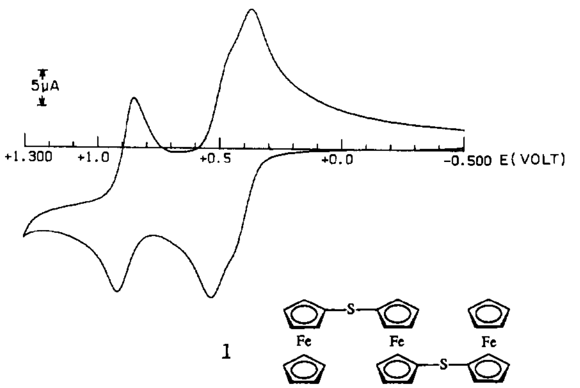

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Fig. 1. Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution containing $[NBu_4]$ $[ClO_4]$ (0.2 mol dm^{-3}) and **1** (9.0×10^{-4} mol dm^{-3}). Scan rate, 0.1 V s^{-1}.

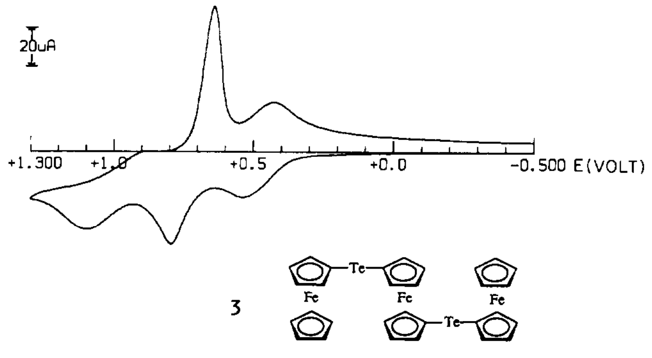

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Fig. 2. Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution containing $[NBu_4][ClO_4]$ (0.2 mol dm^{-3}) and **3** (6.8×10^{-4} mol dm^{-3}). Scan rate, 0.2 V s^{-1}.

exhaustive oxidation at $E_w = +1.0$ V, the colour changes further to yellow-brown. Cyclic voltammograms measured after step-by-step electrolyses as well as reversal coulometric tests show that all three sequential electron removals are chemically reversible. The lack of any blue-green colour typical of iron(III) ferrocenium species in the oxidized products suggests that the HOMO of the present triferrocene molecule is centred mainly on the chalcogen bridge. This is not unexpected in view of the redox behaviour of chalcogena-substituted monoferrocenes [3].

Cyclic voltammetric analysis [4] of the third one-electron anodic process with scan rates between 0.02 and 5.00 V s^{-1} confirms the electrochemical reversibility. The peak-to-peak separation ranges from 59 mV at 0.02 V s^{-1} to 66 mV at 0.2 V s^{-1}, and then increases progressively to 98 mV, probably because of some uncompensated solution resistances. The i_{pc}/i_{pa} ratio is always unity and the current function $i_{pa}/v^{1/2}$ remains constant.

Assignment of the formal electrode potentials of the first two, nearly coupled, one-electron removals was carried out on the basis of the most anodic peak-to-most cathodic peak separation according to the Richardson–Taube method [5], assuming that each one-electron change also displays electrochemically reversible behaviour. For instance, at 0.2 V s^{-1}, this peak-to-peak separation is 140 mV.

A similar redox pattern was exhibited by **2**. The separation between the potentials of the first two electron removals is further less than that of **1**. At a scan rate of 0.2 V s^{-1} it is 94 mV.

The electrochemical response exhibited by **3** (Fig. 2) is puzzling, in that it apparently gives rise to three well separated oxidation steps.

Nevertheless, in macroelectrolysis at $E_w = +0.55$ V the first anodic process again consumes, reversibly, two electrons per molecule. Since the second step manifests electrode adsorption phenomena which are difficult to define, we tentatively assign removal of the third electron to the most anodic process ($E_{pa} = +1.09$ V, $E_{pc} = +0.87$ V). The adsorption processes prevented accurate determination of the chemical stability of $[3]^{3+}$ by controlled-potential electrolysis. In the tellurium-bridged complex **3** the first two electrons are

Table 1

Formal electrode potentials [a] (V vs. SCE) for the consecutive electron-removal steps exhibited by the tri- and tetra-nuclear ferrocene derivatives **1–6** and related molecules

Complex	$E^{0\prime}_{0/+}$	$E^{0\prime}_{+/2+}$	$E^{0\prime}_{2+/3+}$	$E^{0\prime}_{3+/4+}$	Solvent	Reference
1	+0.41	+0.50	+0.89	–	CH_2Cl_2	TW [b]
2	+0.44	+0.49	+0.84	–	CH_2Cl_2	TW [b]
3	+0.46	+0.50	+1.09 [d]	–	CH_2Cl_2	TW [b]
4	+0.46 [c]		+0.75	+0.87	CH_2Cl_2	TW [b]
5	+0.47 [c]		+0.70	+0.82	CH_2Cl_2	TW [b]
6	+0.46 [c,d]		+0.79 [d]	+0.95 [d]	CH_2Cl_2	TW [b]
7	+0.22	+0.44	+0.82	–	CH_2Cl_2/MeCN (1:1)	[6]
8	+0.37	+0.43	+0.68	–	PrCN	[7]
9	+0.16	+0.36	+0.61	+0.89	CH_2Cl_2/MeCN (1:1)	[6]
10	+0.52 [c]		+0.69	+0.82	THF	[7]

[a] For the calculations, see Experimental. [b] This work. [c] Two-electron step. [d] Peak potential value.

removed at practically the same potential. At 0.2 V s^{-1} the peak-to-peak separation is 90 mV.

Table 1 summarizes the redox potentials of the redox changes under discussion, and includes data for the related species **7** and **8** (Scheme 2).

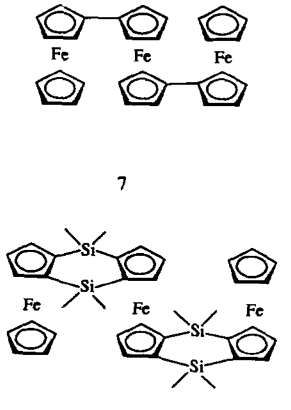
Multiple electron additions to the same molecule are dominated mainly by electronic interaction between the accepting sites and by the resulting electrostatic interactions [5,8]. The greater the electronic communication, the greater is the separation of the redox potentials. For complexes **1–3** we conclude that the small separation of the first two steps indicates that the first two electrons are removed stepwise from the two outer ferrocenyl units. Since the separation of the first two steps decreases in the order $S \geqslant Se > Te$, the shielding ability of the chalcogen bridges towards site interactions decreases in the order $Te \geqslant Se > S$. Finally, the removal of the third electron from the central ferrocene unit is significantly more difficult owing to the double positive charge which is generated by the preceding steps.

In summary, the redox behaviour of complexes **1–3** indicates that the chalcogen bridges substantially quench electronic interaction between the ferrocene–iron centres, in contrast to the high degree of communication found for the directly connected ferrocene units of 1,1'-terferrocene (**7**) [6]. The redox behaviour of the chalcogen-containing complexes **1–3** is more reminiscent of that of the bis(disila)-bridged compound **8** [7].

2.2. Electrochemistry of the tetranuclear complexes 4–6

Fig. 3 shows the cyclic voltammetric response exhibited by the disulphide-bridged complex **4** in dichloromethane solution.

Since controlled-potential coulometry at $E_w = +0.6$ V proves that the first oxidation step reversibly consumes two electrons per molecule, it is evident that the two last electrons are removed separately, corresponding to the two more anodic processes, both of which display directly associated responses in the reverse scan, even though the most anodic one is affected by electrode adsorption phenomena. As in the case of the **1**/[**1**]$^{2+}$ redox change, on exhaustive two-electron removal at the first anodic step, the starting lemon-yellow solution turns golden brown, suggesting a chalcogen-centred process.



Scheme 2.

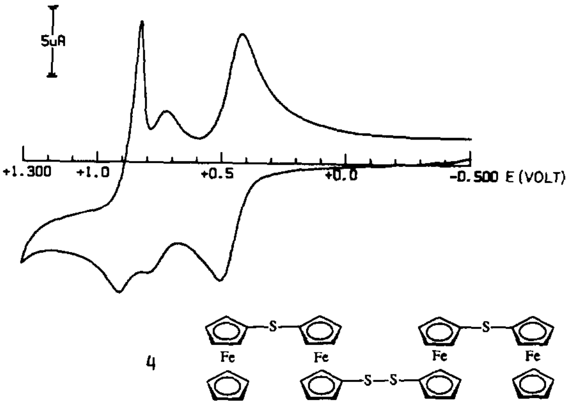


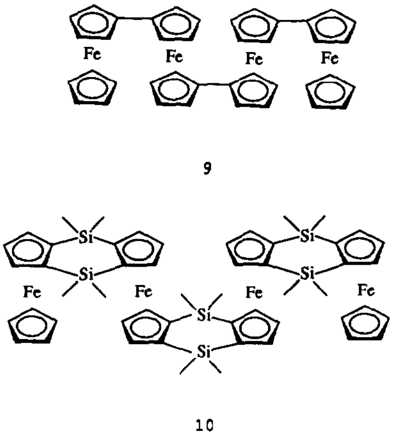
Fig. 3. Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution containing $[NBu_4][ClO_4]$ (0.2 mol dm^{-3}) and **4** (4.5×10^{-4} mol dm^{-3}). Scan rate, 0.1 V s^{-1}.

Analysis of the cyclic voltammograms of the dependence of the first single-stepped two-electron oxidation on scan rate shows that the peak-to-peak separation increases progressively from 72 mV at 0.02 V s^{-1} to 302 mV at 5.00 V s^{-1}, that the i_{pc}/i_{pa} ratio is constant (unity) and that the current function $i_{pa}/v^{1/2}$ remains constant. These data are diagnostic of two one-electron oxidation processes possessing some electrochemical reversibility and occurring at the same formal electrode potential. Again, the large peak-to-peak separation at high scan rates is probably due to uncompensated solution resistances.

The same redox profile is exhibited by the diselenide-bridged complex **5**. In contrast, in the ditelluride-bridged analogue **6**, all three anodic steps suggest chemical complications.

The redox potentials observed for the tetranuclear complexes **4–6** are given in Table 1. The tris(disila)-bridged complex **10** [7] displays a redox behaviour similar to that of the present complexes, whereas 1,1'-quaterferrocene **9** gives rise to four distinct oxidation steps [6] (Scheme 3).

In summary, we conclude that in **4–6** the first two electrons are removed from two non-interacting sites. However, it is well known that binuclear diferrocenyl–chalcogenide and diferrocenyl–dichalcogenide combinations behave as communicating sites, in that they exhibit two separate one-electron oxidations [9–12].



Scheme 3.

Therefore, we speculate that in complexes **4–6** the first two electrons are also withdrawn from the two outer terminal ferrocenyl units.

3. Experimental

The materials and apparatus for electrochemistry have been described previously [3]. All the potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions the one-electron oxidation of ferrocene occurs at $E^{0\prime} = +0.45$ V. The synthesis and spectroscopic characterization of the complexes **1–6** have been reported elsewhere [2].

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