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A Comparative Electrochemical Study of the Iron–Sulfur Cluster Series $Fe_4S_xCp_4$ (x = 4–6) in Benzonitrile

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Abstract

The electrochemical redox behaviour of the compounds $Fe_4S_xCp_4$ (x = 4–6) has been investigated at a platinum electrode in benzonitrile solutions, using pulse polarographic and cyclic voltammetric techniques. In this solvent $Fe_4S_4Cp_4$ exhibits four reversible oxidation reactions, earlier noted in acetonitrile, and a thus far unknown irreversible reduction. $Fe_4S_5Cp_4$ shows two reductions one of which is reversible, and three reversible oxidations. $Fe_4S_6Cp_4$ shows a reversible reduction and two reversible oxidations, and also a third, previously undetected, irreversible one-electron oxidation. Thus far not reported detailed electrochemical data for these compounds (e.g. current functions and reversibility criteria) are measured under the same experimental conditions. In this way a detailed comparative study of the electrochemical properties of the $Fe_4S_xCp_4$ compounds is possible. Some attention is paid to the nature of the decomposition products resulting from the irreversible transitions.

Introduction

The cores of the compounds $Fe_4S_xCp_4{}^n$ (x = 4–6) are built up from iron and inorganic sulfide. As suchlike cores occur at the active sites of a large number of redox proteins [1], one can expect the compounds $Fe_4S_xCp_4$ (x = 4–6) to be able to behave catalytically in electron transfer processes with substrates having various redox potentials.

Earlier electrochemical studies have revealed that the core structure of the cluster compounds $Fe_4S_xCp_4$ (x = 4–6) remains intact in several oxidation states and over a wide potential range [2, 3]. Ferguson and Meyer investigated the redox behaviour of $Fe_4S_4Cp_4$ in acetonitrile [4]. Kubas and Vergamini reported the half-wave potentials of $Fe_4S_5Cp_4$ and $Fe_4S_6Cp_4$ in dichloromethane [5]. In a recent paper we described two new, previously not reported reduction waves shown by $Fe_4S_5Cp_4$ in acetonitrile solution [6].

We intend to study the chemical reactivity of the series $Fe_4S_xCp_4$ (x = 4–6) and its relation with (electronic) structure and electron transfer kinetics. Because differences in structure of these compounds are reflected in their electrochemical properties and because the available data have not been obtained under identical experimental conditions, we have performed a comparative electrochemical study. Benzonitrile turned out to be the most suitable solvent, taking into account the solubility of the compounds, the accessible potential range and the stability of the $Fe_4S_6Cp_4$ series.

Experimental

The cluster compounds $Fe_4S_4Cp_4{}^n$ (n = 0, 1+), $Fe_4S_5Cp_4{}^n$ (n = 0, 2+) and $Fe_4S_6Cp_4$ were synthesized according to literature methods [4, 5]. Tetrabutylammonium hexafluorophosphate was purchased from Fluka (p.a.) and used as received. All solvents were purified according to literature procedures [7]. Benzonitrile (Janssen, 99%) was treated with concentrated HCl, stored over K_2CO_3 and distilled over P_2O_5 under nitrogen. Acetonitrile (Janssen, spectrophotometric grade) was distilled over CaH_2 under nitrogen. Dichloromethane (Merck, reinst) was treated with concentrated H_2SO_4, predried with $CaCl_2$ and distilled over CaH_2 under nitrogen. Toluene was dried over molecular sieves. The voltammograms were recorded at room temperature, unless indicated otherwise. Tetrabutylammonium hexafluorophosphate (TBAH) was used as supporting electrolyte (0.1 mol dm^{-3}). The measurements were made on 0.1 to 1 mM solutions of the electroactive species. All voltammograms were recorded under anaerobic conditions using a conventional three-

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electrode system with a platinum disk working electrode. All potentials reported herein are referred to the ferrocene/ferricinium system measured under the same experimental conditions. The reference electrodes used were a silver wire immersed in a 0.1 M $AgNO_3$ solution in benzonitrile for the measurements in benzonitrile ($E_{1/2}(Fc/Fc^+) = +35$ mV), either an SSCE ($E_{1/2}(Fc/Fc^+) = +398$ mV) or a silver wire immersed in a 0.1 M $AgNO_3$ solution in acetonitrile ($E_{1/2}(Fc/Fc^+) = +50$ mV) for the measurements in acetonitrile and a Ag/AgI electrode (0.05 M Bu_4NI in a 0.4 M Bu_4NClO_4 solution in dichloromethane) [8] for the measurements in dichloromethane ($E_{1/2}(Fc/Fc^+) = +657$ mV). All reference electrodes were separated from the test solution by a Luggin capillary containing the supporting electrolyte. This capillary was positioned as close as possible to the working electrode to minimize iR drop, although also external iR compensation was employed. Cyclic voltammograms were made with a potentiostat PAR Model 173 equipped with an I/E-converter PAR Model 176 and coupled to a universal programmer PAR Model 175. Normal pulse voltammograms were obtained with a polarographic analyzer PAR Model 174A at a scan rate of 5 mV/s with a pulse frequency of 2.0 pulses/s. The recording devices were a Kipp BD91 recorder and a Tectronix 564 B storage oscilloscope.

Results and Discussion

Pulse polarographic and cyclic voltammetric data for the compounds $Fe_4S_xCp_4$ ($x = 4$–6) in benzonitrile solution (0.1 M TBAH) are listed in Table 1. With $(Fe_4S_4Cp_4)(PF_6)$ instead of $Fe_4S_4Cp_4$ as the electroactive compound and $(Fe_4S_5Cp_4)(PF_6)_2$ instead of $Fe_4S_5Cp_4$ the same numerical values and essentially the same *i–E* curves were obtained.

$Fe_4S_4Cp_4$

The four reversible transitions shown by this compound in acetonitrile were initially thought to be one reduction and three oxidations [4]. It is now well established that all four transitions are oxidations [2, 9]. In benzonitrile solution $Fe_4S_4Cp_4$ also exhibits four reversible one-electron oxidations (Table 1 and Fig. 1a). Furthermore, we have been able to observe an irreversible reduction, both in benzonitrile and in acetonitrile solution. This reduction remains irreversible both at lower temperatures (243 K) in a benzonitrile–toluene mixture (the toluene serves to lower the freezing point) and at higher scan rates (20 V/s). The current function i_d/C in PP indicates that one electron is involved. Other criteria, such as the slope of the log-plot in PP and the current function $i_pC^{-1}v^{-1/2}$ in CV (not shown in Table 1), however, point to the involvement of two electrons. These contradictory results are probably caused by the interference of follow up reactions. The irreversibility of the reduction indicates that the $Fe_4S_4Cp_4^{1-}$ species is certainly very unstable at the temperatures considered, and that the cluster structure breaks down immediately after the electron uptake. One of the decomposition products is reoxidized at about 0 mV, as can be seen from the linear sweep voltammograms that were obtained after

TABLE 1. Electrochemical Data for the Series $Fe_4S_xCp_4^n$ ($x = 4$–6) in Benzonitrile (0.1 M Bu_4NPF_6)[a]

Series	Redox couple	Normal pulse voltammetry[b]			Cyclic voltammetry		
		$E_{1/2}$ (V)	Slope[c] (mV)	i_d/C (mA dm^3 mol^{-1})	$E_{1/2}$[d] (V)	E_p[e] (mV)	i_b/i_f
$Fe_4S_4Cp_4^n$	3+/4+	0.925	60	19.6	0.915	90	1.0
	2+/3+	0.42	60	25.1	0.425	65	1.0
	1+/2+	−0.115	60	24.0	−0.11	60	1.0
	0/1+	−0.735	60	23.6	−0.74	60	1.0
	1−/0	−2.015	60	22.7	−2.075[f]		
$Fe_4S_5Cp_4^n$	2+/3+	0.785	60	20.6	0.785	75	1.0
	1+/2+	−0.335	60	22.2	−0.335	60	1.0
	0/1+	−0.65	60	22.7	−0.64	60	1.0
	1−/0	−1.745	65	21.9	−1.72	130	0.8
	2−/1−	−2.175	80	20.9	−2.19[f]		
$Fe_4S_6Cp_4^n$	2+/3+	0.82	65	36.3	0.855[f]		
	1+/2+	−0.17	60	19.0	−0.175	65	1.0
	0/1+	−0.49	60	18.9	−0.49	60	1.0
	1−/0	−1.715	60	19.3	−1.71	85	0.8

[a] Potentials *vs.* the ferrocene/ferricinium couple in the same solvent and electrolyte. $E_{1/2}/Fc/Fc^+) = +35$ mV *vs.* the Ag/Ag$^+$ reference electrode (see 'Experimental'). [b] At a scan rate of 5 mV s^{-1}. [c] Slope of the plot of E *vs.* $\log[(i_d - i)/i]$. [d] At a scan rate of 100 mV s^{-1}; $E_{1/2} = \frac{1}{2}(E_{p,c} + E_{p,a})$. [e] E_p is the cathodic–anodic peak potential separation. [f] Peak potential.

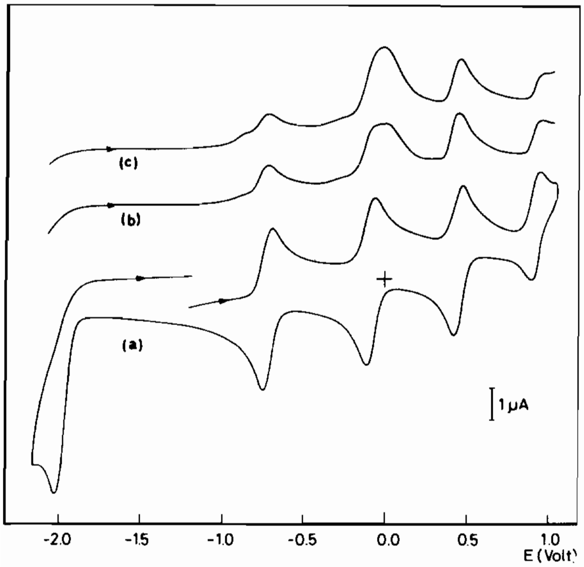

Fig. 1. (a) Cyclic voltammogram of $(Fe_4S_4Cp_4)(PF_6)$ in 0.1 M TBAH benzonitrile solution at a scan rate of 0.1 V s^{-1}. Potentials *vs.* the Fc/Fc^+ couple. (b) Linear sweep voltammogram obtained after the potential had been held at a potential of −2.035 V for 20 s. (c) Linear sweep voltammogram obtained after the potential had been held at −2.035 V for 1 min.

the potential had been kept at −2.035 V for respectively 20 s and 1 min (Fig. 1b and c). Minor peaks, which are possibly due to cluster fragments, appear at −850 and −250 mV.

$Fe_4S_5Cp_4$

In benzonitrile this compound exhibits three reversible one-electron oxidations, one reversible and one irreversible one-electron reduction (Fig. 2a). The same pattern was observed before in acetonitrile [6], except for the 0 → 1− transition being now already reversible at room temperature. For the 0 → 1− transition the ratio i_b/i_f in CV is 0.8 at a scan rate of 100 mV s^{-1}. When the potential is kept at −1.835 V during one minute, cyclic voltammograms are obtained with peaks assignable to small amounts of $Fe_4S_4Cp_4$ and again a large peak at about 0 mV (Fig. 2b). Apparently decomposition of $Fe_4S_4Cp_4^{1-}$ and of $Fe_4S_5Cp_4^{1-}$ leads to the formation of the same species. An explanation for the instability of the mono-anion is that the Fe–Fe bonding interactions are weakened upon reduction and that, as a consequence, one sulfur is expelled from the S_2 group [5, 6].

$Fe_4S_6Cp_4$

Kubas and Vergamini reported that this compound exhibits two reversible one-electron oxidations and one reversible one-electron reduction in dichloromethane [5]. Additionally to these, in benzonitrile a third irreversible oxidation is visible (Fig. 3). This oxidation remains irreversible at higher scan rates (20 V/s). The small re-reduction wave in the backward scan is attributed to a small amount of $Fe_4S_5Cp_4^{3+}$ that has been formed. The current function i_a/C in PP is almost twice as large as for the reversible 0 → 1+ and 1+ → 2+ transitions, and controlled-potential bulk electrolysis at a potential of 900 mV resulted in a current that was still considerable after three equivalents of charge had been passed through the solution. We assume that these contradictory results are caused by complicated decomposition and subsequent oxidation of the reaction products. Upon

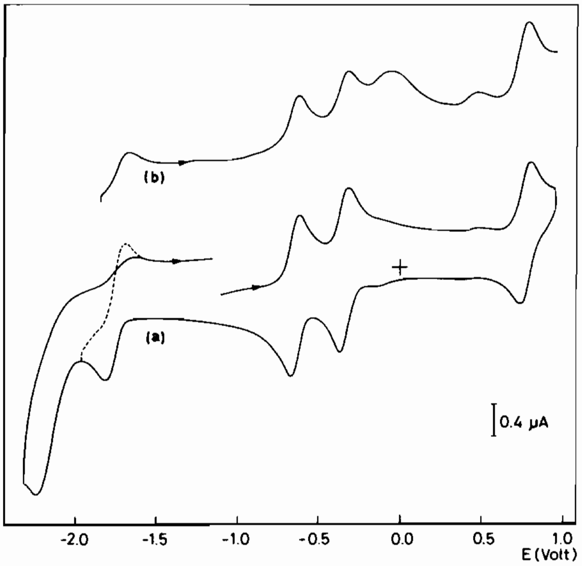

Fig. 2. (a) Cyclic voltammogram of $(Fe_4S_5Cp_4)(PF_6)_2$ in 0.1 M TBAH benzonitrile solution at a scan rate of 0.1 V s^{-1}. Potentials *vs.* the Fc/Fc^+ couple. (b) Linear sweep voltammogram obtained after the potential had been held at −1.835 V for 1 min.

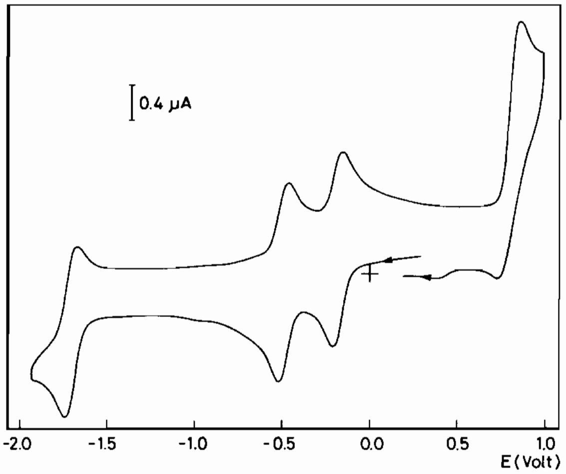

Fig. 3. Cyclic voltammogram of $Fe_4S_6Cp_4$ in 0.1 M TBAH benzonitrile solution at a scan rate of 0.1 V s^{-1}. Potentials *vs.* the Fc/Fc^+ couple.

TABLE 2. A Comparison of the Redox Potentials of the Series $Fe_4S_xCp_4$ (x = 4–6) in Various Solvents as Determined by Using Cyclic Voltammetry (scan rate 100 mV s^{-1})

Compound	Solvent	Reference	Transition					
			2–/1–	1–/0	0/1+	1+/2+	2+/3+	3+/4+
$Fe_4S_4Cp_4$	CH_2Cl_2	this work			−0.73	−0.05	d	d
	CH_3CN [a]	4			−0.73	−0.07	0.48	1.01
	CH_3CN	this work		-2.1^e	−0.73	−0.10	0.43	0.94
	C_6H_5CN	this work		-2.1^e	−0.74	−0.11	0.43	0.92
$Fe_4S_5Cp_4$	CH_2Cl_2 [b]	5			−0.73	−0.43	0.69	
	CH_2Cl_2	this work		−1.76	−0.61	−0.30	d	
	CH_3CN	6	-2.2^e	−1.72	−0.62	−0.33	0.79	
	C_6H_5CN	this work	-2.2^e	−1.72	−0.64	−0.34	0.79	
$Fe_4S_6Cp_4$ [c]	CH_2Cl_2 [b]	5		−1.78	−0.39	−0.09		
	CH_2Cl_2	this work		−1.72	−0.45	−0.14	d	
	C_6H_5CN	this work		−1.71	−0.49	−0.18	0.86^e	

Potentials in volt *vs.* the ferrocene/ferricinium couple (see 'Experimental'). [a] A value $E_{1/2}(Fc/Fc^+)$ = +398 mV *vs.* SSCE was used to convert the original data. [b] A value $E_{1/2}(Fc/Fc^+)$ = +453 mV *vs.* SCE was used to convert the original data. [c] $Fe_4S_6Cp_4$ is insoluble in acetonitrile. [d] Adsorption. See text. [e] Peak potential.

decomposition of $Fe_4S_6Cp_4^{3+}$ both $Fe_4S_4Cp_4^{3+}$ and $Fe_4S_5Cp_4^{3+}$ are formed; in Fig. 3 the small waves at about +450 and +750 mV correspond with the reductions of the two latter species, respectively. When holding the potential at +850 mV for one minute, some unassigned peaks become visible as well. All $Fe_4S_6Cp_4^n$ species are thermally instable, which has been attributed before to steric strain imposed within the molecule [5].

In Table 2 the redox potentials for the series $Fe_4S_xCp_4$ (x = 4–6) in the solvents acetonitrile, benzonitrile and dichloromethane are compared. All potentials are referenced to the ferrocene/ferricinium couple measured under the same experimental conditions [10]. Our own data for $Fe_4S_4Cp_4$ in acetonitrile differ from those reported earlier [4]. We do not have an explanation for this lack of agreement. When looking at our own values the redox potentials in acetonitrile and benzonitrile are the same within experimental error, as could be expected from the dielectric properties of these two solvents which are very much alike [11].

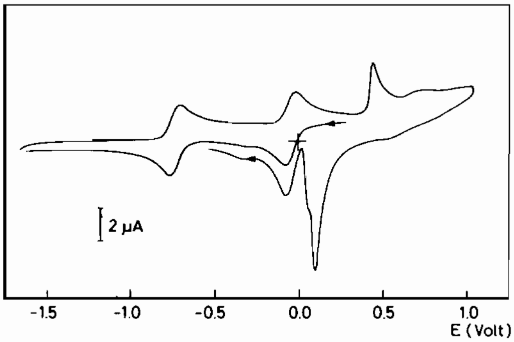

Fig. 4. Cyclic voltammogram of $(Fe_4S_4Cp_4)(PF_6)$ in 0.1 M TBAH dichloromethane solution at a scan rate of 0.1 V s^{-1}. Potentials *vs.* the Fc/Fc^+ couple.

The redox behaviour in dichloromethane is characterized by adsorption phenomena accompanying the 2+ → 3+ transitions. As an illustration a 0.1 V s^{-1} cyclic voltammogram of $(Fe_4S_4Cp_4)(PF_6)$ in dichloromethane is shown in Fig. 4. Recently similar adsorption phenomena were also reported for the iron–selenium cluster $Fe_4Se_4Cp_4$ in dichloromethane [9]. The disagreement between the values found before [5] for $Fe_4S_5Cp_4$ and $Fe_4S_6Cp_4$ in dichloromethane and our own data could well in part be due to the interference of these adsorption effects. When taking into account only our own data a trend is that redox potentials corresponding with the 0 → 1+, 1+ → 2+ and 2+ → 3+ transitions shift slightly in the positive direction in dichloromethane as compared with acetonitrile and benzonitrile whereas the redox potentials corresponding with the 0 → 1– transition shift slightly in the negative direction. All differences $E_{1/2}(CH_2Cl_2) - E_{1/2}(CH_3CN/C_6H_5CN)$, however, are smaller than 100 mV and are comparable to the differences found before for the quasi-solvent independent ferrocene/ferricinium couple [10]. A more comprehensive study of the effects of cluster environment on the redox potentials of these compounds, including an extension of the theoretical model derived before by Kassner and Yang for thiolate-containing cluster compounds is under way [12].

When comparing the $Fe_4S_6Cp_4$ with the $Fe_4S_5Cp_4$ series, it appears that all potentials except for the one corresponding with the 0 → 1– transition are shifted in the negative direction. This indicates that, upon decrease of the number of S_2 groups from two to one, a more easily oxidizable cluster, with enhanced reducing power, is obtained.

TABLE 3. Potential Ranges (in volts) Over Which the $Fe_4S_xCp_4^n$ (x = 4–6) Species Exist in Benzonitrile (*i.e.* the voltage separations between two successive half-wave potentials)

x/n	1–	0	1+	2+	3+	4+
4		1.34	0.63	0.54	0.49	[a]
5	0.47[b]	1.08	0.31	1.12	[a]	
6	[a, b]	1.22	0.32	1.03		

[a]No additional transitions observed before the background limit is reached. [b]Unstable species.

Table 3 lists the voltage separations between successive transitions of the series $Fe_4S_xCp_4^n$ (x = 4–6). A remarkable feature is that the paramagnetic species $Fe_4S_xCp_4^n$ ($x = 5$; n = 1–, 1+ and $x = 6$; n = 1+) exist over much smaller potential ranges than the corresponding diamagnetic ones. This change in half-wave separation implies that more energy is required to remove an electron from a completely filled than from a half-filled HOMO and, presumably, that the molecular orbitals involved in the electron transfers are energetically well separated. This behaviour seems to be related to the presence of the μ-S_2 groups, since in the $Fe_4S_4Cp_4$ series, where only μ-S atoms are present, this feature has disappeared.

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