DOI: 10.1002/ejic.201000619

Synthetic and Electrochemical Studies of [2Fe2S] Complexes Containing a 4-Amino-1,2-dithiolane-4-carboxylic Acid Moiety

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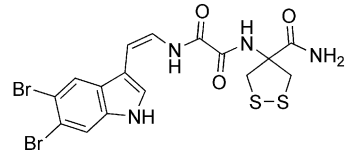
Keywords: Iron / Sulfur / Hydrogenase / Amino acids / Electrocatalysis

In the search for novel [FeFe] hydrogenase model systems several di- and tripeptides containing an 4-amino-1,2-dithiolane-4-carboxylic acid (Adt) moiety or *N*-phenylsulfonyl-Adt-OMe were treated with $Fe_3(CO)_{12}$. The resulting [FeFe] complexes were characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. All complexes were investigated by cyclic voltammetry, and their ability to catalyze the reduction of protons to dihydrogen, as a function of acid concentration, was studied in different solvents.

Introduction

Since the active site of the [FeFe] hydrogenase was elucidated by Peters et al.[1] and Fontecilla-Camps et al.[2] vigorous efforts have been undertaken to model the active site of this enzyme. Numerous model complexes are known and recent progress has been made in mimicking the specific features of the active site of [FeFe] hydrogenase. In particular, the formation of the "rotated" state (formation of a bridging CO ligand and a vacant coordination site on one iron center),[3] the formation of terminal hydrides during catalysis,[4] the establishment of an electron cascade towards the [2Fe2S] subunit,[5] as well as the influence of proton shuffle from an adjacent base towards the iron centres during the electrocatalytic dihydrogen formation[6] are issues that are in the focus of many research groups. However, so far minor attention has been directed towards the use of amino acid containing derivatives for mimicking the enzymatic environment.[7] In continuation of our efforts on [2Fe2S] complexes including an amino acid moiety, 4-amino-1,2-dithiolane-4-carboxylic acid (Adt) derivatives were selected as coordinating ligands. The ligand Adt exhibits a dithiolane ring in the α-position and has been known exclusively as a synthetic building block for a long time.[8] But in 2003 the carboxamide derivative of this conformationally restricted dithiolane was found in a natural occurring dibrominated indole enamide, termed Kottamide E (Scheme 1) that was isolated from the ascidian *Pycnoclavella kottae*.[9]



Scheme 1. Kottamide E containing the carboxamide of Adt.

Since the reaction of carbonyliron complexes with dithiolanes generates stable double chair conformation complexes, Adt could be an ideal precursor molecule for hydrogenase models, offering an internal base, the capability to form noncovalent interactions via the functional group of the side chain[10] and a variety of possible derivatisations.

However, initial attempts with Adt containing [FeFe] model complexes revealed no influence of the pendant base on the catalytic ability of the complexes.[7c] Thus, novel Adt derivatives with additional functional groups were synthesized. A methionine and/or phenylalanine or proline moiety was coupled to the Adt residue, thus building di- and tripeptidic ligands (Scheme 2). Furthermore, a *N*-sulfonyl derivative of Adt offering an acidic NH proton has also been examined (Scheme 2). All dithiolane ligands were treated with $Fe_3(CO)_{12}$ to afford the corresponding [2Fe2S] complexes, and the ability of these compounds to act as [FeFe] hydrogenase model complexes was investigated by cyclic voltammetry. In addition, the electrocatalytical properties of these complexes in different aprotic solvents were compared.

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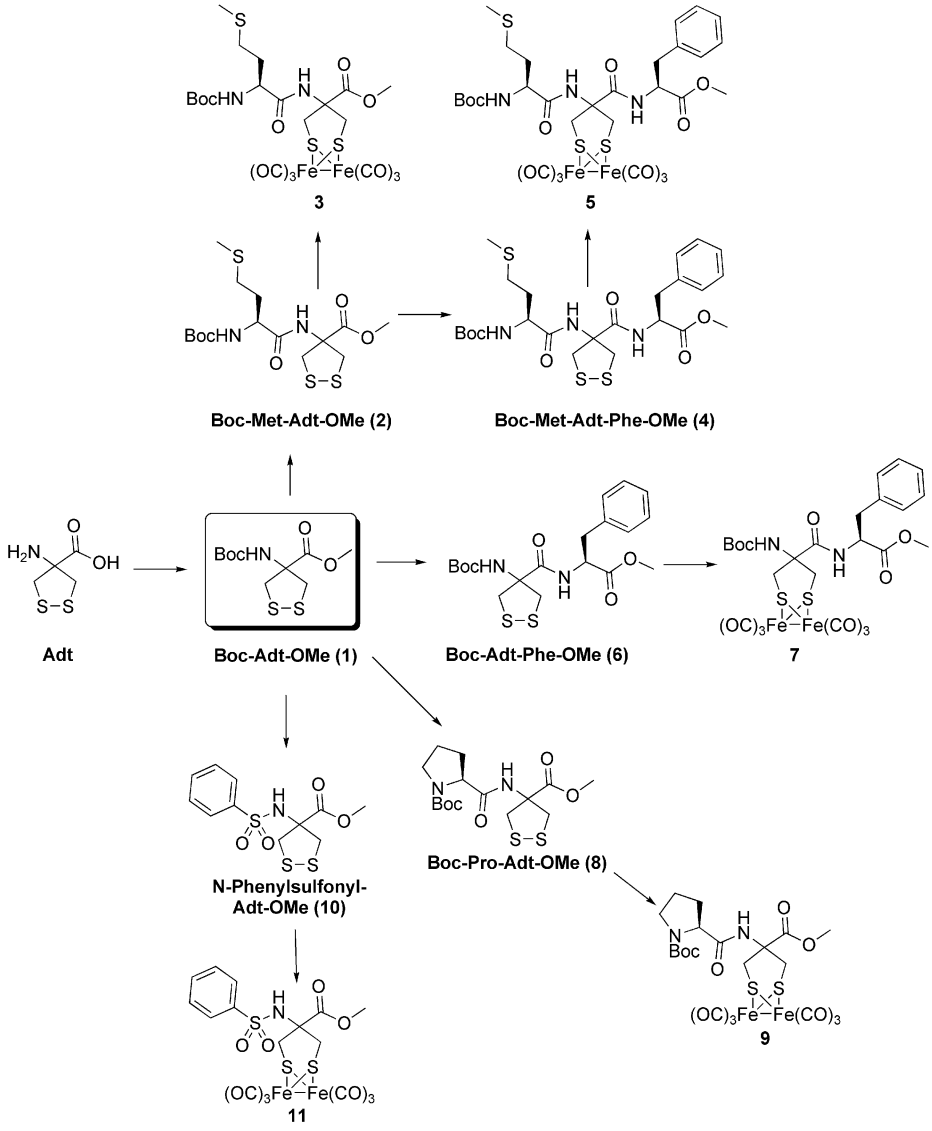
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000619.



Scheme 2. Adt containing ligands and the products of the reactions of these ligands with $Fe_3(CO)_{12}$.

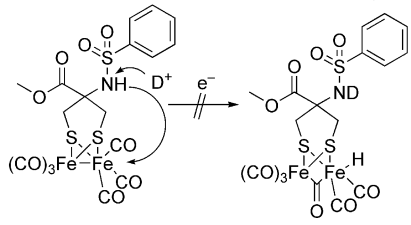
Results and Discussion

The reaction of Boc-Adt-OMe (**1**) with thionyl chloride generates the free amine, which was reacted in situ with 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC), 1-hydroxybenzotriazole (HOBt) and *N*-(*tert*-butoxycarbonyl)-L-methionine to afford the dipeptide **2** (Scheme 2).[12] This molecule possesses a thioether group that enables the formation of [2Fe3S] clusters. The reaction of **2** with $Fe_3(CO)_{12}$ under reflux conditions results in the formation of complex **3** in a moderate yield of 52%. The one- and two-dimensional ^1H and ^{13}C NMR spectra, the *m*/*z* values and isotopic distribution of the mass spectrometry data, as well as elemental analysis revealed the molecular structure of compound **3**. However, no coordination of the methionine sulfur to the iron centre could be observed either by thermal treatment or by the reaction of **3** with trimethylamine *N*-oxide that should force an oxidative cleavage of a CO group[11] and facilitate the coordination of the thioether group.

Compound **2** was treated with sodium hydroxide to generate the associated carboxylic acid, which was used without further purification for the conversion to the tripeptide Boc-Met-Adt-Phe-OMe (**4**) via standard esterification procedures using EDC, HOBt and L-phenylalanine methyl ester.[12] Subsequent reaction of **4** with $Fe_3(CO)_{12}$ afforded the complex **5**. Furthermore, the dipeptide Boc-Adt-Phe-OMe (**6**) and its corresponding [FeFe] complex **7** were synthesized according to the same procedure. Additionally, complexes **3**, **5** and **7** were treated with trifluoroacetic acid (TFA) in an attempt to achieve *N*-Boc-deprotection, however no reaction was observed and no complexes containing a free amino group could be obtained. Thus, we decided to examine the properties of the dipeptide Boc-Pro-Adt-OMe

(**8**) (Scheme 2) in which, unlike in the model compounds **2**, **4** and **6**, linear side chains are not present. Dipeptide **8**, due to the presence of two consecutive cyclic amino acids,[13] should prefer a compact folded backbone conformation with reduced steric interferences in the side chain and therefore display distinct interaction capabilities. *N*-Boc-Proline was treated with H-Adt-OMe to give **8** in moderate yield (47%). Single crystals for X-ray diffraction analysis were obtained by slow evaporation of a solution of **8** in chloroform (see Figure S1). The crystal structure of **8** showed that it is cocrystallized with chloroform and has the expected molecular structure (see Supporting Information). By studying the bond lengths and angles for the Adt part of the compound some interesting features become obvious. The dithiolane ring exhibits two different C–S bond lengths of 178.8(5) and 182.3(6) pm as well as two different C–S–S angles of 92.66(19) and 90.20(19)° (see Table S1). Comparison of the torsion angle C–S–S–C in **1** and **8** revealed an increase from 31.50 to 44.97°, whereas the S–S distance is unchanged being 205.6(3) and 204.6(3) pm, respectively.[12] These data are very similar to those observed for Boc-Adt-Adt-NHMe where the torsion angle (C–S–S–C) is 42.6° and steric reasons have been suggested for the distortion of the dithiolane ring.[13] Unfortunately, all attempts to get single crystals of any of the [FeFe] model complexes were unsuccessful. Reaction of **8** with $Fe_3(CO)_{12}$ resulted in complex **9** (Scheme 2) in good yield (65%), but again attempts to deprotect the peptide with standard reagents (TFA, thionyl chloride, hydrogen chloride) failed. The deprotection of dipeptide **8** with TFA and subsequent reaction with $Fe_3(CO)_{12}$ resulted in a mixture of species that could not be separated.

A different approach was attempted with a sulfonyl group bound to the Adt-OMe residue. Sulfonamides have been known as the largest class of antimicrobial agents for a long time, and have shown to be irreversible inhibitors of cysteine proteases.[14] In addition to their importance in medicinal chemistry,[15] the electron withdrawing properties of the sulfonyl group results in an acidic NH proton, which can be deprotonated under mild conditions.[16] This was confirmed by kinetic studies of the hydrolysis of *p*-nitrophenyl-*o*-methylsulfonamidobenzoate[17] (pK_a = 8.41 in acetonitrile) and *p*-nitrophenyl-*p*-methylsulfonamidobenzoate[18] (pK_a = 7.34 in acetonitrile). Thus a proton shift from the sulfone NH groups to the iron centres is possible. Inspired by these properties, the dipeptide **10** was synthesised and reacted with $Fe_3(CO)_{12}$ in toluene to afford complex **11** in good yield (83%) as an air and moisture stable red solid. To investigate the possible influence of the sulfonamide group on the catalytic mechanism of this complex, NMR investigations were performed in the presence of CD_3COOD. A decrease in the intensity of the NH resonance at δ = 5.71 ppm should be observed due to proton exchange with deuterium. This can occur either via a S_N2 mechanism similar to that discussed by Mandell et al. (Scheme 3)[19] or by dissociation of the N–H bond and subsequent deuteration of the N atom. However, no change in the NMR resonance could be observed, in agreement with IR measurements, with and without acetic acid being present.



Scheme 3. Hypothetical mechanistic pathway for the desired protonation of the [FeFe] core.

Electrochemistry

The cyclic voltammograms (Figure 1) of [FeFe] metal complexes **3**, **5**, **7**, **9** and **11** were recorded in order to observe the electrochemically induced reduction and oxidation properties of these compounds, and to assess their ability to catalyse the formation of dihydrogen from weak acids. A comparison of the electrochemical data is shown in Table 1.

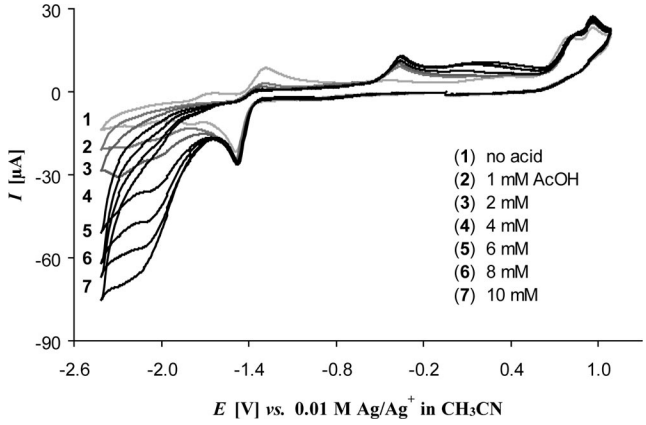


Figure 1. Cyclic voltammograms of complex **9** (1 mM) recorded in the presence of different concentrations of acetic acid.

Table 1. Electrochemical data[a] for the iron complexes discussed herein.

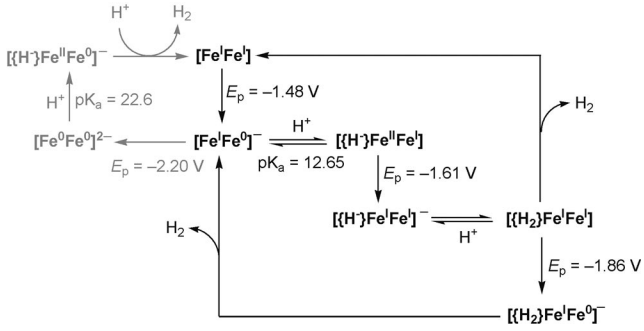
Compound	E_p [Fe^IFe^I]/[$Fe^{II}Fe^I$]	E_p [Fe^IFe^I]/[Fe^0Fe^I]	E_p [Fe^0Fe^I]/[Fe^0Fe^0]
$Fe_2(CO)_6$(Boc-Adt-OMe)[7c]	+0.81[b]	–1.47[b]	–2.09[b]
3	+0.98[b]	–1.52[b]	–1.76[b]
5	+0.95[b]	–1.57[b]	n/a
7	+0.71[b] and +0.94[b,c]	–1.51[b]	–1.89[b]
9	+0.8[b] and +0.97[b,c]	–1.48[b]	–1.81[b]
11	+0.8[b] and +1.0[b,c]	–1.48[b]	–1.72[b]

[a] Potentials given in Volt ± 0.01 vs. 0.01 M Ag/Ag^+ in CH_3CN with 0.10 M [nBu_4N][BF_4]. [b] Irreversible wave. [c] Further oxidation to the [$Fe^{II}Fe^{II}$] state.

Complexes **3**, **5**, **7**, **9** and **11** show quite similar electrochemical properties (Table 1) and as representative example a detailed description will be given for compound **9**. Following a cathodic scan of complex **9** (Figure 1) starting at 0.00 V vs. 0.01 M Ag/Ag^+ in CH_3CN, the cyclic voltammogram reveals an irreversible reduction peak at $E_{p,red}$ = –1.48 V that is attributable to the [Fe^IFe^I]→[Fe^IFe^0]$^-$ pro-

cess. This irreversible signal suggests an EC (E = electrochemical reaction, C = chemical reaction) mechanism whereby the Fe^IFe^I state is converted to $[Fe^IFe^0]^-$ by a one-electron reduction followed by a fast change in the bonding properties within the molecule, which is in good agreement with literature results.[20] This change in bonding properties is best described by the cleavage of the Fe–Fe bond and/or the appearance of a bridging carbonyl group.[20,21] At –1.81 V a further small irreversible reduction wave can be observed, and is attributed to the $[Fe^IFe^0]^- \rightarrow [Fe^0Fe^0]^{2-}$ process in accordance with data collected on $Fe_2(CO)_6$-(Boc-Adt-OMe).[7a] After reversal of the scan, an oxidation peak at –1.23 V occurs, 250 mV more positive than the $[Fe^IFe^I] \rightarrow [Fe^IFe^0]^-$ reduction potential, suggesting that this signal does not arise from the simple re-oxidation of $[Fe^IFe^0]^-$ but from the oxidation of the rapidly formed reaction product. At ca. +0.8–1.0 V the $[Fe^IFe^I]$ oxidation peak can be observed. In addition, in the case of complexes **7** and **9** a second well separated oxidation wave occurs, which can be ascribed to the $[Fe^IFe^{II}]^+ \rightarrow [Fe^{II}Fe^{II}]^{2+}$ process.

In the presence of acetic acid (AcOH) the initial reduction potential at –1.48 V remains constant. Thus, prior to the reduction no protonation of compound **9** takes place (this is equally true for **3**, **5**, **7** and **11**), suggesting no involvement of the ligand amide groups as proton donors. However, with continuous addition of acetic acid a steadily increasing current at around –2.2 V emerged, indicating the electrocatalytic formation of dihydrogen.[22] In agreement with the literature, the second reduction step that creates $[Fe^0Fe^0]^{2-}$ is followed by two protonation reactions leading to the generation of dihydrogen and the simultaneous regeneration of the initial $[Fe^IFe^I]$ state (Scheme 4).[22a]



Scheme 4. Catalytic mechanisms for the electrochemical reactions of [FeFe] complexes in the presence of a weak (grey) and strong acids (black). The E_p values reported are for compound **9**.

When TFA (pK_a = 12.65 in CH_3CN)[23] is used in the voltammetry experiments instead of acetic acid (pK_a = 22.6 in CH_3CN),[23] no shift in the $[Fe^IFe^I] \rightarrow [Fe^IFe^0]^-$ reduction potential could be observed (Figure 2), confirming that TFA is not able to remove the Boc protecting group from the proline nitrogen, as also seen in the synthesis experiments. Nevertheless, the cyclic voltammograms (Figure 2) are strongly altered compared to those recorded in the presence of AcOH. It is known that, in contrast to weak acids,[22] the one-electron reduction product $[Fe^0Fe^I]$ can react very fast with protons from strong acids like TFA to give a $[\{H^-\}Fe^{II}Fe^I]$ assembly (Scheme 4).[22b] For low TFA concentrations (< 4 mM) the reduction to $[HFe^IFe^I]$ is followed by a second protonation ($[\{H_2\}Fe^IFe^I]$), resulting in the release of dihydrogen at around –1.6 V. Thus, an ECEC mechanism is suggested in the presence of TFA (< 4 mM) in accordance with the results found by Pickett et al.[24] At high concentrations of TFA (> 4 mM) a new catalytic reduction signal can be observed, which continuously shifts to more negative potentials, ending up at –1.86 V when the concentration of TFA is 10 mM. This behaviour can be explained by further reduction of $[\{H_2\}Fe^IFe^I]$ resulting in the formation of dihydrogen and regeneration of $[Fe^0Fe^I]^-$ (Scheme 4).[24]

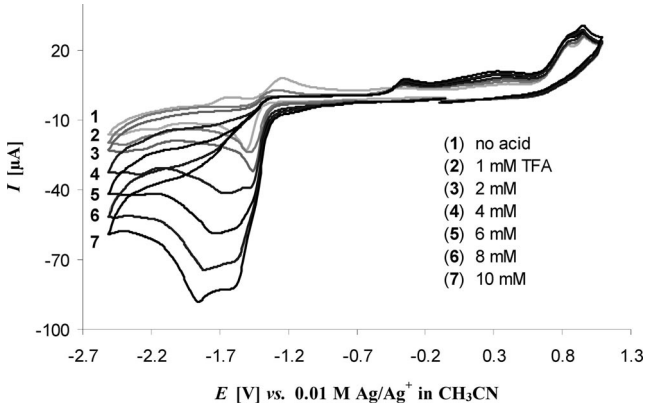


Figure 2. Cyclic voltammograms of complex **9** (1 mM) recorded in the presence of different concentrations of trifluoroacetic acid.

To obtain further information about the parameters that affect the potential at which dihydrogen is formed, and the redox properties of the [FeFe] complexes, cyclic voltammetry measurements of complex **9** were repeated in the aprotic solvents dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and dichloromethane (CH_2Cl_2) in the presence of 5 and 10 mmol AcOH, the solvent leads to an alteration in the acid strength [pK_a = 13.2 in DMF; pK_a = 12.3 in DMSO] as compared to CH_3CN.[25,26] To allow for comparison with the data obtained in CH_3CN, the reduction potentials of AcOH in these solvents were investigated in the absence of the complex (Table 2). In contrast to the strong acetic acid reduction signal at around –2.3 V in CH_3CN, the respective spectra in DMF and DMSO revealed almost no dihydrogen development up to –2.7 and –2.9 V vs. 0.01 M Ag/Ag^+ in CH_3CN, respectively, values that are near to the solvent cut off potentials. In the case of the CH_2Cl_2 voltammogram a small reduction peak at around –2.1 V can be observed (solvent cut off at around –2.2 V).

Without the addition of AcOH the redox potential of the $[Fe^IFe^I] \rightarrow [Fe^IFe^0]^-$ reduction of complex **9** is similar in all investigated solvents. Addition of 5 mmol AcOH to a DMF solution of **9** results in a continuous increase in the current starting at ca. –2.0 V, but not in a distinct reduction signal (Figure 3). Furthermore, the intensity of the catalytic cur-

Table 2. Comparison of electrochemical reduction of AcOH in different solvents in the absence and in the presence of complex **9**.[a]

Solvent	E_p (H^+/H_2)	E_p (H^+/H_2) in the presence of **9**
CH_3CN	–2.3	shoulder at –2.1
DMF	< –2.7	no distinct reduction peak
DMSO	< –2.9	no distinct reduction peak
CH_2Cl_2	–2.1	shoulder at –2.1

[a] Potentials in V vs. 0.01 M Ag/Ag^+ in CH_3CN containing 0.10 M [nBu$_4$N][BF_4] as the supporting electrolyte.

rent increases only slightly when the acid concentration is increased from 5 to 10 equiv., and nearly no difference could be observed when the concentration is changed from 10 to 15 mmol AcOH. With DMSO as the solvent, **9** exhibited similar electrochemical behaviour as in DMF solution, again no correlation between the AcOH concentration and the catalytic current was observed. The scan recorded in CH_2Cl_2 shows a shoulder at around –2.1 V associated with the catalytic transformation of protons to dihydrogen (Figure 3), and a stepwise increase of the catalytic current. Thus, with respect to the characterisation of the electrocatalytical properties, only CH_2Cl_2 is comparable to CH_3CN, however with the limitation that the cut off potential is far more positive at around –2.2 V vs. 0.01 M Ag/Ag^+ in CH_3CN.

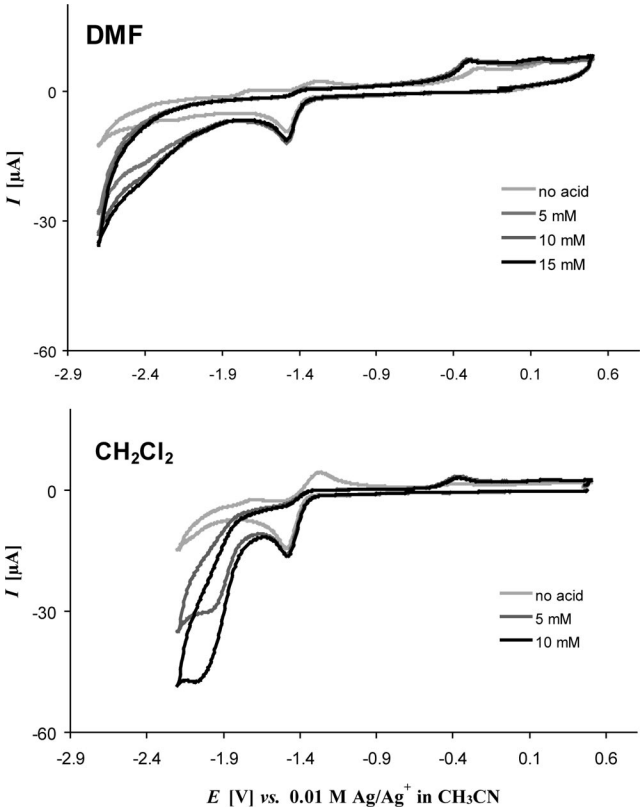


Figure 3. Cyclic voltammograms of complex **9** (1 mM) recorded in the presence of acetic acid in DMF (top) and CH_2Cl_2 (bottom).

Conclusions

Diiron dithiolato compounds containing Adt have been prepared in good yields, and can be considered as [FeFe] hydrogenase model compounds. The *N*-Boc-protected amino acid backbones of these novel di- and tripeptidic complexes do not influence the electrochemical formation of dihydrogen in the presence of AcOH or TFA. This behaviour was also observed in the case of a sulfonamide complex containing an acidic NH proton. A comparative study of the electrochemical properties of compound **9** in DMSO, DMF, CH_2Cl_2 and CH_3CN revealed a very similar redox response of the complex in all solvents, but the dihydrogen formation strongly depends on the solvent. Only in the case of CH_2Cl_2 is the catalytical current associated with dihydrogen formation comparable to that observed with the standard solvent CH_3CN, whereas DMF and DMSO do not appear to be suitable solvents for the characterisation of the electrocatalytical properties of [2Fe2S] complexes.

Experimental Section

General: All reactions were carried out in an argon atmosphere. Toluene and THF were dried with KOH and distilled from sodium/benzophenone. Chemicals were received from Fluka or Acros and used without further purification. Compounds **1**, **2**, **4** and **6** as well as Boc-Pro-OH were synthesized following literature procedures.[12,27] Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates (detection under UV light at 254 nm) and FC (flash chromatography) on Fluka silica gel 60. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AVANCE 200 MHz or 400 MHz spectrometer, whereby the splitting of the proton resonances are defined as s (singlet), d (doublet), t (triplet) and m (multiplet). Chemical shifts are given in parts per million with reference to an internal standard, $CHCl_3$ or $SiMe_4$. Infrared spectra were obtained from KBr pellets with a Perkin–Elmer 2000 FT-IR instrument or Perkin–Elmer 983 spectrophotometer. The intensity of the signals are assigned as vs (very strong), s (strong), m (medium) and w (weak). Electron impact mass spectrometry (MS) was carried out at 70 eV with a Finnigan SSQ710 or Q-TOF Micro instrument (Micromass, Waters) with desorption electron ionisation (DEI), fast atom bombardment (FAB) or electron spray ionisation (ESI) mode. Expected and experimental isotope distributions were compared. Elemental analyses (C, H, N, S) were carried out on a LECO CHNS-931 instrument or on a Fisons EA-1108 apparatus. Prior to the elemental analyses, all samples were dried under high vacuum for at least one day, and the remaining amounts of hexane are in agreement with the amounts determined from ^{1}H NMR spectroscopy.

[(Boc-Met-Adt-OMe)Fe$_2$(CO)$_6$] (3): Boc-Met-Adt-OMe (**2**) (25 mg, 0.061 mmol) and $Fe_3(CO)_{12}$ (31 mg, 0.061 mmol) were dissolved in dry toluene (20 mL) and refluxed for 30 min. The solvent was evaporated under reduced pressure and the crude product was purified by FC (THF/hexane = 1:3); yield 22 mg (52%) as a red solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.82 (m, 1 H, N*H*Boc), 4.90 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, N*H*-Adt), 4.30 (m, 1 H, C*H*), 3.66 (s, 3 H, OCH_3), 3.06 and 2.77 (2d, $^2J_{H,H}$ = 14.2 Hz, 2 H, CCH_AH$_B$S), 2.52 (t, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2SCH$_3$), 2.40 and 2.27 (2d, $^2J_{H,H}$ = 13.4 Hz, 2 H, CCH$_A$$H_B$S), 2.11 (s, 3 H, SC$H_3$), 2.02–1.83 (m, 2 H, C$H_2$CH) 1.41 [s, 9 H, C(C$H_3$)$_3$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 207.2 (*C*O), 172.0 [*C*(O)OCH$_3$], 170.7 [*C*(O)NH], 156.2

[*t*BuO*C*(O)NH], 80.7 [*C*(CH$_3$)$_3$], 61.5 (SCH$_2$*C*CH$_2$S), 53.4 (O*C*H$_3$), 53.1 (*C*HNHBoc), 30.3 (*C*H$_2$CH), 30.0 (S*C*H$_2$C*C*H$_2$S), 29.7 (*C*H$_2$SCH$_3$), 28.3 [C(*C*H$_3$)$_3$], 15.2 (S*C*H$_3$) ppm. MS (FAB in *meta*-nitrobenzyl alcohol): *m*/*z* = 691 [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 3423 (m), 2960 (m), 2924 (m), 2853 (m), 2076 (vs), 2036 (vs), 1996 (vs), 1740 (s), 1686 (s) cm^{-1}. $C_{21}H_{26}Fe_2N_2O_{11}S_3$·1.7 hexane (690.35): calcd. C 44.78, H 6.00, N 3.35, S 11.50; found C 44.56, H 6.19, N 3.42, S 11.76.

[(Boc-Met-Adt-Phe-OMe)Fe$_2$(CO)$_6$] (5): Boc-Met-Adt-Phe-OMe (**4**) (44 mg, 0.081 mmol) and $Fe_3(CO)_{12}$ (41 mg, 0.081 mmol) were dissolved in dry THF (40 mL) and refluxed for 45 min. The solvent was evaporated under reduced pressure and the crude product was purified by FC (THF/hexane = 1:1); yield 29 mg (42%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.14 (m, 5 H, $H_{aromatic}$), 6.98 (s, 1 H, N*H*-Adt), 5.09 (m, 1 H, N*H*Boc), 4.84 [m, 1 H, C*H*C(O)OCH$_3$], 4.71 (m, 1 H, C*H*NHBoc), 4.22 (s, 3 H, OC*H*$_3$), 3.71 (m, 4 H, SC*H*$_2$C), 3.49 (m, 2 H, C*H*$_2$Ph), 3.12 (m, 2 H, C*H*$_2$SCH$_3$), 2.58 (m, 2 H, C*H*$_2$CH$_2$S), 2.10 (s, 3 H, SC*H*$_3$), 1.49 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.3 (*C*O), 171.5 [*C*(O)OCH$_3$], 167.7 [CH*C*(O)NH], 155.9 [O*C*(O)NH], 132.3, 130.8, 129.9, 128.2 ($C_{aromatic}$), 80.8 [*C*(CH$_3$)$_3$], 68.1 (SCH$_2$*C*CH$_2$S), 53.8 (*C*HCH$_2$Ph), 53.6 (*C*HNHBoc), 52.3 (O*C*H$_3$), 37.9 (*C*H$_2$Ph), 30.3 (SCH$_2$*C*H$_2$CH), 30.2 (S*C*H$_2$C*C*H$_2$S), 29.3 (*C*H$_2$SCH$_3$), 28.2 [C(*C*H$_3$)$_3$], 15.2 (S*C*H$_3$) ppm. MS (Micro-ESI in CHCl$_3$/CH$_3$OH): *m*/*z* = 860 [M + Na]$^+$. IR (KBr): $\tilde{\nu}$ = 3418 (s), 2955 (m), 2924 (s), 2850 (m), 2074 (vs), 2035 (vs), 1989 (vs), 1931 (w), 1693 (vs), 1514 (m), 1504 (m) cm^{-1}. $C_{30}H_{35}Fe_2N_3O_{12}S_3$·0.5 hexane (837.53): calcd. C 45.01, H 4.81, N 4.77, S 10.92; found C 45.11, H 4.98, N 4.62, S 11.05.

[(Boc-Adt-Phe-OMe)Fe$_2$(CO)$_6$] (7): Boc-Adt-Phe-OMe (**6**) (25 mg, 0.059 mmol) and $Fe_3(CO)_{12}$ (30 mg, 0.059 mmol) were dissolved in dry toluene (20 mL) and the dark green solution was stirred under reflux for 30 min. The solvent was evaporated under reduced pressure and the crude product was purified by FC (THF/hexane = 1:3); yield 28 mg (67%) as a red solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.24–6.96 (m, 5 H, $H_{aromatic}$), 6.64 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, N*H*CH), 4.69 (m, 2 H, N*H*Boc and NHC*H*), 3.66 (s, 3 H, OC*H*$_3$), 3.04 (d, $^3J_{H,H}$ = 4.4 Hz, 2 H, CHC*H*$_2$), 2.92 and 2.76 (2d, $^2J_{H,H}$ = 14 Hz, 2 H, C*H*$_A$H$_B$S), 2.40 and 2.20 (2d, $^2J_{H,H}$ = 14.6 Hz, 2 H, CH$_A$*H*$_B$S), 1.41 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 207.0, 206.6 (*C*O), 171.5 [*C*(O)NH], 170.7 [*C*(O)OCH$_3$], 153.3 [*t*BuO*C*(O)NH], 135.5, 129.2, 127.2, 125.5 ($C_{aromatic}$), 81.8 [*C*(CH$_3$)$_3$], 61.6 (SCH$_2$*C*CH$_2$S), 53.4 (NH*C*H), 52.4 (O*C*H$_3$), 37.9 (CH*C*H$_2$), 30.3 (S*C*H$_2$C*C*H$_2$S), 28.1 [C(*C*H$_3$)$_3$] ppm. MS (Micro-ESI in CHCl$_3$): *m*/*z* = 729 [M + Na]$^+$. IR (KBr): $\tilde{\nu}$ = 3371 (m), 3315 (m), 2955 (m), 2927 (m), 2855 (w), 2074 (vs), 2036 (vs), 2000 (vs), 1750 (s), 1690 (s), 1649 (s) cm^{-1}. $C_{25}H_{26}Fe_2N_2O_{11}S_2$·0.6 hexane (706.33): calcd. C 45.32, H 4.57, N 3.70, S 8.46; found C 45.46, H 4.56, N 3.42, S 8.10.

Boc-Pro-Adt-OMe (8): Thionyl chloride (130 μL) was added to a solution of Boc-Adt-OMe (**1**) (500 mg, 1.79 mmol) in methanol (10 mL) at 0 °C. The solution was heated to 50 °C and stirred for 6 h, followed by removal of the solvent under reduced pressure. The remaining residue (HCl·H-Adt-OMe) was dissolved in dimethylformamide (10 mL) at 0 °C and 1-hydroxybenzotriazole (HOBt) (306 mg, 2.26 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (380 mg, 1.98 mmol) and Boc-Pro-OH (488 mg, 2.26 mmol) were added to the solution. After 20 min at 0 °C triethylamine (0.32 mL, 2.30 mmol) was added, and the solution was stirred for additional 17 h at room temperature. Water (3 mL) was added and after 30 min the solution was twice extracted with ethyl acetate (20 mL). The combined organic phases were extracted with 10% citric acid, saturated $NaHCO_3$ and water. After drying the solution with Na_2SO_4 and removal of the solvent under reduced pressure, the crude product was purified by FC (ethyl acetate/hexane = 35:65); yield 318 mg (47%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1 H, N*H*), 4.29 (m, 1 H, C*H*), 3.74 (s, 3 H, OC*H*$_3$), 3.52 (m, 2 H, NC*H*$_2$), 3.33 (m, 4 H, SC*H*$_2$CC*H*$_2$S), 2.32–2.01 (m, 1 H, CHCH$_2$C*H*$_2$), 1.85 (m, 3 H, CH*C*H$_2$CH$_2$ and CHCH$_2$C*H*$_2$), 1.45 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1 [*C*(O)OCH$_3$], 170.1 (*C*ONH), 155.8 (*t*BuO-*C*ONH), 80.8 [*C*(CH$_3$)$_3$], 70.7 (SCH$_2$*C*CH$_2$S), 60.1 (*C*H), 53.2 (O*C*H$_3$), 47.6 (N*C*H$_2$), 47.0 (S*C*H$_2$C*C*H$_2$S), 30.8 (CH*C*H$_2$CH$_2$), 28.3 [C(*C*H$_3$)$_3$], 24.3 (CHCH$_2$*C*H$_2$) ppm. MS (DEI): *m*/*z* = 376 [M]$^+$. IR (KBr): $\tilde{\nu}$ = 3274 (s), 3219 (s), 3054 (m), 2975 (s), 2877 (m), 1748 (s), 1682 (s), 1543 (s), 1479 (m), 1424 (s), 1289 (s) cm^{-1}. $C_{15}H_{24}N_2O_5S_2$ (376.50): calcd. C 47.85, H 6.43, N 7.44, S 17.03; found C 48.05, H 6.69, N 7.17, S 17.04.

[(Boc-Pro-Adt-OMe)Fe$_2$(CO)$_6$] (9): Boc-Pro-Adt-OMe (**8**) (103 mg, 0.27 mmol) and $Fe_3(CO)_{12}$ (138 mg, 0.27 mmol) were dissolved in dry toluene (40 mL) and refluxed for 90 min. The solvent was evaporated under reduced pressure and the crude product was purified by FC (THF/hexane, 1:1); yield 116 mg (65%) as a red solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.89 (s, 1 H, N*H*), 4.38 (m, 1 H, C*H*), 3.62 (s, 3 H, OC*H*$_3$), 3.28 (m, 2 H, NC*H*$_2$), 2.57 (m, 2 H, SC*H*$_A$H$_B$), 2.24 (m, 3 H, SCH$_A$*H*$_B$ and CHC*H*$_2$CH$_2$), 1.85 (m, 3 H, CHC*H*$_2$CH$_2$ and CHCH$_2$C*H*$_2$), 1.47 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 207.3 (*C*O), 172.4 [*C*(O)OCH$_3$], 171.1 [*C*(O)NH], 156.6 (*t*BuO*C*ONH), 80.7 [*C*(CH$_3$)$_3$], 61.6 (SCH$_2$*C*CH$_2$S), 59.2 (*C*H), 53.2 (O*C*H$_3$), 46.7 (N*C*H$_2$), 29.4 (S*C*H$_2$C*C*H$_2$S), 26.3 [C(*C*H$_3$)$_3$], 24.6 (CH*C*H$_2$CH$_2$), 22.3 (CHCH$_2$*C*H$_2$) ppm. MS (Micro-ESI in CH$_2$Cl$_2$/CH$_3$OH): *m*/*z* = 679 [M + Na]$^+$. IR (KBr): $\tilde{\nu}$ = 2966 (w), 2930 (w), 2867 (w), 2076 (vs), 2036 (vs), 1999 (vs), 1742 (m), 1639 (m), 1410 (m) cm^{-1}. $C_{21}H_{24}Fe_2N_2O_{11}S_2$·0.3 hexane (656.27): calcd. C 40.15, H 4.17, N 4.11, S 9.40; found C 40.24, H 4.21, N 4.06, S 9.30.

***N*-Phenylsulfonyl-Adt-OMe (10):** Thionyl chloride (17 μL, 0.23 mmol) was added to a solution of Boc-Adt-OMe (**1**) (64 mg, 0.23 mmol) in dry MeOH (1.5 mL) at 0 °C. The solution was heated to 50 °C and stirred for 3 h. Removal of the solvent under reduced pressure afforded H-Adt-OMe·HCl (50 mg), which was used in the next step without further purification. H-Adt-OMe·HCl was suspended in dry CH_2Cl_2 (2 mL) and phenylsulfonyl chloride (36 μL, 0.28 mmol) and triethylamine (0.11 mL, 0.79 mmol) were added. The mixture was stirred at room temp. for 24 h and then at 40 °C for 4 h. After evaporation of the solvent under reduced pressure, the residue was purified on silica gel (3 g) using CH_2Cl_2 as the eluent; yield 38 mg (51%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.94 (m, 5 H, $H_{aromatic}$), 5.71 (s, 1 H, N*H*), 3.67 (s, 3 H, OC*H*$_3$), 3.61 (d, $J_{H,H}$ = 12.0 Hz, 2 H, 2 × SC*H*$_A$H$_B$), 3.42 (d, $J_{H,H}$ = 12.0 Hz, 2 H, 2 × SCH$_A$*H*$_B$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.2, 133.1, 129.1, 127.1 ($C_{aromatic}$), 73.5 (SCH$_2$*C*CH$_2$S), 53.4 (O*C*H$_3$), 47.3 (S*C*H$_2$C*C*H$_2$S) ppm. MS (ESI): *m*/*z* = 342 [M + Na]$^+$. IR (KBr): $\tilde{\nu}$ = 3250 (m), 3226 (s), 1747 (vs), 1453 (s), 1324 (m), 1295 (s), 1154 (s), 1087 (s) cm^{-1}. $C_{11}H_{13}NO_4S_3$ (319.44): calcd. C 41.36, H 4.10, N 4.39, S 30.12; found C 41.31, H 4.11, N 4.42, S 30.16.

[(*N*-Phenylsulfonyl-Adt-OMe)Fe$_2$(CO)$_6$] (11): *N*-Phenylsulfonyl-Adt-OMe (**10**) (7 mg, 0.022 mmol) and $Fe_3(CO)_{12}$ (12 mg, 0.022 mmol) were dissolved in dry toluene (20 mL) and refluxed for 1.5 h. The solvent was evaporated under reduced pressure and the dark brown crude product was purified by FC (THF/hexane = 1:3); yield 11 mg (83%) of a red solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.79–7.58 (m, 5 H, $H_{aromatic}$), 3.67 (s, 1 H, N*H*), 3.52

(s, 3 H, OCH_3), 2.71 (d, $^2J_{H,H}$ = 14.8 Hz, 2 H, SCH_AH$_B$), 2.53 (d, $^2J_{H,H}$ = 14.8 Hz, 2 H, SCH$_A$$H_B$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 207.0, 206.7 (*C*O), 169.3 [*C*(O)OCH$_3$], 139.9, 133.4, 129.2, 127.7 ($C_{aromatic}$), 63.6 (SCH$_2$*C*CH$_2$S), 53.6 (*C*H$_3$), 27.8 (S*C*H$_2$C*C*H$_2$S) ppm. MS (DEI): *m*/*z* = 543 [M – 2CO]$^+$, 515 [M – 3CO]$^+$, 487 [M – 4CO]$^+$, 459 [M – 5CO]$^+$, 431 [M – 6CO]$^+$. IR (KBr): $\tilde{\nu}$ = 3431 (s), 3066 (w), 2955 (m), 2922 (m), 2852 (m), 2077 (vs), 2036 (vs), 2002 (vs), 1743 (s) cm^{-1}.

Electrochemistry: Cyclic voltammograms were measured in a three-electrode cell with a 2.0 mm diameter glassy carbon disc working electrode, a platinum auxiliary electrode, and a Ag/Ag$^+$ reference electrode containing 0.01 M $AgNO_3$/CH_3CN. The solvent contained 0.1 M [*n*Bu$_4$N][BF$_4$] as the supporting electrolyte. Measurements were performed at room temp. using an EG & G PARC 273A potentiostat/galvanostat. Deaeration of the sample solutions was accomplished by passing a stream of argon through the solutions for 5 min prior to the measurements, and the solutions were kept under argon for the duration of the measurements. To monitor the stability of the reference electrode ferrocene was used as an internal standard ($E_{1/2}$ = +0.087 vs. 0.01 M $AgNO_3$ in CH_3CN).[28]

Structure Determinations: The intensity data for **8** were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[29,30]

Crystal Data for 8: $C_{15}H_{24}N_2O_5S_2{\cdot}2CHCl_3$, M_r = 615.22 g mol^{-1}, colourless prism, size 0.05 × 0.05 × 0.04 mm^3, monoclinic, space group $P2_1$, a = 9.2374(4), b = 11.6975(7), c = 13.6656(6) Å, β = 106.68(3)°, V = 1414.47(22) Å^3, T = –90 °C, Z = 2, $\rho_{calcd.}$ = 1.444 g cm^{-3}, μ (Mo-K_α) = 7.84 cm^{-1}, F(000) = 632, 9433 reflections within the limits h(–11/11), k(–14/15), l(–17/15), measured in the range 2.89° ≤ θ ≤ 27.48°, completeness θ_{max} = 99.3%, 5786 independent reflections, R_{int} = 0.0503, 3857 reflections with $F_o > 4\sigma(F_o)$, 307 parameters, 1 restraint, $R_{1obsd.}$ = 0.0677, $wR_{2obsd.}$ = 0.1713, R_{1all} = 0.1076, wR_{2all} = 0.1970, GOF = 1.007, Flack parameter: –0.14(10), largest difference peak and hole: 1.218 and –0.693 e Å^{-3}. The structure was solved by direct methods (SHELXS)[31] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[32] All hydrogen atom positions were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[32] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. CCDC-775460 (for **8**) contains 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.

Supporting Information (see also the footnote on the first page of this article): Crystallographic data.

Acknowledgments

The authors thank the Studienstiftung des deutschen Volkes for financial support in form of a PhD grant (to U.-P. A.), and M. Rudolph for valuable discussions.

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Received: June 3, 2010
Published Online: October 4, 2010

