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Diiron Complexes with a [2Fe3S] Core Related to the Active Site of [FeFe]H_2ases

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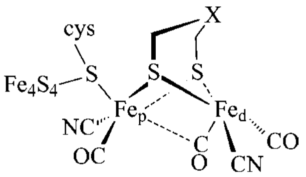
Six-membered heterocycles, 1,4-dithiane and 1,4-thioxane, were treated with $[Fe_2(CO)_6(\mu\text{-pdt})]$ (pdt = propanedithiolate) in order to synthesise [2Fe3S] complexes with well positioned heteroatoms as potential base. Monosubstituted compounds of general formula $[Fe_2(CO)_5L(\mu\text{-pdt})]$ (L = 1,4-dithiane, 1,4-thioxane) were mainly obtained and characterised by ^1H NMR, IR, elemental analysis and X-ray diffraction studies. Electrochemical behaviour of these monosubstituted derivatives was investigated by cyclic voltammetry. An original tetranuclear cluster with a [4Fe8S] core was also isolated as a minor product and structurally characterised.

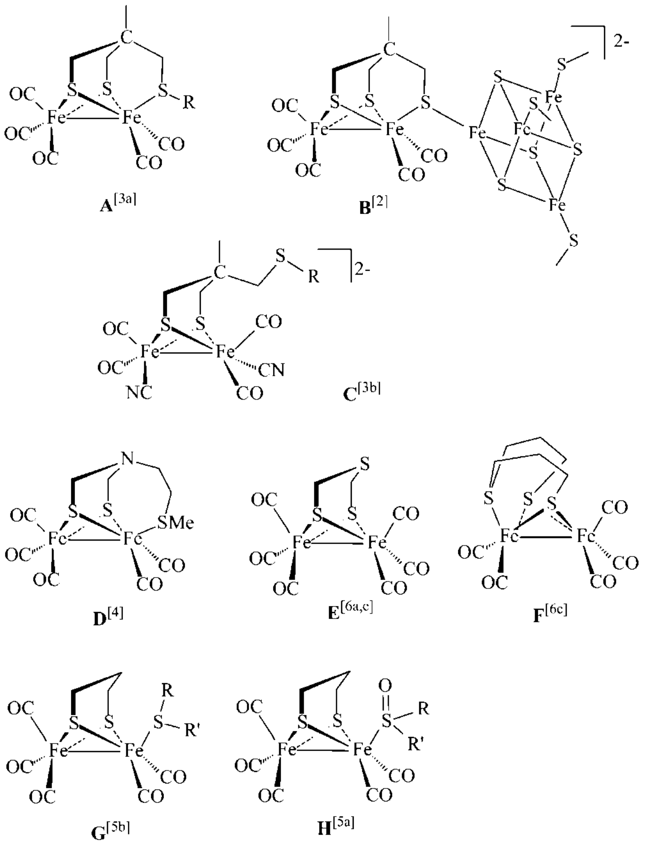
Introduction

The chemistry and electrochemical behaviour of carbonyl-dithiolato-diiron complexes with a [2Fe2S] core have been recently widely explored in reason of the resemblance of such organometallic species with the active site of [FeFe]-hydrogenases.[1] A better understanding of the activity of such a natural site is still required to elaborate sulfur–iron aggregates that could efficiently electrocatalyze the reduction of protons. In this context, it is worth noting that fewer examples of bioinspired diiron molecules with a [2Fe3S] core have been reported despite the fact these species have a sulfur environment very close to that of the natural site (Scheme 1).



Scheme 1. A schematically view of the H-cluster of [FeFe]H_2ases.

Such a sulfur environment has been modeled by using monodentate thioethers and propane- or aza-dithiolate-bridging ligands with various thiol or thioether functionalities, binding one iron atom (Scheme 2).[2–5] Other systems featuring thiadithiolate bridges have been also reported recently.[6]



Scheme 2. Complexes **A**–**H** containing various thiol and/or thioether functionalities, and modelling the [2Fe3S] core of the H-cluster.[2–6]

In another connection, recent studies of systems with azadithiolate bridges[7] or flexible diphosphanes,[8–9] such as {PNP $[(R_2PCH_2)_2NR']$ and $P^R{}_2N^{R'}{}_2$ $[(RPCH_2NR')_2]$},

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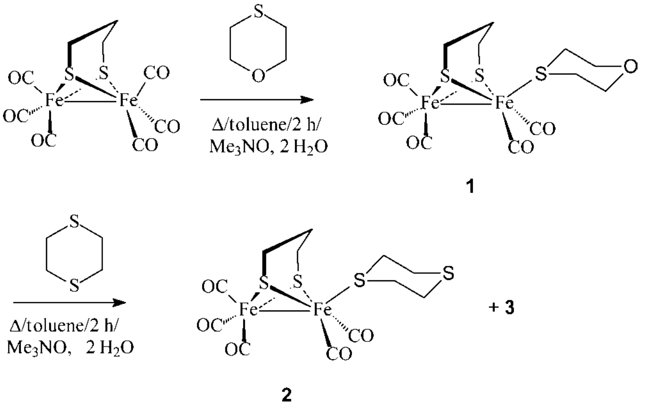
have suggested that the presence of a proton relay should be necessary for an efficient activation of proton reduction/hydrogen oxidation.

In the course of our work concerning the understanding of the activity of the H-cluster and the design of diiron electrocatalysts we have elaborated molecules in which a [2Fe3S] core is combined with six-membered heterocyclic sulfur ligands with well positioned heteroatoms, such as 1,4-dithiane ($C_4H_8S_2$) and 1,4-thioxane (C_4H_8OS). We report here results concerning the formation of monosubstituted complexes with a [2Fe3S] core and that of an unexpected [4Fe8S] cluster. The electrochemical behaviour of the bimetallic species is briefly examined.

Results and Discussion

The reaction of [$Fe_2(CO)_6$(μ-pdt)] with 3 equiv. of 1,4-thioxane or 1,4-dithiane and 2 equiv. of $Me_3NO,2H_2O$ in refluxing thf for 18 h gave monosubstituted derivatives **1** and **2** (Scheme 3).



Scheme 3. Synthesis of **1**–**3**.

Compound **1** was the sole isolated product of the reaction with 1,4-thioxane and it was synthesised with a fair yield (57%), whereas **2** was obtained in a moderate yield (37%) with small amounts of a by-product **3** (< 3%). The lowering of the carbonyl IR frequencies of **1**, and **2**, relative to those of [$Fe_2(CO)_6$(μ-pdt)], is consistent with the replacement of one carbonyl group by a better σ-donor ligand. ^{1}H NMR spectra of **1** and **2** show the expected signals of six-membered heterocycles and of the propanedithiolate bridge in a 1:1 ratio.[10,11] The $^{13}C\{^1H\}$ NMR spectrum displays in the carbonyl region typical signals of a monosubstituted pentacarbonyl species [$Fe_2(CO)_5L$(μ-pdt)] with a singlet by 210 ppm for the non-substituted {$Fe(CO)_3$} moiety and a broad signal by 213 ppm for the substituted fragment {$Fe(CO)_2L$}. Compared to previous work, it is worth noting that here no species with bidentate or bridging 1,4-dithiane and 1,4-thioxane was observed.[11] Single crystals of complexes **1** and **2** were obtained from dichloromethane/hexane mixtures at –15 °C. The crystal structures of **1** and **2** were determined by X-ray crystallography (Table 2) and are shown in Figure 1. Selected bonds and angles are listed in Table 1. Compounds **1** and **2** have similar molecular structures (Figure 1 and Table 1). **1** and **2** are structurally analogous to other monosubstituted pentacarbonyldiiron(I) dithiolato-bridged species [$Fe_2(CO)_5L$(μ-pdt)] with two eclipsed {$Fe(CO)_3$} and {$Fe(CO)_2L$} moieties bridged by a propanedithiolate group. The geometry around each iron atom is a distorted square-pyramid supplemented by a Fe–Fe single bond. 1,4-Dithiane and 1,4-dithioxane are coordinated in a monodentate fashion, in apical position, through a sulfur atom. In the solid state, both of these heterocycles adopt a chair conformation.

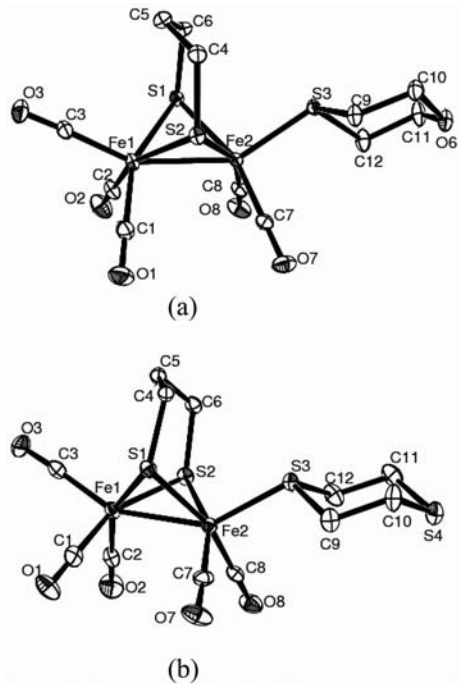


Figure 1. ORTEP diagram of compounds **1** (a) and **2** (b) depicted with 30% thermal elliposïds.

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **2**.

Distances [Å] and angles [°]	1	2
Fe1–Fe2	2.5018(5)	2.5036(12)
Fe1–S1	2.2732(6)	2.2770(17)
Fe1–S2	2.2664(6)	2.2723(17)
Fe2–S1	2.2650(6)	2.2638(17)
Fe2–S2	2.2593(6)	2.2653(17)
Fe2–S3	2.2522(6)	2.2538(16)
C10–X (X = S4, O6)	1.419(3)	1.792(6)
C11–X (X = S4, O6)	1.420(3)	1.797(7)
Fe2–S2–Fe1/Fe2–S1–Fe1	67.118(19)/66.907(19)	66.97(5)/66.92(5)

The reaction of [$Fe_2(CO)_6$(μ-pdt)] with 1,4-dithiane afforded also a side-product **3** which was isolated by column chromatography with very low yields (< 3%). X-ray analysis of single crystals of **3** reveals an unusual tetranuclear derivative, formulated as [$Fe_4(CO)_6(S_2C_3H_6)_4$] (Figure 2). **3** contains four chemically inequivalent iron atoms arranged so that the central Fe1–Fe2–Fe3 and Fe2–Fe3–Fe4 angles are 153.55(8) and 178.99(8)°, respectively. The Fe1–Fe2 bond [2.505(2) Å] is bridged by a bidentate propanedithiolate group. Three carbonyl groups bonded to Fe1 complete its coordination sphere, that may be described as a distorted square-pyramid. The Fe2–Fe3 core [2.546(2) Å] is bridged by three sulfur atoms (S3, S4, S5) of three different dithiolate ligands, the other sulfur atoms (S6, S7, S8) of these groups bridge the Fe3 and Fe4 atoms. Five sulfur atoms (S1, S2, S3, S4, S5) define a square-pyramid centered on Fe2 supplemented by two Fe–Fe single bonds. The geometry around Fe3 could be described as an octahedron with three chelated propanedithiolate ligands. The Fe3–Fe4 distance of 3.014(3) Å suggests that there is no direct bond between these two atoms. Three carbonyl ligands complete the octahedral geometry around Fe4. Electron-counting rules suggest a structure with two Fe–Fe bonds (Fe1–Fe2 and Fe2–Fe3) and a $\{Fe^{I}–Fe^{II}–Fe^{III}–Fe^{II}\}$ assembly. It has to be noted that examples of original tetranuclear iron thiolate clusters with fused [2Fe3S] cores have been very recently reported.[12] Similarly, some related $\{Fe_3(pdt)(CO)_4\}$ chains have been recently described.[13]

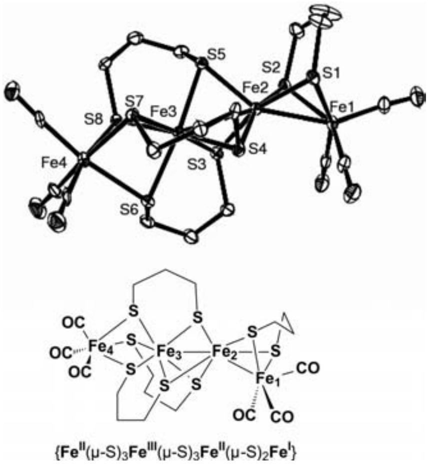


Figure 2. Schematic view, and molecular structure of $[Fe_4(CO)_6(S_2C_3H_6)_4]$ (**3**).

The formation of **3** was reproducible but its mechanism remains unclear. Attempts to obtain this species with higher yields were unsuccessful. The formation of traces of **3** was also observed when $[Fe_2(CO)_6(\mu\text{-pdt})]$ is reacted with propanedithiolate in the presence of an excess (3 equiv.) of $Me_3NO,2H_2O$.

The redox properties of **1** and **2** were shortly examined by cyclic voltammetry (CV) in $CH_3CN/[NBu_4][PF_6]$ at room temperature. Voltammograms of **1** and **2** exhibit very similar features (Figure S1 in Supporting Information and Figure 3). Compound **1** is reduced at $E_{p,red}$ = –1.67 V and oxidized at $E_{p,ox}$ = 0.26 V vs. Fc. The primary reduction of **1** involves two electrons[14] and this process is completely irreversible even at fast scan rates and low temperatures. This indicates that the electron transfer is coupled to fast chemical reactions whose product is detected by an oxidation at ca. –1.20 V on the reverse scan. It has to be pointed out that the primary reduction of **1** and **2** occurs in the same potential range[15] as that of the all-CO parent compound, $[Fe_2(CO)_6(\mu\text{-pdt})]$, despite the replacement of one carbonyl group by a σ-electron-donating ligand, such as thioxane and dithiane. The electrocatalytic activity of compounds **1** and **2** for proton reduction was investigated in CH_3CN/Bu_4NPF_6 solutions with increasing concentrations of toluenesulfonic acid (HOTs, p*K*a ≈ 8) (Figure 3). The voltammetric peak associated with the primary reduction of **1** increased continuously upon increasing the acid concentration, consistent with a catalytic process that consumes acid. The intimate mechanism of this process was not studied further.

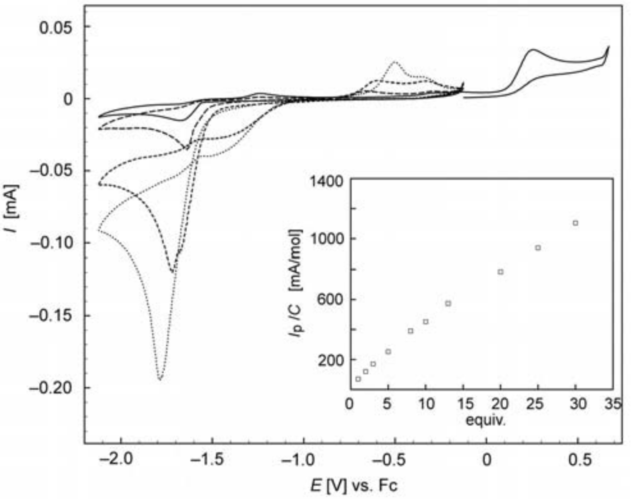


Figure 3. Cyclic voltammograms of **1** (1.1 mM) in $CH_3CN/[NBu_4][PF_6]$ before (plain) and after addition of 1, 5 and 8 molar equiv. HOTs (dot). $v = 0.1\ V\,s^{-1}$.

Conclusions

The reactivity of 1,4-dithiane and 1,4-thioxane with $[Fe_2(CO)_6(\mu\text{-pdt})]$ was explored. Two monosubstituted products $[Fe_2(CO)_5L(\mu\text{-pdt})]$ {L = κ^1(*S*)-1,4-dithiane, κ^1(*S*)-1,4-thioxane} were isolated. An investigation of their electrochemical behaviours reveal that both of them possess an electrocatalytic activity in the presence of proton. An unusual tetranuclear derivative with a [4Fe8S] core was isolated and structurally characterised.

The use of the six-membered cyclic thiomorpholine, C_4H_8SNH, as a base-containing ligand that would act as a proton relay at a [2Fe3S] core, and the extension of such a study to the reactivity of $[Fe_2(CO)_6(\mu\text{-pdt})]$ towards smaller thiocycle reagents, such as thiirane, C_2H_4S, or thietane, C_3H_6S, that have the capacity to sustain C–S bond cleavage and bond recombination at sulfur-rich organometallic centres,[11] are now under consideration.

Experimental Section

General Procedures: All the experiments were carried out under an inert atmosphere, using Schlenk techniques. $[Fe_2(CO)_6(\mu\text{-pdt})]$ was prepared according to reported procedures.[16] The ^1H NMR spectra were recorded at room temperature in $CDCl_3$ or C_6D_6 solution with a Bruker AMX 400, AC300 and DRX 500 spectrometers and were referenced to $SiMe_4$ (^1H). The infrared spectra were recorded on a Nicolet Nexus Fourier transform spectrometer. Chemical analyses were made by the "Service de Microanalyses I.C.S.N.", Gif-sur-Yvette (France).

The electrochemical equipment consisted either in an Autolab PGSTAT12 driven by the GPES software or a PAR 273 driven by the M270 software. The cell and electrodes were as described previously.[17] All the potentials (text and figures) are quoted against the ferrocene–ferrocenium couple; ferrocene was added as an internal standard at the end of the experiments.

Crystal data (Table 2) for compound **1**–**3** were collected on an Oxford Diffraction X-Calibur-2 CCD diffractometer, equipped with a jet cooler device and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved and refined by standard procedures.[18]

Table 2. Crystallographic Data for complexes **1**–**3**.

	1	**2**	**3**·C_5H_{12}
Empirical formula	$C_{12}H_{14}Fe_2O_6S_3$	$C_{12}H_{14}Fe_2O_5S_4$	$C_{23}H_{36}Fe_4O_6S_8$
Formula weight	462.11	478.17	888.40
Temperature /K	170(2)	170(2)	170(2)
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	8.8715 (8)	8.8205 (10)	12.4540 (8)
b /Å	9.9199 (7)	10.3845 (12)	12.5693 (7)
c /Å	10.2913 (9)	10.6139 (15)	12.7913 (8)
α /°	74.650 (7)	109.690 (11)	75.818 (5)
β /°	80.891 (7)	97.744 (10)	72.909 (5)
γ /°	87.776 (6)	90.857 (9)	62.296 (6)
V /Å^3	862.35 (3)	905.10 (19)	1680.54 (18)
Z	2	2	2
ρ_{calc} /Mgmm^{-3}	1.780	1.755	1.756
μ /mm^{-1}	2.068	2.081	2.225
Crystal size /mm	0.30×0.12×0.04	0.15×0.06×0.02	0.10×0.06×0.03
Range of θ /°	2.87–28.28	3.23–20.81	2.99–22.72
Reflections measured	8214	5008	7567
R_{int}	0.0210	0.0546	0.0708
Unique data/parameters	4273/208	1808/208	3815/372
R_1 [$I > 2\sigma(I)$]	0.0282	0.0399	0.0653
R_1 (all data)	0.0406	0.0623	0.1026
$W R_2$ (all data)	0.0770	0.0631	0.1661
Goodness of-fit on F^2	1.032	1.012	0.986
$\Delta\rho_{\max}$,$\Delta\rho_{\min}$ /eÅ^{-3}	0.520, –0.460	0.313, –0.304	0.609, –0.604

CCDC-793695 (for **1**), -793696 (for **2**) and -793697 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 1–2: In a typical procedure, [$Fe_2(CO)_6(\mu\text{-}S_2C_3H_6)$] (500 mg, 1.29 mmol), two equiv. of Me_3NO, $2H_2O$ (288 mg, 2.59 mmol) and three equiv. of 1,4-thietane (465 mg) or 1,4-thioxane (362 µL) were heated in refluxing THF (50 mL). After 4 h, the solvent was removed and the obtained residue was chromatographed on a silica gel column. Complexes **1** and **2** were eluted with hexane/dichloromethane mixtures. A red-brown fraction containing **1** or **2** was collected and these two products were obtained as red-brown powders (**1**, 346 mg, 58%; **2**, 228 mg, 37%) after the solvent has been removed. In experiments involving 1,4-dithiane, a second red fraction was collected and afforded the complex **3** with very low yields (15–30 mg, 1.5–3%).

1: IR (CH_2Cl_2): $\tilde{\nu}_O$ = 2048 (sh), 2041 (s), 1985 (vs), 1967 (sh), 1927 (w) cm^{-1}. ^{1}H NMR (C_6D_6, 298 K): δ = 3.21 [br. m, 4 H, O(CH_2)$_2$], 2.08 [br. m, 4 H, S(CH_2)$_2$], 1.67 [br. m, 3 H, S(CH_2)$_3$S], 1.28 [br. m, 2 H, S(CH_2)$_3$S], 1.16 [br. m, 1 H, S(CH_2)$_3$S] ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ = 213.2 [br., Fe(CO)$_2$L], 210.8 [Fe(CO)$_3$], 67.7 [O(CH_2)$_2$], 38.5 [S(CH_2)$_2$], 30.6, 23.7 [S(CH_2)$_3$S] ppm. $C_{12}H_{14}Fe_2O_6S_3$ (462.11): Calcd. C 31.16, H 3.03; found C 30.77, H 3.87.

2: IR (CH_2Cl_2): $\tilde{\nu}_O$ = 2052 (s), 2044 (sh), 1987 (vs), 1972 (sh), 1930 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ = 3.06 [br. m, 4 H, S(CH_2)$_2$], 2.98 [br. m, 4 H, S(CH_2)$_2$], 2.15 [br. m, 2 H, S(CH_2)$_3$S], 1.87 [br. m, 3 H, S(CH_2)$_3$S], 1. 64 [br. m, 1 H, S(CH_2)$_3$S] ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ = 213.5 [br., Fe(CO)$_2$L], 210.7 [Fe(CO)$_3$], 41.4 [S(CH_2)$_2$], 28.9 [S(CH_2)$_2$], 30.6, 23.8 [S(CH_2)$_3$S] ppm. $C_{12}H_{14}Fe_2O_5S_4$ (478.17): Calcd. C 30.11, H 2.92; found C 31.02, H 3.58.

3: IR (CH_2Cl_2): $\tilde{\nu}_O$ = 2083 (s), 2033 (sh), 2020 (s), 1950 (w) cm^{-1}.

Supporting Information (see also the footnote on the first page of this article): one Figure of cyclic voltammograms of compound **1** and **2** in CH_3CN/[NBu_4][PF_6] before and after addition of HOTs.

Acknowledgments

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