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Note

Redox behavior of the iron–sulfur cluster $[Fe_4Cp_4S_5][PF_6]_2$ in protic organic solvents and aqueous micellar solutions

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Abstract

The structural and electronic stabilities of the title compound have been investigated in CH_3CN–CH_3OH (100–0% to 0–100%) and in aqueous Triton X-100 micelles, by cyclic voltammetry and electronic absorption and EPR spectroscopies. The iron–sulfur cluster has been located in the peripheral polar zone of the micelle, where H_2O molecules are also present. When incorporated in the micelle, the cluster shows satisfactory stability and appears to react, at its most reduced state, with the unsaturated substrate 4-methyl-1-cyclohexene.

Keywords: Electrochemistry; Iron–sulfur complexes; Cluster complexes; Aqueous micelles

1. Introduction

Iron–sulfur clusters in proteins function most often as electron transfer catalysts [1]. However, attempts to use the related synthetic models as electron transfer catalysts in aqueous solutions have often been unsuccessful, mainly because of the clusters' instability under hydrolytic reaction conditions [2]. This instability, particularly strong at the $[4Fe–4S]^{3+}$ oxidation state, has been attributed to the polar [3] and basic [4] properties of the aqueous solvent. The use of micelles seems to provide the most promising systems to increase the cluster stability in protic media [5–7], since it is well established that micelles provide hydrophobic environments similar to those of enzymes [8]. The iron–sulfur synthetic systems used so far in micelles are of the $[Fe_4S_4(SR)_4]^{2-}$ type, with SR = L-$SCH_2CH(CO_2Na)NHCOC_{17}H_{35}$ or SC_6H_4-*p*-n-C_8H_{17}, where long aliphatic chains have been added to the thiolates to improve the cluster solubility in the detergent. These systems have been shown to catalyze an electron transfer reaction towards acridine derivatives [6] and n-pentylazide [7].

As part of our continuing interest in iron–sulfur–cyclopentadienyl cluster chemistry, we have shown that $Fe_4(Cp)_4S_5$ and $Fe_4(MeCp)_4S_5$ (Cp = cyclopentadienyl, MeCp = 1-methylcyclopentadienyl) can be reversibly reduced or oxidized by several electrons, while remaining structurally intact [9,10]. This type of cluster, where the iron–sulfur core is characterized by the presence of three sulfides and one disulfide group, is therefore potentially a good candidate for redox based reactivity studies. We report here the electrochemical and spectroscopic studies of the structural and electronic stabilities of $Fe_4(Cp)_4S_5$, as a function of its overall oxidation state, first in the protic organic medium (CH_3CN/CH_3OH), then in aqueous micellar solutions. Preliminary results of its interaction with 4-methyl-1-cyclohexene are also reported.

2. Experimental

$[Fe_4(Cp)_4S_5][PF_6]_2$ and $Fe_4(Cp)_4S_4$ were prepared according to the literature [11]. All solvent purifications, electrochemical and spectroscopic experiments were performed under an argon atmosphere. The supporting electrolyte Bu_4NPF_6, the buffer solutions and Triton X-100 were used as received (Fluka or Merck). Acetonitrile and methanol were distilled over CaH_2, aqueous solutions were thoroughly degassed. Electrochemical (cyclic voltammetry, controlled potential electrolysis) measurements were performed in a conventional three-electrode cell, using a PAR 273 potentiostat/galvanostat.

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Electrolyses to generate $[Fe_4(Cp)_4S_5][PF_6]$ and $Fe_4(Cp)_4S_5$ were performed at −0.174 and −0.300 V/SCE, respectively. With the organic solvents, platinum working and counter electrodes were used, together with a saturated calomel reference electrode. In the aqueous micellar solutions, as no redox phenomena could be observed on a platinum electrode, carbon felt (Le Carbone Lorraine, Gennevilliers, France) was instead chosen as the working electrode, because of its high conductivity and large active surface. Aqueous micellar solutions (at 5% in Triton X-100, pH 3–11) of the iron–sulfur cluster were prepared either by first dissolving the latter in the surfactant (7 mg of $[Fe_4(Cp)_4S_5][PF_6]_2$ in 1.6 g of Triton X-100) before addition of water (28.5 ml of the appropriately buffered solution) to form the micellar solution, or by introducing the cluster, dissolved in a minimum amount of acetonitrile (9.5 mg of $[Fe_4(Cp)_4S_5][PF_6]_2$ in 1 ml CH_3CN), in the already formed aqueous micelles (50 ml) by vigorous stirring. Spectroelectrochemical experiments were carried out with a modified OTTLE-type cell [12]. Electronic absorption spectra were measured with a Hewlett-Packard 8452A diode array spectrophotometer. EPR spectra were recorded on a Varian E 109 spectrophotometer operating at ~9 GHz. Samples were cooled in a stream of helium gas, the temperature of which was regulated by an Oxford Instruments ESR 900 cryostat.

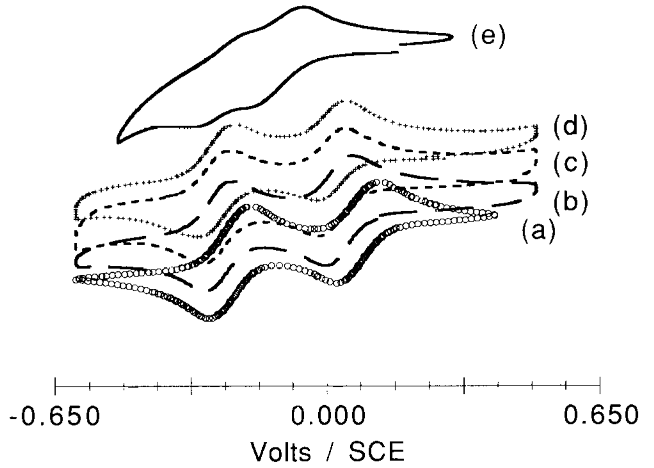

Fig. 1. Cyclic voltammograms of $[Fe_4(Cp)_4S_5]^{2+}$ in CH_3CN–CH_3OH at 100–0% (a); 75–25% (b); 25–75% (c); 0–100% (d); and in aqueous Triton X-100 micellar solution, pH 4 (e).

3. Results and discussion

The cyclic voltammetry profile of the redox behavior of $[Fe_4(Cp)_4S_5]^{2+}$ in the presence of increasing amounts of methanol (from 0 to 100%) is presented in Fig. 1(a)–(d), and the corresponding $E_{1/2}$ values are reported in Table 1. Only the 2+/1+ and 1+/0 redox couples are observed, since the presence of methanol prevents any observation of the higher oxidation states 3+/2+ redox couple. The increasing presence of methanol does not modify significantly the reversibility of both redox processes, indicating thereby that the cluster remains stable in a protic medium, at three oxidation states. The redox potentials are somewhat shifted to lower values (by 40 to 50 mV) when compared to acetonitrile solutions [9]. Such a preferential solvation by CH_3OH may be attributed either to a hydrogen bonding in-

Table 1
Electrochemical and EPR data for the $[Fe_4(Cp)_4S_5]^{2+/1+/0}$ series

	Redox couple		
	$[Fe_4(Cp)_4S_5]^{2+/1+}$ $E_{1/2}$(V/SCE) [c]	$[Fe_4(Cp)_4S_5]^{1+/0}$ $E_{1/2}$(V/SCE) [c]	$[Fe_4(Cp)_4S_5]^{1+}$ g_1; g_2; g_3
CH_3CN–CH_3OH [a]			
100–0	0.07(100) [d]	−0.23(105)	2.120; 1.999; 1.970
75–25	0.03(60)	−0.26(65)	
50–50	0.03(90)	−0.27(90)	
25–75	0.02(70)	−0.27(60)	
0–100	0.02(75)	−0.27(95)	
Micelles at pH [b]			
3	−0.12(40)	−0.26(50)	
4	−0.13(40)	−0.26(50)	
5	−0.13(70)	−0.27(50)	2.114; 1.998; 1.969
7	−0.13(60)	−0.27(40)	2.119; 2.000; 1.968
9	−0.13(60)	−0.28(40)	2.120; 2.000; 1.971
11	−0.14(60)	−0.28(40)	

[a] Electrolyte: 0.1 M Bu_4NPF_6.

[b] In the aqueous solutions, the addition of buffer solutions to adjust the pH was sufficient to ensure a reasonable conductivity.

[c] Sweep rate: 100 mV s^{-1}.

[d] Values in parentheses after the half-wave potentials correspond to the cathodic–anodic peak potential separation.

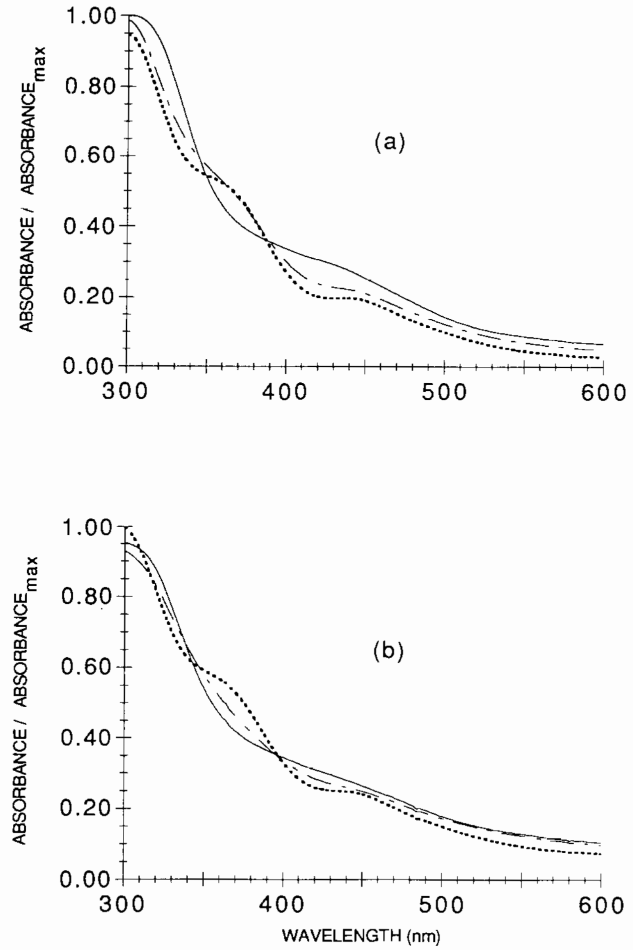

Fig. 2. Electronic absorption spectra of $[Fe_4(Cp)_4S_5]^{2+}$ (dotted line), $[Fe_4(Cp)_4S_5]^{1+}$ produced by electrolysis at −0.174 V/SCE (broken line) and $[Fe_4(Cp)_4S_5]^0$ produced by electrolysis at −0.300 V/SCE (full line) in aqueous Triton X-100 micellar solution (pH 4, cluster concentration 0.05 mM) (a), and in CH_3CN (cluster concentration 0.125 mM) (b).

teraction with the sulfurs of the Fe–S cluster, or to a donating effect from the oxygens of the solvent to the formally positively charged iron atoms of the Fe_4S_5 core. In effect, despite the steric hindrance of the Cp rings, an increase of the coordination number at the iron atoms cannot be excluded, as this is already the case for one of the irons of the Fe_4S_5 core [13,14].

Fig. 1(e) shows the cyclic voltammogram of $[Fe_4(Cp)_4S_5]^{2+}$ in an aqueous micellar solution at pH 4, on a carbon felt electrode. Again, only two redox couples are observed. The chemical stability of the cluster at all three oxidation states at room temperature was verified by a spectroelectrochemical study of each of these states generated by electrolysis, and also by checking the EPR of the paramagnetic monocationic species. The electronic spectra of the micellar $[Fe_4(Cp)_4S_5]^{2+/1+/0}$ species are presented in Fig. 2(a) (for comparison purposes, the electronic spectra of the same oxidation species in acetonitrile are also reported, in Fig. 2(b)). Three absorption bands are visible, in the ranges 300–310 (26 000 M^{-1} cm^{-1}), 350–360 (13 500 M^{-1} cm^{-1}) and 430–450 (5100 M^{-1} cm^{-1}) nm. The bands at 350–360 and 430–450 nm were assigned to the $S_2 \rightarrow Fe$ and $S \rightarrow Fe$ charge-transfer transitions, respectively. In effect, the 350–500 nm energy range is characteristic of the iron–sulfur chromophore [15]. Moreover, the feature at 350–360 nm is most apparent in the dication $[Fe_4(Cp)_4S_5]^{2+}$, decreases in intensity in the monocationic species $[Fe_4(Cp)_4S_5]^{1+}$ and has disappeared in the neutral cluster $[Fe_4(Cp)_4S_5]^0$. Previous analyses [9,11] of the variation of the structural and NMR data with the 2+/1+/0 reduction process have shown that this coincides with the lengthening of the Fe–Fe bonds and with a change in the coordination mode, from μ_4 to μ_3, of the S_2 group between the monocationic and the neutral cluster. The transition at 350–360 nm appears thus to be characteristic of a μ_4 coordination mode of the S_2 sulfurs on the iron atoms. The higher energy absorption band, at 300–310 nm, was assigned to the $Cp \rightarrow Fe$ charge-transfer transition, by comparison with the electronic absorption parameters (in acetonitrile) of the parent $[Fe_4(Cp)_4S_4]^{3+/2+/1+/0}$ series (two absorption bands, at 300 and 460 nm, data not shown). When the micellar solutions containing either $[Fe_4(Cp)_4S_5]^{2+}$ or $[Fe_4(Cp)_4S_5]^{1+}$ or $[Fe_4(Cp)_4S_5]^0$ were left in the air for over 20 h, no change was observed in their electronic spectra, which suggests that the Fe–S cluster is effectively protected by the micelle from any hydrolysis reaction. The EPR spectrum of the paramagnetic species ($S=1/2$) $[Fe_4(Cp)_4S_5]^{1+}$ in the micellar solution shows a rhombic signal with g values (see Table 1) which are very similar to those observed for the same species in the acetonitrile solution [9]. This is a further indication that the electronic properties of the cluster in the aqueous micelle remain identical to those in the organic solution.

The redox potentials of the cluster in micellar solutions remain unchanged when the proton concentration is varied from pH 3 to 11 (see Table 1). Thus, one can assume that, different from other iron–sulfur clusters $(Fe_4S_4(SR)_4)^{2-}$ with SR = L-$SCH_2CH(CO_2Na)$-$NHCOC_{17}H_{35}$ or SC_6H_4-p-n-C_8H_{17}) in micelles [5–7], $Fe_4(Cp)_4S_5$ has no direct interaction with any protons. One reason for this may reside in the difference between the ligands, since the Cp rings cannot undergo any hydrogen bonding. Also, the redox potential of the 1+/0 process hardly varies when the protic acetonitrile/methanol medium is replaced by the micelle (see Table 1). On the contrary, the 2+/1+ process is significantly shifted to more negative potentials (by about −160 mV). The surprisingly strong stabilization of the most oxidized state of the cluster can be explained by the electron-donating effect of the oxygen atoms, that belong to the oxyethylene groups present in the hydrophilic

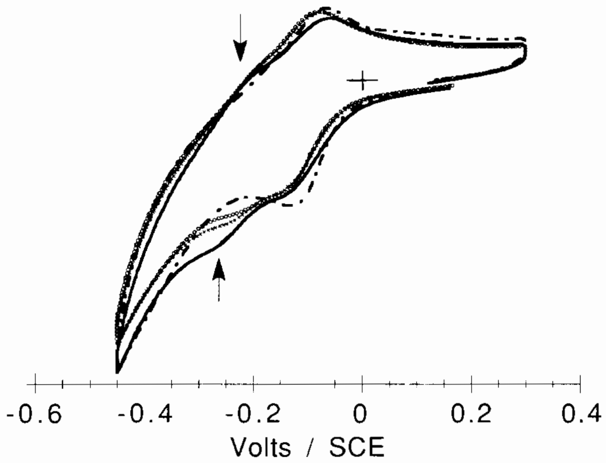

Fig. 3. Cyclic voltammogram of $[Fe_4(Cp)_4S_5]^{2+}$ in aqueous Triton X-100 micellar solution (pH 4, cluster concentration 0.05 mM) in the absence (full line), in the presence of 4-methyl-1-cyclohexene: 100 μl (crosses line); 200 μl (dotted line), and after 10 min electrolysis (dashed line) at −0.30 V.

section of the micelle. In effect, the basic oxygens may interact with the iron atoms, which appear to be the most electron-deficient sites in the $[Fe_4(Cp)_4S_5]^{2+}$ species; indeed, three of the iron atoms have been shown to be most affected by the electrons' abstraction (shortening of the Fe–Fe bond distances, decrease of the isomer shifts) [14]. This provides an indication as to the cluster localization within the micelle, namely that it is probably not in the hydrophobic inner part, but rather in the peripheral polar zone, where the cluster is stabilized by its interaction with the oxygen atoms of the Triton X-100, and where water molecules have also been shown to be present [16]. This is therefore a favorable situation to test whether this type of clusters has any electron transfer reactivity towards unsaturated substrates. Acetophenone, diphenylacetylene, 1-octene and 4-methyl-1-cyclohexene were investigated as the final electron acceptor in the micelles. In the case of the last substrate, the cyclic voltammogram of $[Fe_4(Cp)_4S_5][PF_6]_2$ shows the progressive disappearance of the 1+/0 redox couple upon addition of increasing amounts of substrate (see Fig. 3). After an electrolysis of the final solution for 10 min at −0.30 V/SCE, so that all the cluster may be reduced to $Fe_4(Cp)_4S_5$, only the 2+/1+ wave is clearly present, while the 1+/0 wave has totally disappeared. This result suggests that the neutral $Fe_4(Cp)_4S_5$ cluster has formed an adduct with the substrate (the corresponding redox wave has moved out of the potential window). Further experiments are planned to identify any reduced products.

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