Fe–S complexes containing five-membered heterocycles: novel models for the active site of hydrogenases with unusual low reduction potential†‡

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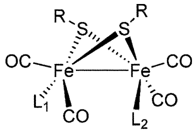
Three biomimetic 2Fe2S complexes $[\{(\mu\text{-SCH}_2)_2\text{NCH}_2(2\text{-C}_4\text{H}_3\text{O})\}](\text{Fe}_2(\text{CO})_6)$ (**6a**), $[\{(\mu\text{-SCH}_2)_2\text{NCH}_2(2\text{-C}_4\text{H}_3\text{S})\}](\text{Fe}_2(\text{CO})_6)$ (**6b**) and $[\{(\mu\text{-SCH}_2)_2\text{NCH}_2(5\text{-Br-2-C}_4\text{H}_2\text{S})\}\text{Fe}_2(\text{CO})_6]$ (**6c**) were prepared as models for the active site of Fe-only hydrogenase by the convergent process from $[(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6]$ and *N*,*N*-bis(hydromethyl)-2-furan and thiophene. The structures of these complexes were identified spectroscopically and crystallographically. The electrochemical behavior of the complexes **6a** and **6c** was unique as they showed catalytic proton reduction with a low reduction potential at −1.13 and −1.09 V *vs* Fc/Fc$^+$, respectively, in the presence of HClO_4.

Introduction

The Fe-only hydrogenases are important enzymes which catalyze the reduction of protons to molecular hydrogen in numerous microorganisms.[1,2] Since the elucidation of the structures of the Fe-only hydrogenases isolated from *Desulfovibrio desulfuricans* and *Clostridium pasteurianum*,[3,4] transition metal sulfides have been the subject of much research aimed at structural and functional mimics of the Fe-only hydrogenase active site. While the natural enzymes catalyze proton reduction at potentials around −0.4 V *vs* NHE (*ca.* −1 V *vs* Fc/Fc$^+$),[5] the early synthetic models such as **1a**, containing cyanide ligands,[6] required potentials below −2 V. Similarly, the mixed cyanide–phosphine **1b**[7] and the bisphosphine complexes **1c**[8,9] required very negative potentials for reduction. For the all carbonyl complex **1d**, less negative potentials had been measured around −1.7 V,[7,9–11] as might be expected. It was found that the reductive potential of a mixed phosphine–cyanide complex **1b** moved to *ca.* −1.6 V on protonation by a strong acid.[8,12] In addition, catalytic hydrogen evolution could be detected at −1.4 V. A similar behavior was observed for bisphosphine complexes.[8] By contrast, addition of acid to the carbonyl complexes had little effect on the reductive potentials.[9,13]

It has been suggested by recent crystallographic, spectroscopic and theoretical studies that the structure of the bond between the two iron atoms of H-cluster might be azadithiolate (ADT).[14–16] The possibility of nitrogen functionalization induces the potential for a great structural versatility, and a few 2Fe2S model compounds with an aryl or alkyl substituent on the N-bridged atom have been synthesized.[11,17–20] After protonation, the nitrogen-bridged complex itself lowered the reduction potential from around −1.6 V to between −1.16 (strong acid)[11] and −1.36 V (acetic acid).[18] Hydrogen evolution could be observed around −1.5 V with strong acid and −1.6 V with acetic acid. With benzyl as a substituent on the nitrogen, the phenyl group seemed to have an influence on the reductive potential and with a furan group, a reduction potential of −1.13 V was observed,[21] which was getting very close to the potentials of the hydrogenases.



1a $L_1 = L_2 = \text{CN}$
1b $L_1 = \text{Me}_3\text{P}$, $L_2 = \text{CN}$
1c $L_1 = L_2 = \text{Me}_3\text{P}$
1d $L_1 = L_2 = \text{CO}$

Chart 1

Obviously, the introduction of an electron-rich five-membered heterocycle (furan and thiophene) on the Fe–S cluster may influence the reduction potentials of the complexes. Direct attachment to the N-bridged atom can increase its electron density, make the protonation easier, and lead finally to the less negative reduction potential. The incorporation of the 5-membered heterocycle can also be realized through one carbon atom between the N-bridged atom and the heterocycle, which seems more synthetically easy. In addition, the electron negative oxygen of the furan ring may capture a proton by forming a hydrogen bond. However, very few studies have systematically varied the genre of heterocycles. At the early stage of this study, we observed the low reduction potential at −1.13 V caused by the furan-containing 2Fe2S complex in the strong acidic conditions. This observation encouraged us to explore the thiophene-attached 2Fe2S system. Moreover, the introduction of a halogen atom to the heterocycle can provide a possible way to connect the photosensitizer to Fe-only hydrogenase active site model compounds *via* a Pd-catalyzed coupling reaction. Bromine was identified as an ideal candidate. Herein, we report on the synthesis, structure and electrochemical properties of the furan-containing complex **6a** and thiophene-containing complexes **6b** and **6c**.

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† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Details of the electrochemical studies of **6a–6c** and bulk electrolysis. See DOI: 10.1039/b615037c

Results and discussion

Synthesis and characterization

The readily accessible complexes **6a** and **6b** were prepared in a moderate yield according to literature methods by the reaction of [(μ-S_2)$Fe_2(CO)_6$] with 2-aminomethylfuran (**2a**) and 2-aminomethylthiophene (**2b**), respectively (Scheme 1).[21,22] After lithiation of [(μ-S_2)$Fe_2(CO)_6$] and subsequent H–Li exchange reaction, the resulting [(μ-HS)$_2$$Fe_2(CO)_6$] reacted with the diol [($HOCH_2$)$_2$$NCH_2$(2-$C_4H_3X$) (X = O, S)] derived from the hydroxymethylation of **2a** and **2b** to give the 5-membered heterocyclic 2Fe2S derivatives **6a** and **6b** in good yields. It is worth noting that the synthesis is different from the usual procedure, where the reaction was performed between these two compounds [(μ-LiS)$_2$$Fe_2(CO)_6$] and the dichloromethyl amine. Since the chloromethylation reagent $SOCl_2$ decomposed the diol products, **3a** and **3b**, we selected to use the direct reaction of complex **5** with **3a** and **3b**. Attempts to functionalize the thiophene group of **6b** by bromination with Br_2 led to the decomposition of the starting substance. The use of the less aggressive reagent *N*-bromosuccinimide (NBS) resulted, to our surprise, in the generation of the starting complex **4** and the mechanism will not be discussed here. The final preparation of **6c** was obtained from 2-aminomethyl-5-bromothiophene (**2c**), which was obtained from the hydroxymethylation of 5-bromothiophene with (CH_2O)*n* and NH_4Cl at 70 °C by a procedure similar to that used for complex **6b** (Scheme 1).

Complexes **6a–6c** were purified directly by column chromatography and characterized by ^{1}H NMR, ^{13}C NMR, IR and MS spectrometry. The API-ES positive mode mass spectra show the parent ion peaks at m/z 468 $[M + H]^+$ for **6a**, 484 $[M + H]^+$ for **6b**, and 562 $[M + H]^+$ for **6c**. The IR spectra of complexes **6a**, **6b** and **6c** all show three strong CO bands in the region of 1990–2080 cm^{-1}. Table 1 shows a comparison of CO bands for complexes **6a**, **6b** and **6c** and a related diiron aryl-azadithiolate [{(μ-SCH_2)$_2$$NCH_2$(2-$BrC_6H_4$)}$Fe_2(CO)_6$].[20] The values of CO bands of complexes **6a**, **6b** and **6c** are quite similar to those reported for the analogues.

Molecular structure

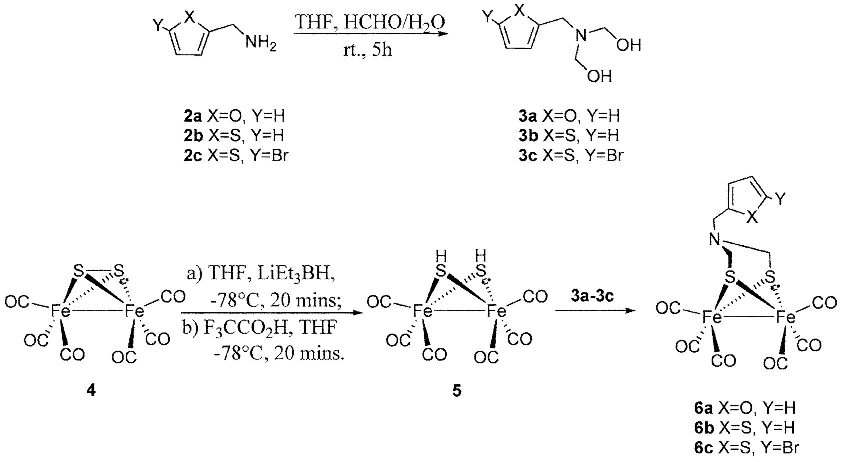
The molecular structures of complexes **6a**, **6b** and **6c** were further confirmed by X-ray crystallography and are shown by ORTEP diagrams in Fig. 1. According to the single-crystal X-ray diffraction analysis, their structures are similar to the active site of Fe-only hydrogenases,[3,4] with the usual distorted square-pyramidal geometry around the iron centre.[17,23–26] The sum of the C–N–C angles around N of complexes **6a**, **6b** and **6c** are 334.5, 332.2 and 340.2° respectively, consistent with an sp^3-hybridization of the N atom. The methylene group between the heterocycles and the N-bridged atom allows the substituted group flexibility compared to the rigid structure of phenyl-substituted ADT-bridged diiron complexes, accordingly influencing the bond angles in the corresponding position. The change of heteroatom does not influence the structures of **6a** and **6b** to any great extent except for the heteroatom position. However, when compared to the aryl-substituted hydrogenase model [{(μ-SCH_2)$_2$$NCH_2$(2-$BrC_6H_4$)}$Fe_2(CO)_6$],[20] the changes seem obvious. In addition to an sp^3-hybridization of the N-bridged atom instead of an sp^2-hybridization for complexes **6a**, **6b** and **6c**, the length of bonds also changed significantly. For example, the range of the C–S bond in complex **6c** is 1.808(4)–1.826(4) Å, much less than that of [{(μ-SCH_2)$_2$$NCH_2$(2-$BrC_6H_4$)}$Fe_2(CO)_6$] (1.863(5)–1.866(5) Å).

Table 1 A comparison of CO bands of analogous diiron heterocyclic-azadithiolate complexes

Complex	CO bands/cm^{-1}	Ref.
6a	2073, 2031, 1995	This work
6b	2073, 2031, 1994	This work
6c	2072, 2031, 1994	This work
[{(μ-SCH_2)$_2$$NCH_2$(2-$BrC_6H_4$)}$Fe_2(CO)_6$]	2074, 2035, 1997	20

Furthermore, it is interesting to note that the conformations of the two complexes **6b** and **6c** are different in the solid state, which changes from periplanar to gauche. In addition, the nonbonding C···N distance between the N-bridged atom and the nearest carbonyl carbon atom is 3.03 Å for **6b**, 2.997 Å for **6a** and 3.101 Å for **6c**. In comparison to other complexes reported, the Fe–Fe bond length is shorter by 0.1 Å, but the Fe–S bond lengths are longer. The change in solid state is mostly due to the electron withdrawing property of the Br atom.

There is a simple packing and no hydrogen bond in the crystal cell packing graphs of complexes **6b** and **6c**, with the exception of



Scheme 1 Synthetic route for complexes **6a–6c**.

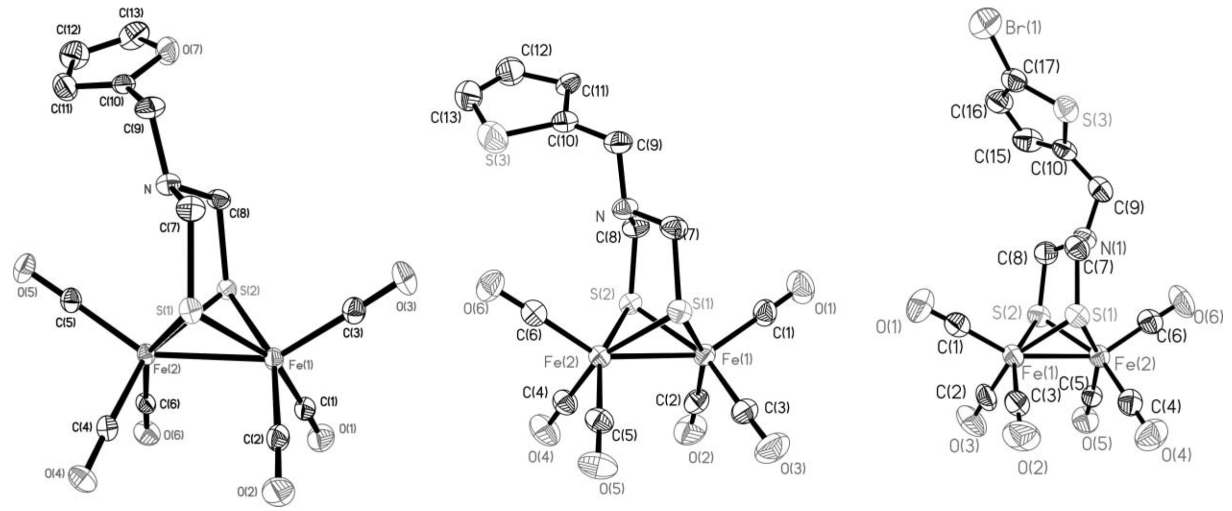


Fig. 1 Molecular structure (ellipsoids at 30% probability level) of **6a**, **6b** and **6c**. Selected distances (Å) and angles (°) for **6a**: Fe–Fe, 2.5127(8), Fe–S, 2.2391(8)–2.2535(9), Fe–C, 1.784(3)–1.808(3), S–C, 1.818(3)–1.825(3), N–C, 1.439(3)–1.472(3), C(8)–N–C(9), 112.4(2), C(7)–N–C(9), 109.45(19), C(8)–N–C(7), 112.3(2); for **6b**: Fe–Fe, 2.5126(6); Fe–S, 2.2476(8)–2.2505(9); Fe–C, 1.784(3)–1.813(4); S–C, 1.820(3)–1.825(3); N–C, 1.441(4)–1.477(4); C(8)–N–C(7), 112.0(3); C(8)–N–C(9), 110.3(3); C(7)–N–C(9), 109.9(3); for **6c**: Fe–Fe, 2.5042(13); Fe–S, 2.2448(15)–2.2571(15); Fe–C, 1.760(5)–1.811(5); S–C, 1.808(4)–1.826(4); N–C, 1.441(5)–1.473(5); C(8)–N–C(7), 113.6(4); C(8)–N–C(9), 113.8(3); C(7)–N–C(9), 112.8(3).

complex **6a**. In the crystal of complex **6a**, there is one molecule in the asymmetric unit and inversion-related molecules are linked to form dimers by C–H···O hydrogen bonds between the alpha-position H13A atom of the furan and an adjacent carbonyl O6 atom at $(-x, 1 - y, -z)$ with C13···O6 3.485(4), H13A···O6 2.56 Å and C13–H13A···O6 is 173°.

Protonation

The protonation of complexes **6a**, **6b** and **6c** showed similar behaviour. When the protonation occurred under the effect of excess $HClO_4$ in CH_3CN, the color of the solution changed from red to orange. The protonation products in CH_3CN were characterized by ^1H NMR and IR correspondingly as shown in Fig. 2. With regard to complexes **6a**, **6b** and **6c**, there was no peak at $\delta < 0$ ppm in the ^1H NMR, indicating that the protonation was occurring on the N-bridged atom rather than the formation of μ-H. The peaks of the thiophene proton and the methylene proton between thiophene and the N-bridged atom were generally shifted to a lower magnetic field than the parent complexes. With the exception of the methylene ($-NCH_2S-$) peaks in the proximity of the ADT nitrogen ($-NCH_2S-$), these were split from 3.34 into 4.20 and 3.27 ppm in a ratio of 1 : 1 for complex **6b**, with an incomplete split but a lower magnetic field shift from 3.32 to 3.72 ppm for corresponding peaks in complex **6c**, and also with an incomplete split from 3.38 to 3.66 ppm for **6a**. The signal at δ 5.37 ppm for complex **6b** and 7.20 ppm for complex **6c** were derived from excess $HClO_4$, which was difficult to eliminate even after repeatedly washing the protonation product with solvent.

As expected, the ν(CO) IR bands shifted when the protonation on N-bridged atom occurred,[11,17,20] and there were suitable shifts of 10–17 cm^{-1} for complex **6a** from 2073, 2031, 1995 cm^{-1} to 2087, 2048, 2011 cm^{-1}, from 2074, 2030, 1995 cm^{-1} to 2084, 2040, 2011 cm^{-1} for complex **6b** and from 2072, 2031, 1994 cm^{-1} to 2086, 2046, 2009 cm^{-1} for complex **6c**. The spectral data further indicated that protonation occurred on the bridging N atom.

For complexes **6a**, **6b** and **6c**, the role of the protonated nitrogen functionality is probably twofold. Above all, the reductive potential of the system should be reduced, simply by the introduced positive charge. In addition, the closeness of the proton on the nitrogen to the iron atoms allows for proton coupled electron transfer,[27] which is likely to reduce the potential.[28] The role of the aromatic substituents in the complexes such as **6a** and **6b** is open to speculation. It could form a hydrogen bond to the proton on the nitrogen with the heteroatom[21], as shown in Fig. 3. This kind of hydrogen bond should be fairly weak, with a bond energy of a few kcal mol^{-1}, but such a bond could still be sufficient to help in fine-tuning the reductive potential of the system.

Electrochemistry

The iron core plays a vital role in the formation of Fe–H hydride and the process of H_2 evolution. Thus, the electrochemical character of **6a**, **6b** and **6c** was investigated by cyclic voltammograms (CVs). The irreversible oxidation peaks in CVs for complexes **6a**, **6b** and **6c** appeared at +0.71, +0.65 and +0.72 V (*vs* Fc/Fc^+) for the $Fe^IFe^I/Fe^{II}Fe^I$ couple, consistent with the reported description.[9] In addition, coulometry was performed to establish that one electron was transferred in the irreversible process. Quasi-reversible reduction peaks were observed at −1.55, −1.64 and −1.54V (*vs* Fc/Fc^+), respectively, for the $Fe^I Fe^I/Fe^IFe^0$ couple (Table 2). The oxidation potential of **6b** was less positive than that of **6a** and **6c**, indicating that it was easier to oxidize. The reduction potential of **6b** was more negative than **6a** and **6c** by around 100 mV, identifying a decreased reduction capability. These observations suggested that the methane group near the heterocycle may increase the electron density in the π system by donating electrons by hyperconjugation (σ conjugation), and slightly decrease the nuclear electron density of the Fe through the three atoms (N, C, S). Such an effect can be increased by the oxygen atom in furan and bromine atom on the thiophene, resulting in less negative reduction potentials. Although the heterocycle is far

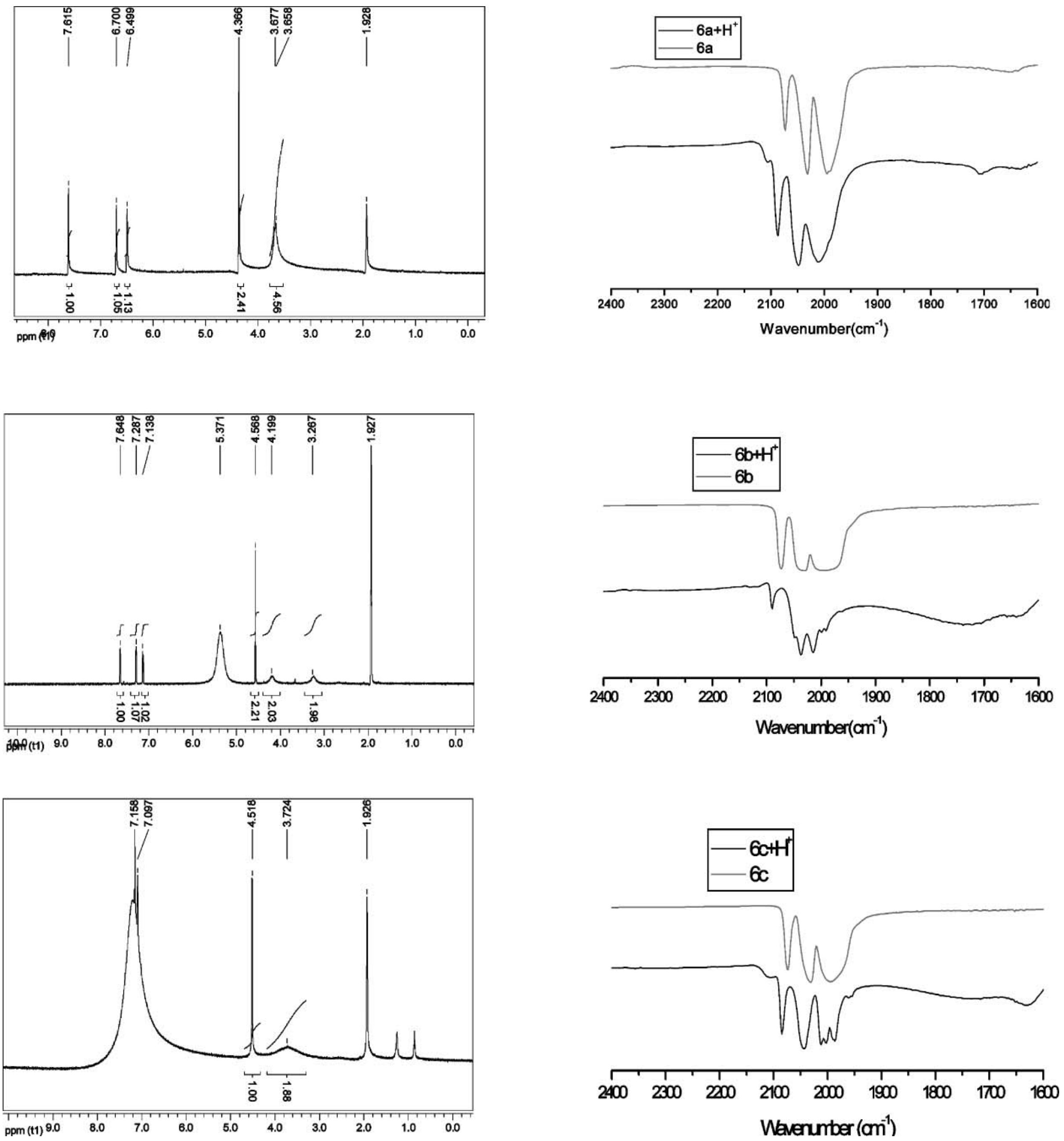


Fig. 2 ^{1}H NMR and IR of the protonation of **6a**, **6b** and **6c**.

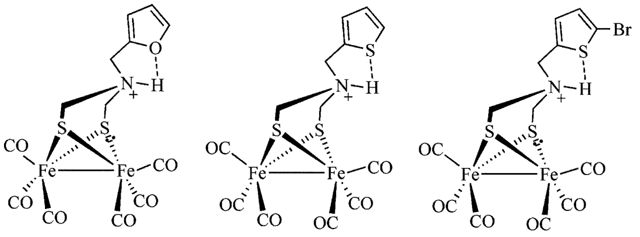


Fig. 3 The possible conformation of complexes **6a**, **6b** and **6c** after protonation.

from the 2Fe2S center, it does have a considerable effect on the redox potential.

The catalytic proton reduction of complexes **6a**, **6b** and **6c** was investigated through cyclic voltammetry on addition of $HClO_4$ in CH_3CN under CO, with the concentration of 0–8 mM, respectively (Fig. 4). The voltammograms of **6a–6c** with 1 equiv. of $HClO_4$ showed new reduction peaks more positive than those of the Fe^IFe^I/Fe^IFe^0 couple, which indicated the catalytic proton reduction.[12] The second reduction peak still indicated the presence of Fe^IFe^I/Fe^IFe^0 couple. With increasing concentration of acid, the current intensity of the first reduction peak increased notably, and the potential shifted toward more negative potential, as expected for catalytic proton reduction.[29] When the acid concentration reached over 4 mM, the new peak showed a sharp negative shift, and the potential change was great. The reason cannot be explained at present, although

Table 2 The redox potentials of **6a–6c** in MeCN[a]

Complex	$Fe^IFe^I/Fe^{II}Fe^I$ (V)	Fe^IFe^I/Fe^IFe^0 (V)
6a	+0.71	−1.55 −1.33
6b	+0.65	−1.64 −1.36
6c	+0.72	−1.54 −1.33

[a] nBu_4NPF_6 (0.1 M in CH_3CN; scan rate: 0.1 V s^{-1}; working electrode: glassy carbon electrode of diameter 3 mm; reference electrode: non-aqueous Ag/Ag$^+$ electrode (0.01 M $AgNO_3$ in CH_3CN); counter electrode: platinum wire.

similar observations have been recorded in the literature.[30,31] Moreover, the reduction potential of the Fe^IFe^I/Fe^IFe^0 couple shows negative shifts (*ca.* 20, 60 and 30 mV) for **6a–6c**. Bubbles could be observed on the surface of the glassy carbon disk electrode (surface area: 1.17 cm^2) during the recording of the electrolysis with controlled potentials at −1.2, −1.3 and −1.2 V, respectively, for the three complexes, which were identified as H_2 by GC. H_2 evolution as a result of bulk electrolysis has been reported recently.[11–13,31] The isolated protonated product, identified by ^{1}H NMR and IR spectroscopy, showed that the protonation of the complexes occurred on the bridging nitrogen atom first, suggesting a chemical–electrochemical–chemical–electrochemical (CECE) process.

In contrast to the redox behavior of the furan-containing complex **6a**, where the catalytic electrochemical reduction of the proton was at −1.13 V (*vs* Fc/Fc$^+$),[21] the thiophene-containing analogues **6b** and **6c** exhibited catalytic reduction potential at −1.20 and −1.09 V, respectively, as shown in Fig. 4. It seemed that the introduction of a bromine atom did have a favourable effect on the acid catalyzing proton reduction. To the best of our knowledge, −1.09 V was the most positive potential recorded for 2Fe2S-hexacarbonyl model compounds, which was 40 mV lower than that of complex **6a** and 90 mV lower than that of $[\{(\mu\text{-}SCH_2)_2NCH_2(p\text{-}BrC_6H_5)\}Fe_2(CO)_6]$.[11] Since these potentials are getting closer to those of the natural hydrogenases and also coming into a range where reduction by an excited photosensitizer of Ru(bpy)$_3$-type is becoming possible, even small improvements are important.

Experimental

Reagents and instruments

The reactions and operations involving organometallic complexes were carried out under a dry, oxygen-free nitrogen atmosphere. THF was dried and distilled by standard methods. Formaldehyde solution was analytical pure, and NBS was recrystallized in distilled water at room temperature. Commercially available reagents, 2-thiophenemethanamine, 5-bromothiophene and $[Fe(CO)_5]$ were used without further purification. The reagent $LiEt_3BH$ was purchased from Aldrich. $[(\mu\text{-}HS)_2Fe_2(CO)_6]$ and $[(\mu\text{-}LiS)_2]Fe_2(CO)_6]$ were prepared according to literature procedures.[11,13] IR spectra were recorded on a JASCO FT/IR 430 spectrophotometer. Proton and ^{13}C NMR spectra were collected on a Varian INOVA 400 NMR spectrometer. Elemental analyses were performed on a Carlo Erba MOD-1106 elemental analyzer. Diffraction measurements were made on a Siemens SMART CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal data and parameters for data collection and refinement are listed in Table 3. CCDC reference numbers 245082, 266225 and 276211. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615037c

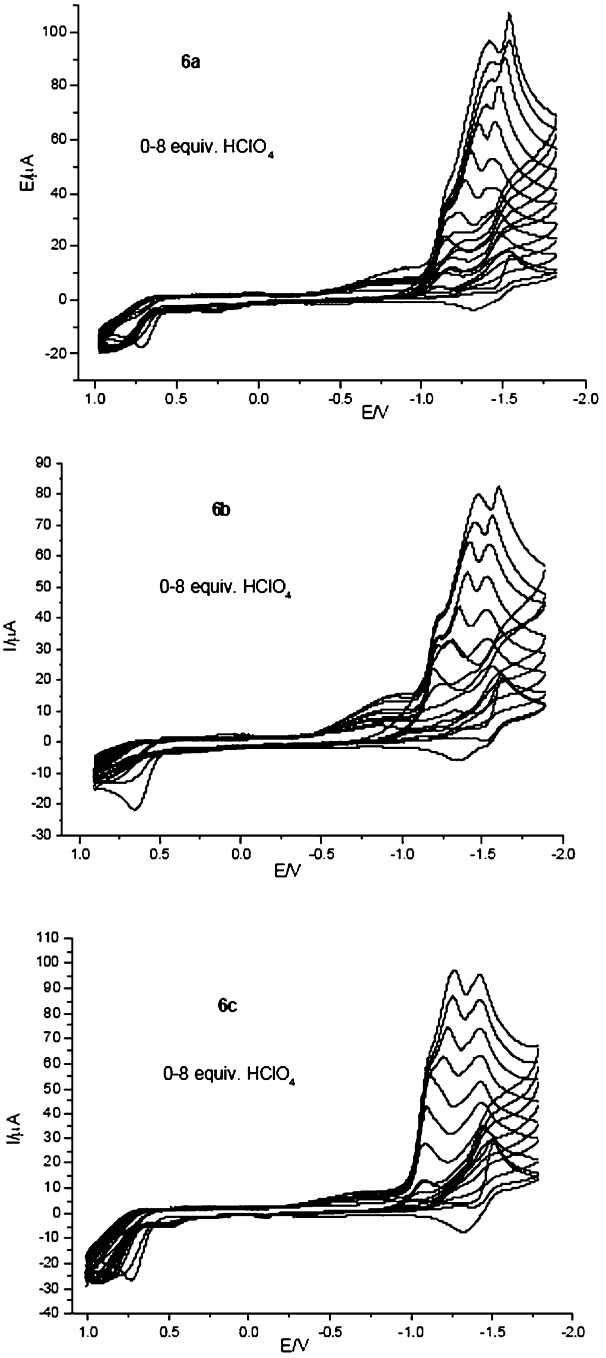


Fig. 4 Cyclic voltammograms of **6a**, **6b** and **6c** with $HClO_4$ (0–8 mM) for the catalytic proton reduction. Sample concentration is 1.0 mmol in 0.05 M $n\text{-}Bu_4NPF_6$–CH_3CN, scan rate 100 mV s^{-1}, working electrode: glassy carbon, reference electrode: Ag/Ag$^+$. All potentials are *versus* Fc/Fc$^+$.

Synthesis of $[\{(\mu\text{-}SCH_2)_2NCH_2(2\text{-}C_4H_3O)\}Fe_2(CO)_6]$ (6a). A solution of **3a** (1.57 g, 10 mmol), prepared from **2a** (0.97 g,

Table 3 Crystal data for complexes **6a–6c**

	6a	**6b**	**6c**
Formula	$C_{13}H_9Fe_2\ NO_7S_2$	$C_{13}H_9Fe_2\ NO_6S_3$	$C_{13}H_8BrFe_2NO_6S_3$
M_w	467.03	483.09	561.99
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	*C*2/*c*	*P*2(1)/*c*
a/Å	7.5684(15)	25.2878(17)	9.160(4)
b/Å	10.878(2)	7.5720(5)	18.101(8)
c/Å	12.426(3)	22.6997(15)	12.148(6)
α/°	111.59(3)	90.00	90.00
β/°	96.93(3)	121.103(10)	109.265(8)
γ/°	108.30(3)	90.00	90.00
V/Å^3	870.2(3)	3721.7(4)	1901.3(15)
Z	2	8	4
ρ_{calcd}/g m^{-3}	1.782	1.724	1.963
T/K	273(2)	273(2)	273(2)
μ/mm^{-1}	1.941	1.923	3.986
F[000]	468	1936	1104
Reflns collected/unique	7286/3804	11269/4356	11402/4300
Feflns observed [$I > 2\sigma(I)$]	3361	3514	2402
Parameters	226	226	235
GOF (on F^2)	1.027	1.041	0.790
$R1$ [$I > 2\sigma(I)$]	0.0335	0.0427	0.0433
w$R2$ [$I > 2\sigma(I)$]	0.0935	0.1284	0.0747

10 mmol) and HCHO–H_2O (2 ml, 20 mmol) in THF (20 ml) was added to a THF solution (20 ml) of **5**, freshly derived from [(μ-S)$_2$Fe$_2$(CO)$_6$] (**4**) (0.344 g, 1.0 mmol), reacted with LiEt$_3$BH (1 M in THF, 1.0 ml, 1.0 mmol) and F_3CCO_2H (0.076 ml, 1.0 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C, then at room temperature for 2 h. During the course of the reaction, the color of the solution turned dark red. After evaporation of the solvent, the crude product was purified by column chromatography with silica gel using hexane as the eluent to give complex **6a** as a red solid (0.19 g, 39%). Recrystallization in hexane afforded crystals of **6a** suitable for X-ray crystallographic study. ESI-MS: *m*/*z*: 467.9 [M + H]$^+$; IR *ν*(CO): 2073, 2031, 1995 cm^{-1}; ^{1}H NMR (CD$_3$CN) *δ* 7.39 (s, 1H), 6.32 (s, 1H), 6.19 (s, 1H), 3.74 (s, 2H), 3.38 (s, 4H) ppm; ^{13}C NMR (CDCl$_3$) *δ* 207.9, 150.3, 142.9, 119.5, 109.0, 54.4, 52.5 ppm. Anal. Calcd for $C_{13}H_9NO_7S_2Fe_2$: C 33.43, H, 1.94, N 3.00. Found: C, 33.44; H, 1.97; N, 3.08%.

Protonation of complex 6a. To a solution of complex **6a** (100 mg) in CHCl$_3$ (3 ml) was added 8 μL HClO$_4$. The solution was stirred for 10 min. The red solution turned to a lighter red and a yellow-orange solid was precipitated. The solvent was decanted and the solid was washed three times with hexane and dried *in vacuo*. The N-protonated product was obtained in 65% yield (65 mg). MS (API-ES): *m*/*z* 467.9 (M$^+$); IR *ν*(CO) : 2087, 2048, 2011 cm^{-1}. ^{1}H NMR (CD$_3$CN): *δ* 7.62 (s, 1H), 6.70 (s, 1H), 6.50 (s, 1H), 4.36 (s, 2H), 3.66 (d, *J* = 3.6 Hz, 4H) ppm.

Synthesis of [{(μ-SCH$_2$)$_2$NCH$_2$(2-C$_4$H$_3$S)}Fe$_2$(CO)$_6$] (6b). A solution of di-(hydroxymethyl)-thiopheneanamine (1.73 g, 10 mmol), prepared from 2-aminomethyl thiophene (1.13 g, 10 mmol) and HCHO–H$_2$O (2 ml, 20 mmol) in THF (20 ml), was added to a THF solution (20 ml) of [(μ-HS)$_2$Fe$_2$(CO)$_6$], freshly derived from [(μ-S$_2$) Fe$_2$(CO)$_6$] (0.344 g, 1 mmol), LiEt$_3$BH (1.0 M in THF 20 ml, 1.0 mmol) and F_3CCO_2H (0.076 ml, 1.0 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C, then 2 h at room temperature, until the color of the solution turned dark red. After evaporation of the solvent, the crude product was purified by column chromatography with silica gel using hexane as the eluent to give complex **6b** as a red solid (0.18 g, 37%). Recrystallization in hexane afforded crystals suitable for X-ray crystallographic study. ESI-MS: *m*/*z* 483.9 [M + H]$^+$; IR *ν*(CO) 2073, 2031, 1994 cm^{-1}; ^{1}H NMR (CD$_3$CN) *δ* 7.26 (s, 1H), 6.94 (s, 1H), 6.86 (s, 1H), 3.91 (s, 2H), 3.34 (s, 4H) ppm; ^{13}C NMR (CDCl$_3$) *δ* 207.9, 139.1, 127.0, 126.1, 77.2, 56.5, 52.3 ppm. Anal. Calcd for $C_{13}H_9NO_6S_3Fe_2$: C 32.32, H, 1.88, N 2.90. Found: C, 32.38; H, 2.05; N, 2.88%.

Protonation of [{(μ-SCH$_2$)$_2$NCH$_2$(2-C$_4$H$_3$S)}Fe$_2$(CO)$_6$] (6b). To a solution of complex **6b** (100 mg) in CHCl$_3$ (3 ml) was added HClO$_4$ (8 μL). After the solution was stirred for 10 min, the red solution turned to a lighter red and a yellow-orange solid was precipitated. The solvent was decanted and the solid was washed three times with hexane and dried *in vacuo*. The N-protonated product was obtained in 62% yield (62 mg). IR *ν*(CO) 2084, 2040, 2011 cm^{-1}. ^{1}H NMR (CD$_3$CN): *δ* 7.65 (d, *J* = 5.2 Hz, 1H), 7.29 (d, *J* = 3.2 Hz, 1H), 7.14 (t, *J* = 4.0 Hz, 1H), 4.57 (s, 2H), 4.20 (s, 2H), 3.27 (s, 2H) ppm.

Synthesis and protonation of [{(μ-SCH$_2$)$_2$NCH$_2$(2-(5-Br–C$_4$H$_2$S)Fe$_2$(CO)$_6$)} (6c). (5-Bromothiophene-2-yl)methanamine (3.4 g, 18 mmol) was prepared from the commercial available product 5-bromothiophene (24.5 g, 151 mmol) reacting with HCHO–H$_2$O (12.4 g, 413 mmol) and ammonium chloride (11.2 g, 211 mmol) in acetic acid (5 g, 5 ml) at 70 °C for 3 h. A solution of di-(hydroxymethyl)-(5-bromothiophene-2-yl) anamine (2.52 g, 10 mmol), prepared from 2-aminomethyl-5-bromothiophene (1.91 g, 10 mmol) and HCHO–H$_2$O (2 ml, 20 mmol) in THF (20 ml), was added to a THF solution (20 ml) of [H$_2$S$_2$Fe$_2$(CO)$_6$], freshly derived from [(μ-S$_2$) Fe$_2$(CO)$_6$] (0.344 g, 1 mmol), LiEt$_3$BH (1.0 M in THF 20 ml, 1.0 mmol) and F_3CCO_2H (0.076 ml, 1.0 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C, then 2 h at room temperature, until the color of the solution turned dark red. After evaporation of the solvent, the crude product was purified by column chromatography with silica gel using hexane as the eluent to give complex **6c** as a red solid (0.19 g, 35%). ESI-MS: m/z: 561.8 $[M + H]^+$; IR ν(CO): 2072, 2031, 1994 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.88 (s, 1H), 6.62 (s, 1H), 3.82 (s, 2H), 3.32(s, 4H) ppm; ^{13}C NMR ($CDCl_3$) δ 207.8, 141.0, 129.8, 127.2, 77.2, 56.7, 52.1 ppm; Anal. Calcd for $C_{13}H_8BrFe_2NO_6S_3$: C 27.78, H, 1.43, N 2.49. Found: C, 28.00; H, 1.59; N, 2.60%. The orange solid N-protonated product of **6c** from **6c** (100 mg, 0.18 mmol) was obtained in a similar manner to that of **6b** (yield: 65 mg, 65%). IR ν(CO): 2086, 2046, 2009, 2002, 1987 cm^{-1}. ^1H NMR (CD_3CN): δ 7.16 (d, J = 3.6 Hz, 1H), 7.09 (d, J = 3.6 Hz, 1H), 4.52 (s, 2H), 3.72 (s, 4H) ppm.

Crystallographic parameters of complexes **6a–6c** are listed in Table 3.

Electrochemical studies of complexes 6a–6c. The acetonitrile (Aldrich, spectroscopy grade) used for electrochemical measurements was dried with molecular sieves and then freshly distilled from CaH_2 under N_2. A solution of 0.1 M n-Bu_4NPF_6 (Fluka, electrochemical grade) in CH_3CN was used as electrolyte, which was degassed by bubbling with dry CO for 10 min before measurement. Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat at a scan rate of 100 mV s^{-1}. CVs were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 3- and 1-μm diamond pastes and sonicated in ion-free water for 10 min. The reference electrode was a non-aqueous Ag/Ag^+ electrode (0.01 M $AgNO_3$ in CH_3CN) and the auxiliary electrode was a platinum wire.

Conclusions

In summary, three heterocycle-containing diiron azadithiolate hexacarbonyl complexes have been synthesized as biomimetic models for the active site of Fe-only hydrogenases. This study provides a new addition to Fe–S chemistry and shows the potential for great structural diversity. The most remarkable feature of this heterocyclic system is the low reduction potential after addition of $HClO_4$, −1.09 V *vs* Fc/Fc^+, about the same as that recently obtained for a related complex[32] where two CO ligands have been replaced by phosphines. This has obviously resulted from the introduction of a bromine on the thiophene ring. The synthesis of these complexes would allow future access to six-membered analogues for evaluation of their redox potentials. Attempts to reach values even closer to the natural hydrogenases are in progress.

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