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Note

Carboxy-functionalized dithiolate di-iron complexes related to the active site of Fe-only hydrogenase

Vijendran Vijaikanth [b], Jean-François Capon [a], Frédéric Gloaguen [a], François Y. Pétillon [a], Philippe Schollhammer [a,*], Jean Talarmin [a]

[a] UMR CNRS 6521, Chimie, Electrochimie Moléculaires et Chimique Analytique, UFR Sciences et Techniques Université de Bretagne Occidentale, CS 93837, 29238 BREST-Cedex 3, France
[b] Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N1N4

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Abstract

Reactions of the di-iron complex $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ with carboxy-functionalized dihalide derivatives $(XCH_2)_2R$ ($X = Cl$, $R = NC_6H_4CH_2CO_2CH_3$; $X = Br$, $R = C_6H_3COOH$, $C_6H_3COON(COCH_2)_2$) gave new functionalized dithiolate di-iron complexes $[Fe_2(\mu\text{-}SRS)(CO)_6]$ ($R = (CH_2)_2NC_6H_4CH_2CO_2CH_3$ (**1**), $(CH_2)_2C_6H_3COOH$ (**2**), $(CH_2)_2C_6H_3COON(COCH_2)_2$ (**3**)) in low yields. The azadithiolate complex **1** has been characterized by a single crystal X-ray diffraction analysis and studied by electrochemical methods.

Keywords: Hydrogenase; Di-iron complex; Carboxy-functionalized dithiolate; Molecular structure; Electrochemistry

1. Introduction

Hydrogen has been identified as a potential clean and renewable energy source for the future. In the last few years, structural determinations of the [FeFe] hydrogenase, one of the enzymes that catalyze the reversible reaction $2H^+ + 2e^- = H_2$, have prompted several fundamental studies on synthetic organometallic iron–sulfur assemblies. These works were developed in the hope to get a better understanding of the chemistry of the di-iron active subsite and to determine the minimal structural requirements for hydrogenase activity in view to provide alternative catalysts and electrocatalysts for efficient hydrogen production [1]. Studies on immobilized catalysts are of importance in this context [2]. Immobilization of a molecule onto an electrode can be achieved through, for example, the formation of a covalent amide link by coupling substrates having ester functionnality with amine groups of a surface-modified electrode [3]. Recently, we decided to explore this strategy to attach an organometallic 2Fe2S site through an adequately funtionalized dithiolate bridge to an electrode (Scheme 1) [4].

This led us to investigate the syntheses of a series of hexacarbonyl di-iron complexes with carboxy-functionalized dithiolate bridges. Such systems can be obtained by reacting dithiols with $[Fe_3(CO)_{12}]$ and carboxy-substituted dithiol di-iron systems have been recently reported [5]. The synthesis of di-iron dithiolate complexes can be also performed by functionalization of the di-iron disulfide species $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ by treatment with various organic halides [6–10]. In addition, straightforward condensation of $[Fe_2(\mu\text{-}SH)_2(CO)_6]$ with RNH_2 and CH_2O or $RN(CH_2OH)_2$ affords also N-substituted azadithiolate compounds [11]. We wish to report here our attempts to prepare new carboxy-functionalized di-iron compounds by addition of dihalide derivatives $(XCH_2)_2R$ [$X = Cl$, $R = NC_6H_4CH_2CO_2CH_3$; $X = Br$, $R = C_6H_3COOH$, $C_6H_3COON(COCH_2)_2$] to dinuclear anionic species $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$.

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* Corresponding author.
E-mail address: schollha@univ-brest.fr (P. Schollhammer).

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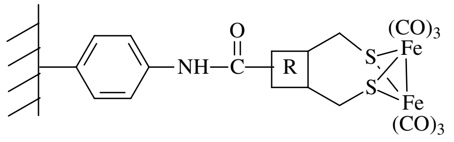
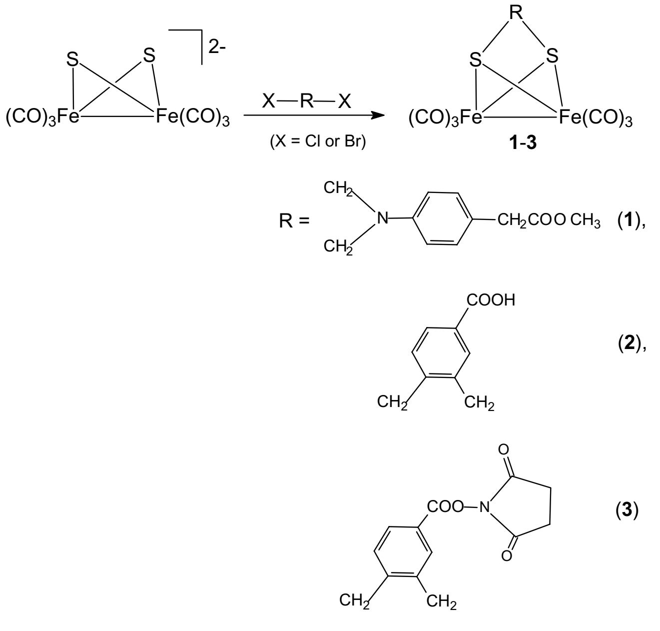


Scheme 1.

2. Results and discussion

Complexes $[Fe_2(\mu\text{-SRS})(CO)_6]$ [$R = (CH_2)_2NC_6H_4CH_2CO_2CH_3$ (**1**), $(CH_2)_2C_6H_3COOH$ (**2**), $(CH_2)_2C_6H_3COON(COCH_2)_2$ (**3**)] were obtained in low yields by treatment of $[Fe_2(CO)_6(\mu\text{-S})_2]^{2-}$ with dihalide $(XCH_2)_2R$ [$X = Cl$, $R = NC_6H_4CH_2CO_2CH_3$; $X = Br$, $R = C_6H_3COOH$, $C_6H_3COON(COCH_2)_2$] following a known procedure [6,7] (Scheme 2). Compounds **1**–**3** were characterized by IR and ^1H NMR spectroscopy. Three typical strong bands between 2075 and 1998 cm^{-1} are observed in the terminal carbonyl region of the infrared spectrum of the complexes in tetrahydrofuran. In addition, the detection of new bands between 1800 and 1700 cm^{-1} accords with the presence of carboxy-functionalized groups. ^1H NMR spectra of **1**–**3** confirm the nature of the dithiolate bridge $\{(SCH_2)_2R\}$. Indeed, the ^1H NMR spectrum of **1** in CD_3CN shows two doublets related to the aromatic group (7.20 and 6.79 ppm) and three singlets with intensities of 4, 3 and 2 for both $S\text{–}(CH_2)_2\text{–}N$ (4.41 ppm) and $CH_2CO_2CH_3$ (3.62 and 3.54 ppm) groups, respectively. ^1H NMR spectra of **2** and **3** display between 8.13 and 6.25 ppm three signals (two doublets and one singlet) assigned to the aromatic protons of the dithiolate bridge. The nature of the carboxyl group is revealed by the observation of a broad acidic proton signal at 11.4 ppm for **2**, and that of a singlet at 2.91 ppm for the four protons of the *N*-hydroxysuccinimide ester group in **3**. The dissymmetry of the bridge in **3** is shown by the observation in $CDCl_3$ of a doublet and a doublet of doublet at 3.18 ppm and 3.93 ppm, respectively, for $S\text{–}CH_2\text{–}Ar$ groups.



Scheme 2.

The formulation of **1** was confirmed by a X-ray diffraction study of a single crystal obtained from hexane/dichloromethane solution. The analysis indicates, as expected, a distorted square-pyramidal coordination at each 18-electron iron centre and the well-known butterfly structure found in related dithiolate di-iron complexes [6–9,11,12] (Fig. 1a). **1** contains a single Fe–Fe bond [2.5044(8) Å] which is bridged by the two sulfur atoms of the azapropanedithiol group. The structure of **1** features two fused six-member rings, Fe2–S1–C7–N1–C8–S2 and Fe1–S1–C7–N1–C8–S2, which adopt boat and chair conformation, respectively. The N-carboxyl group lies in an axial position and the sum of C–N–C angles (C7–N1–C8, C8–N1–C9, C9–N1–C7) around N1 is 356.7°, indicating a noticeable flattening of the trigonal pyramid about N1. It is worth noting that the proton of one bridging methylene $\{N\text{–}CH_2\text{–}S\}$(C7) is involved in a bifurcated hydrogen bond to one oxygen atom (O7) of the carboxy function ($H7\cdots O7 = 2.454(3)$ Å) (Fig. 1(b)).

The electrochemical behavior of **1** has been studied in acetonitrile. A $CH_3CN\text{–}Bu_4NPF_6$ solution of **1** is reduced at −1.57 V versus Fc+/0 (Fig. 2), consistent with the data reported for other di-iron complexes bearing an azadithiolate bridge substituted with an aryl group [7d]. Compounds where the substituent of the azadithiolate bridge is an alkyl group are reduced at a potential about 0.1 V more negative [11e]. It is also relevant to note that the reduction of the azadithiolate-bridged complex **1** occurs at a potential about 0.1 V less negative and appears chemically less reversible than that of the corresponding propanedithiolate-bridged derivative under otherwise similar experimental conditions. Upon addition of 1 molar equiv. toluenesulfonic acid (HOTs, $pK_a \sim 8$), the voltammogram shows two new reduction events at −1.32 V and −1.53 V, respectively (Fig. 2). The first reduction peak is ascribed to the reduction of the protonated form of **1** (the most likely protonation site in **1** being the nitrogen atom of the azadithiolate bridge [7d]). The origin of the second reduction peak cannot be explained at present, although similar observations have recently been reported (Fig. 4 bottom in Ref. [11c]). Upon increasing the acid concentration, the height of the first reduction wave increases and shifts to negative potentials merging with the second reduction wave. Such an electrochemical behavior could result from an electrocatalytic proton reduction [7d].

In summary, attempts to synthesize carboxy-functionalized di-iron dithiolate complexes have been developed in this work, but it appeared difficult to obtain them from the di-iron disulfide $[Fe(CO)_6(S)_2]^{2-}$. Despite this, three new members of the hexacarbonyl di-iron dithiolate series were isolated and characterized. The grafting of the *N*-hydroxysuccinimide ester compound **3** via an amide

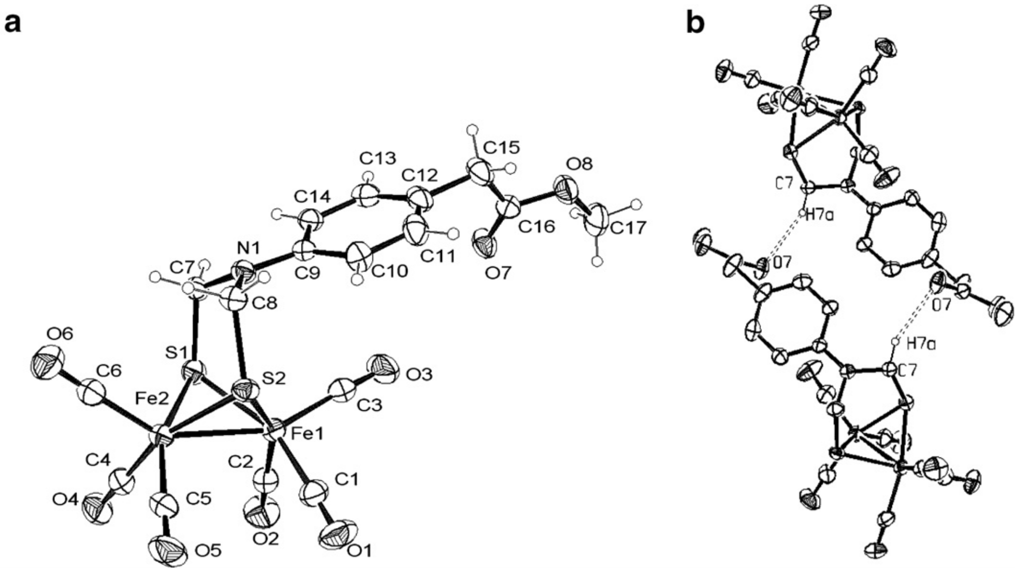


Fig. 1. (a) A view of a molecule of **1** showing 30% ellipsoids (b) hydrogen bonding between two molecules in the unit cell. Selected distances and angles (Å and °): Fe1–Fe2 2.5044(8), Fe1–S1 2.2634(10), Fe1–S2 2.2678(11), Fe2–S1 2.2588(11); Fe2–S2 2.2703(10), S2–C8 1.863(3), S1–C7 1.859(4), N1–C9 1.408(4), N1–C8 1.414(4), N1–C7 1.433(4), O8–C16 1.333(4), O8–C17 1.429(5), O7–C16 1.176(4), C8–S2–Fe1 113.14(12), C8–S2–Fe2 107.99(12), Fe1–S2–Fe2 66.99(3), C7–S1–Fe2 109.79(12), C7–S1–Fe1 112.19(11), Fe2–S1–Fe1 67.26(3), C9–N1–C8 120.8(3), C9–N1–C7 121.5(3), C8–N1–C7 114.4(3), C16–O8–C17 115.4(3), N1–C7–S1 116.2(2), N1–C8–S2 115.1(2), O7–C16–O8 124.1(4), O7–C16–C15 126.4(3), O8–C16–C15 109.5(3).

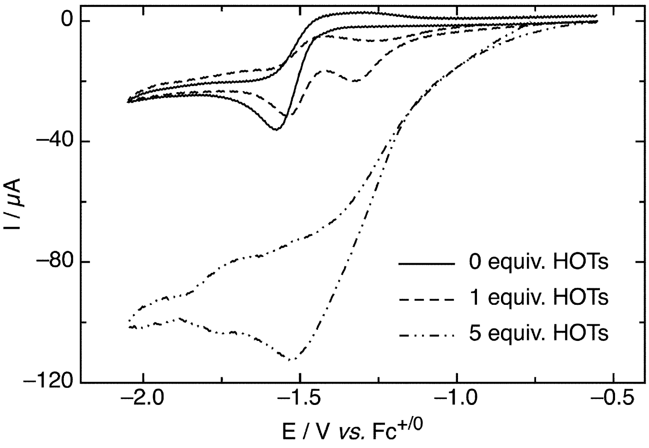


Fig. 2. Cyclic voltammograms of a N_2-purged 2 mM solution of complex **1** in CH_3CN–Bu_4NPF_6 with increasing concentration of HOTs. First negative going scan at 0.1 V s^{-1} recorded at a glassy carbon disk 0.3 cm in diameter.

link to a carbon electrode has been reported previously [4]. This study revealed the decomposition of the modified electrode in acidic media and seems to end up this approach.

3. Experimental

3.1. General procedures

All reactions were performed under an atmosphere of argon or dinitrogen using conventional Schlenk techniques. Solvents were deoxygenated and dried by standard methods. Literature methods were used for the preparation of 3,4-bis(bromomethyl)benzoic acid and its *N*-hydroxysuccinimide ester [13,14], $NH_2C_6H_4CO_2CH_3$ [15] and $[Fe_2S_2(CO)_6]$ [16]. *N*,*N*-di(chloromethyl)amine$(ClCH_2)_2$-$NC_6H_4CH_2CO_2CH_3$ was obtained from reaction of paraformaldehyde with $NH_2C_6H_4CH_2CO_2CH_3$, followed by chlorination with thionyl chloride, according to a procedure previously described [7a]. All other reagents were purchased commercially. Chemical analyses were performed by the Service de Microanalyse du CNRS, Gif sur Yvette (France). The ^1H NMR spectra were recorded at room temperature with a Bruker AC 300 or AMX 400 spectrometers and were referenced to $SiMe_4$. The infrared spectra were recorded on a Nicolet Nexus Fourier transform spectrometer. Cyclic voltammetry experiments were carried out as recently described elsewhere [18].

3.2. Syntheses of $[Fe_2(\mu\text{-}SRS)(CO)_6]$ ($R = (CH_2)_2NC_6H_4CH_2CO_2CH_3$ (**1**), $(CH_2)_2C_6H_3COOH$ (**2**), $(CH_2)_2C_6H_3COON(COCH_2)_2$ (**3**))

In a typical procedure, a red solution of $[Fe_2(\mu\text{-}S_2)(CO)_6]$ (344 mg, 1 mmol) in THF (20 mL) was treated at −78 °C with a 1 mol L^{-1} solution of superhydride, $LiBEt_3H$, in THF (2 mL, 2 mmol). This mixture was stirred 10 min and the solution turned to green. A solution of 1.5 equiv. of a dihalide reagent $[(ClCH_2)_2NC_6H_4$-$CH_2CO_2CH_3$: 393 mg; $(BrCH_2)_2C_6H_3COOH$: 462 mg; $(BrCH_2)_2C_6H_3COON(COCH_2)_2$: 593 mg] in THF (5 mL) was then added and the coloration of the mixture changed readily to red. This solution was allowed to warm to room temperature. The solvent was then evaporated and the resulting residue was extracted with diethylether (2×20 mL). After evaporation of Et_2O the solid was purified by chromatography on silica gel column with mixtures of hexane–dichloromethane or dichloromethane–THF as eluents. Compound **1** was eluted with hexane:dichloromethane (50:50 and 40:60) solutions and **2** and **3** were eluted with a dichloromethane–THF (95:5) mixture. **1**–**3** were obtained as red solids (yields after workup: **1**, 140 mg, 26%; **2**, 70 mg, 14%;**3**, 40 mg, 7%).

$(ClCH_2)_2NC_6H_4CH_2CO_2CH_3$: ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.29 (d, 2H, $J_{HH} = 8.8$ Hz, C_6H_4), 7.20 (d, 2H, $J_{HH} = 8.8$ Hz, C_6H_4), 5.53 (s, 4H, $N(CH_2)_2S_2$), 3.69 (s, 3H, $CH_2CO_2CH_3$), 3.60 (s, 2H, $CH_2CO_2CH_3$).

1: ^{1}H NMR (CD_3CN, 25 °C; δ): 7.20 (d, 2H, $J_{HH} = 8.0$ Hz, C_6H_4), 6.79 (d, 2H, $J_{HH} = 8.0$ Hz, C_6H_4), 4.41 (s, 4H, $(SCH_2)_2N$), 3.62 (s, 3H, $CH_2CO_2CH_3$), 3.54 (s, 2H, $CH_2CO_2CH_3$). IR (THF, cm^{-1}): 2075(s), 2037(vs), 1999(vs), 1724(s) ν(CO). Anal. Calc. for $C_{17}H_{13}NFe_2O_8S_2$: C, 38.1; H, 2.4; N, 2.6. Found: C, 37.5; H, 2.4; N, 2.6%.

2: ^{1}H NMR (CD_3COCD_3, 25 °C; δ): 11.4 (s, br, 1H, $C_6H_3CO_2H$), 8.13 (s, 1H, C_6H_3), 7.98 (d, 1H, $J_{HH} = 7.2$ Hz, C_6H_3), 7.64 (d, 1H, $J_{HH} = 7.2$ Hz, C_6H_3), 4.88 (s, 2H, $(SCH_2)_2C_6H_3$), 4.85 (s, 2H, $(SCH_2)_2C_6H_3$). IR (THF, cm^{-1}): 2073(m), 2037(vs), 1998(s), 1723(w) ν(CO).

3: ^{1}H NMR ($CDCl_3$, 25 °C; δ): 7.92 (d, 1H, $J_{HH} = 8.0$ Hz, C_6H_3), 7.84 (s, 1H, C_6H_3), 7.23 (d, 1H, $J_{HH} = 8.0$ Hz, C_6H_3), 3.93 (dd, $J_{HH} = 13.0$ Hz, 2H, $(SCH_2)_2C_6H_3$), 3.18 (d, $J_{HH} = 13.0$ Hz, 2H, $(SCH_2)_2C_6H_3$), 2.91(s, 4H, $COON(COCH_2)_2$). IR (THF, cm^{-1}): 2074(m), 2039(vs), 1999(s), 1773(m), 1747(s) ν(CO).

3.3. X-ray crystallography

Crystal data for **1**, $C_{17}H_{13}Fe_2NO_8S_2$, F. wt. 535.10, 20 °C, $\lambda = 0.71073$ Å, monoclinic, space group $P2_1/c$, $a = 8.1031(12)$, $b = 11.3667(16)$, $c = 23.698(3)$ Å, $\beta = 103.062(15)$, $V = 2126.3(5)$ Å^3, $Z = 4$, $D_{calc} = 1.672$ g cm^{-3}, $\mu = 1.604$ mm^{-1}, crystal size $0.24 \times 0.17 \times 0.035$ mm, $\theta_{max} = 33.3$ °. 23276 intensities were measured on a Oxford Diffraction X-Calibur-2 CCD diffractometer equipped with a jet cooler device. After empirical absorption corrections (ψ-scans, transmission factors 0.89422–0.53564) and averaging [$R_{int} = 0.0822$] the structure was solved by direct methods and refined by full-matrix least-squares on F^2 [17]. Adjustment of 277 parameters gave $R(F) = 0.0520$, $wR(F^2) = 0.1172$ for 7548 data with $[I > 2\sigma(I)]$ and $R(F) = 0.1581$, $wR(F^2) = 0.1477$ for all unique reflections. $|\Delta\rho| < 0.517$ e Å^{-3}.

Acknowledgments

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Appendix A. Supplementary material

CCDC 648154 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.042.

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