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Functionalized Sugars as Ligands towards Water-Soluble [Fe-only] Hydrogenase Models

Ulf-Peter Apfel,[a] Yvonne Halpin,[b] Michael Gottschaldt,*[c] Helmar Görls,[a] Johannes G. Vos,*[b] and Wolfgang Weigand*[a]

Dedicated to Professor Jan Reedijk on the occasion of his 65th birthday

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Only a small number of water-soluble iron carbonyl type model compounds for the active centre in [Fe-only] hydrogenase are known, and these models are mainly prepared by substitution of one of the CO ligands. In this publication we present new water-soluble models for [Fe-only] hydrogenase that contain a peripherally bound sugar residue. Compounds were prepared in which the 1,3-disulfanyl-2-propyltetra-*O*-acetyl-β-D-glucopyranoside unit is coordinated to the iron carbonyl core through either a sulfur or a selenium bridgehead atom. Electrochemical results for both types of compounds reveal hydrogen gas evolution from acetic acid and water.

Introduction

Since the elucidation of the structure of [Fe-only] hydrogenase in *Desulfovibrio desulfuricans* and *Clostridium pasteurianum*,[1] much effort has been devoted to synthesize structural and functional models of its catalytic centre.[2] Because the involvement of a bis(mercaptomethyl)amine bridge at the coordination site of the iron centres is not yet clarified, other dithiolates (SCH_2XCH_2S, X = CH_2, O, S) have been studied as bridging ligands in these model complexes.[3] It was shown that an amino functionality was not essential for catalytic activity.[4] Up to now, all model systems exhibit similar problems: too negative potentials for H_2 development from protons (ca. –1.6 V) during electrocatalysis and insolubility in water. The use of sugar residues should strongly increase the hydrophilicity and should allow hydrogen gas formation in aqueous systems, which is sparsely known in the literature.[5] Water would provide the advantage to serve as both the solvent and the proton source, as is the case under physiological conditions. The advantages for the use of sugars, therefore, are self evident. Bound to a metal centre, sugars are able to improve water solubility, and additionally, they may create hydrogen bonds, which may have an influence on the catalytic cycle of hydrogen gas evolution. To form complexes with a [2Fe2S] unit like in natural hydrogenase, it is necessary to introduce sulfur into the ligand molecule. Another important aspect of these studies is clarification of the role of the sulfur bridgehead atoms observed in natural systems. In this study, the more electropositive homologous selenium was incorporated to produce compounds with [2Fe2Se] moieties, and these compounds were compared with their [2Fe2S] sulfur analogues. Only a very small number of [2Fe2Se] complexes are known.[6]

Results and Discussion

The synthetic approach taken in the synthesis of both the sulfur- and selenium-containing model compounds is shown in Scheme 1. Starting from β,β′-dibromoisopropyltetra-*O*-acetyl-β-D-glucopyranoside (**1**),[7] thioacetate **2** was synthesized in 49% yield by treatment with an excess amount of potassium thioacetate at room temperature.[8] The usual way to deprotect the thioacetate groups with sodium hydroxide[9] would result in deprotection of the sugar hydroxy groups and is therefore not applicable to obtain dithiol **3**. Selective cleavage of the *S*-acetyl groups could be realized by treatment of **2** with hydrazine and acetic acid in dimethylformamide over a period of 4 d by stirring at room

[a] Institut für Anorganische und Analytische Chemie, Friedrich-Schiller Universität Jena,
August-Bebel-Straße 2, 07743 Jena, Germany
Fax: +49-3641-948102
E-mail: wolfgang.weigand@uni-jena.de
[b] Solar Energy Conversion SRC, School of Chemical Sciences, Dublin City University,
Dublin 9, Ireland
E-mail: han.vos@dcu.ie
[c] Institut für Organische und Makromolekulare Chemie, Friedrich-Schiller Universität Jena,
Humboldtstraße 10, 07743 Jena, Germany
E-mail: Michael.Gottschaldt@uni-jena.de
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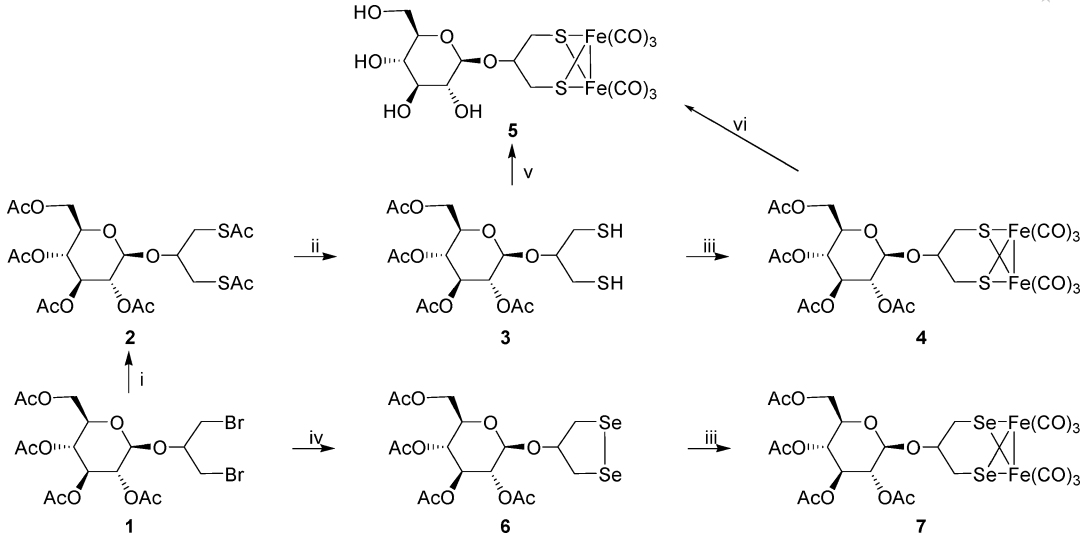

Scheme 1. Synthesis of the sugar-substituted iron carbonyl complexes by starting from dibromide **1**. Reagents and conditions: (i) KSAc, acetone; (ii) $N_2H_4{\cdot}2H_2O$/HOAc; (iii) $Fe_3(CO)_{12}$, toluene; (iv) Na_2Se_2, ethanol/thf; (v) 1. NaOMe, 2. $Fe_3(CO)_{12}$; (vi) NaOMe.

temperature to yield dithiol **3** in 59%.[10] After treatment of 1,3-disulfanyl-2-propyl-tetra-*O*-acetyl-β-D-glucopyranoside (**3**) with $Fe_3(CO)_{12}$ in toluene under reflux conditions[11] only one compound could be isolated. The ^{1}H NMR spectrum of **4** shows two doublets at 2.89–2.85 and 2.69–2.65 ppm and a pseudo triplet (doublet of doublets) at 1.56–1.41 ppm. ^{1}H,^{1}H-COSY measurements suggest that these signals can be assigned to the diastereotopic methylene protons adjacent to the thiolato groups. Two resonances are visible for the methylene carbon atoms in the ^{13}C NMR spectrum at δ = 28.5 and 27.2 ppm. Mass spectrometry shows a stepwise fragmentation of three CO groups and two iron atoms. The $[M - 3CO]^+$ peak at m/z = 648 further confirms the structure of compound **4**.

By diffusion of pentane into a dichloromethane solution of complex **4** crystals suitable for X-ray single-crystal structure analysis could be obtained (Figure 1). Compound **4** crystallized in the noncentrosymmetric space group $P2_1$. The two Fe centres are distorted octahedrally and coordinated by CO ligands and a 1,3-ditholato-2-propyltetra-*O*-acetyl-β-D-glucopyranoside bridge. The angles C1–C2–C3, S1–C1–C2 and S2–C3–C2 are around 115°, which is unexpectedly high in comparison to a regular sp^3 hybridized atom (109.5°). An explanation for this is given in the literature and can be described by the *Rule of Bent*.[12,13] Also, the distances C1–C2 and C2–C3 are slightly shortened (Table 1). The sugar ring exhibits a chair conformation and is arranged in the axial position to the [2Fe2S] centre.

Treatment of compound **4** with sodium methoxide in methanol led to deprotected complex **5**, which decomposes within hours in protic solvents. Additionally, **3** was deprotected by treatment with sodium methoxide in methanol and converted into **5** with $Fe_3(CO)_{12}$ by heating at reflux in thf for 2 h to give a red-coloured product that is soluble in water and methanol. ^{1}H NMR spectroscopy and mass spectrometry indicate that compound **5** was formed. To prepare selenium-containing sugar complex **7**, dibromide **1** was

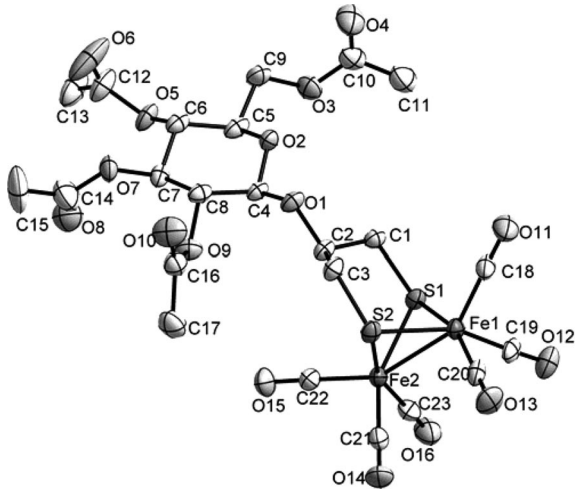

Figure 1. ORTEP view (50% probability) of one of the molecules in the structure of **4**. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for compound **4**.

Fe1–Fe2	2.5150(10)	C1–C2	1.487(8)
Fe1–S1	2.2480(16)	C2–C3	1.507(8)
Fe1–S2	2.2554(17)	S1–C1	1.832(5)
Fe2–S1	2.2730(16)	S2–C3	1.829(5)
Fe2–S2	2.2571(17)	C2–O1	1.435(6)
S1–Fe1–S2	85.12(6)	C1–C2–C3	114.1(5)
S1–Fe2–S2	84.59(6)	C1–C2–O1	110.2(4)
S1–C1–C2	114.4(4)	C3–C2–O1	105.4(4)
S2–C3–C2	115.8(4)		

treated with sodium diselenide, freshly prepared from sodium borohydride and selenium in ethanol, to give **6** in 30% yield.[14] Reaction of **6** with $Fe_3(CO)_{12}$ gave complex **7** as a red solid. The structure as drawn in Scheme 1 was confirmed by ^{1}H, ^{13}C and ^{77}Se{^{1}H} NMR spectroscopic measurements. Comparison of the proton resonances of com-

pound **4** and **7** reveal no important differences. The ^{13}C NMR spectra differ for the resonances of the methylene carbon atoms. The carbon resonances of **7** are found at higher field ($\Delta\delta \approx 10$ ppm) relative to those of **4** and are shifted from 28.5/27.2 ppm in **4** to 17.9/16.4 ppm in **7**, caused by the higher shielding of the carbon nucleus by the more electropositive selenium. Additionally, the $[M]^+$ peak at m/z = 850.6 in the ESI-MS and the CO bands between 2069 and 1991 cm^{-1} in the IR spectrum support the structure. Deprotection of **7** was carried out in situ as outlined below. According to the ^1H and ^{13}C NMR spectra, no epimerization of a β- to α-glycoside was observed.

Electrochemistry

Sulfur-Containing Complexes

Cyclic voltammetry of compound **4** exhibits one irreversible anodic process and several cathodic processes (Figure S1). The iron centres undergo an irreversible oxidation, E_{pa} = +1.09 V, which is assigned to the $[Fe^IFe^I] \rightarrow [Fe^{II}Fe^I] + e^-$ process, as described for the propylendithiolato (PDT)-bridged diiron complex $[(\mu\text{-PDT})Fe_2(CO)_6]$.[12,15,16] The first cathodic wave observed (E_{pc} = –1.50 V) is attributed to the $[Fe^IFe^I] + e^- \rightarrow [Fe^0Fe^I]$ process. The second cathodic wave with a reduction potential of –1.89 V may be ascribed to the $[Fe^0Fe^I] + e^- \rightarrow [Fe^0Fe^0]$ process, as was reported for similar compounds.[16]

To investigate the catalytic proton reduction ability of **4**, cyclic voltammetry was studied in the presence of a weak acid (HOAc, 1–10 mmol in acetonitrile; Figure 2). An increase in the current intensities of the reduction potentials upon addition of an acid is a characteristic feature for a catalytic electrochemical process, and in these cases the formation of hydrogen gas. As previously reported in the literature, other compounds that facilitate catalytic proton reduction exhibited a positive shift in their reduction potential upon addition of acetic acid.[13] No positive shift was observed for **4**. The peak current, however, experienced a substantial increase with the first aliquot of acid (1 mmol), whereas each increment thereafter led only to a slight increase in current. An irreversible wave of low intensity was observed (≈–1.23 V) after the initial addition of acid and experiences a slight increase in current with increments of HOAc thereafter.

An equimolar amount of sodium methoxide ($NaOCH_3$) was added to deprotect the sugar hydroxy groups in compound **4** by standard deacylation (Scheme 1, step vi) to yield **5**, and this enabled the in situ investigation of the free sugar in the CV cell.[17] Sodium methoxide is a redox inactive compound. It exhibits poor solubility in acetonitrile, and as a result of this, it was previously dissolved in a minimal amount of methanol and added to the solution prior to HOAc addition. No shift in potential was observed and the reversibility of the process remained the same (Figure S2). A broad cathodic wave is observed in the spectrum at approximately –1.5 V with a current intensity that weakens with every successive voltage cycle. A return wave is observed for this process, which reached a stable state after the third cycle. A decrease in the current intensity of the first reduction was observed when 1 mmol of acid was added. However, with each sequential increment of HOAc the current intensity of the deprotected sugar reduction experienced a steady increase, which may suggest an electrochemical catalytic process (Figure 3). There was no anodic shift in the reduction potential. The weak, broad cathodic wave seen in Figure 3 disappears with the addition of the acid.

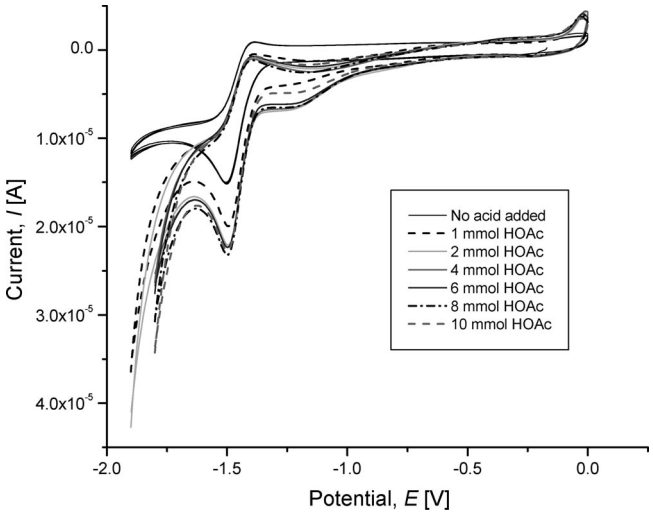

Figure 2. Cyclic voltammograms of **4** (1 mmol) with HOAc (0–10 mmol) in acetonitrile (vs. Ag/Ag^+ reference electrode).

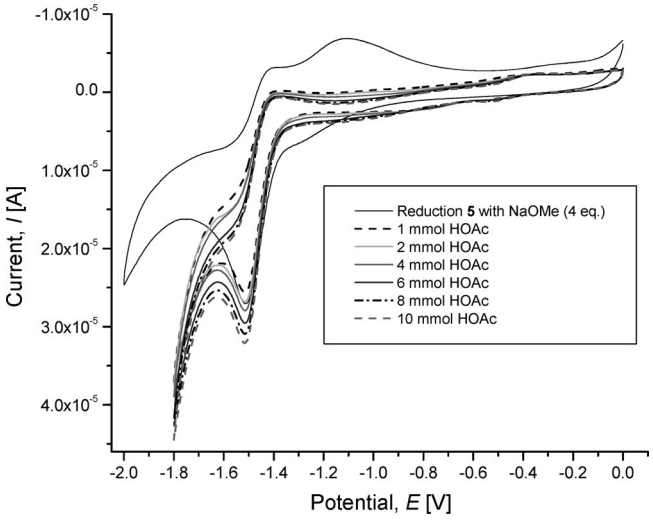

Figure 3. Cyclic voltammograms of **5** (1 mmol) with HOAc (0–10 mmol) in acetonitrile (vs. Ag/Ag^+ reference electrode).

Following the addition of HOAc to the complex and investigation of the catalytic proton reduction, a 5:1 mixture of water/acetonitrile (ACN) was added to the solution to examine any changes in the voltage in the electrochemistry. As a result of adding water the current intensity increased and led to a shift in the reduction potential at –1.5 to –1.6 V. Complex **5** was not stable in protic solvents such as methanol and water. This can be seen in the CV (Figure 4).

By adding 4.5 mL of H_2O/ACN (5:1) the reduction potential at –1.5 V, typical for the reduction of Fe^IFe^I to Fe^0Fe^I, disappeared, which indicates the decomposition of **5**.

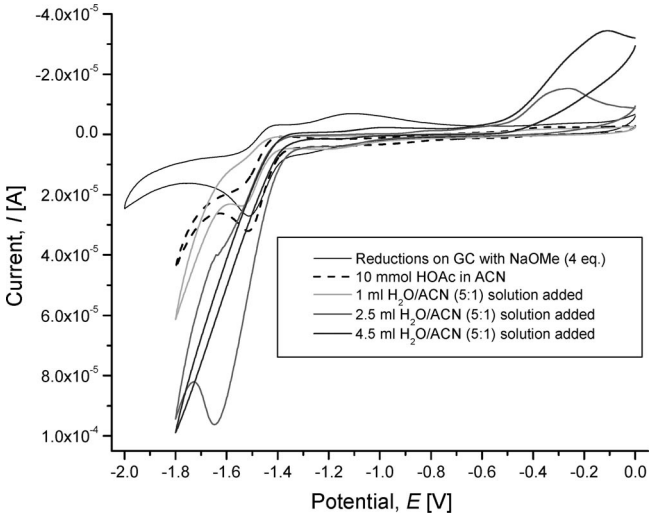

Figure 4. Cyclic voltammograms of **5** detailing the effect of H_2O on the catalytic proton reduction.

Selenium-Containing Complexes

Selenium analogue compound **7** undergoes an irreversible oxidation at +0.97 V, exhibiting a cathodic shift of 120 mV relative to the oxidation potential of **4**. A cathodic wave was observed at –1.46 V, which is attributed to the $[Fe^IFe^I] + e^- \rightarrow [Fe^0Fe^I]$ process. A second reduction wave is observed, E_{pc} = –2.02 V, which can be ascribed to the $[Fe^0Fe^I] + e^- \rightarrow [Fe^0Fe^0]$ process (Figure S3).

The catalytic proton reduction of **7** was investigated through the addition of HOAc (Figure 5). As observed for **4**, the reduction potential of the selenium analogue does not shift anodically. Following the addition of 1 mmol of acid, an increase in the peak current at –1.5 V was observed, which slightly increased with additional aliquots of HOAc. This rise in the current (ca. –1.8 V) suggests catalytic H_2 development.

Compound **7** was treated with sodium methoxide to yield the deprotected sugar complex in analogy to **5** as a precursor molecule of a potential water-soluble hydrogenase model. The cyclic voltammetry of the deprotected sugar complex showed behaviour similar to that of **5**. Again no positive or negative shift was observed, and the reversible process remained the same (Figure S4). A broad anodic wave appeared, but it disappeared after the addition of HOAc. The influence of the added acetic acid was studied and evidence for H_2 development at –1.8 V was found (Figure 6).

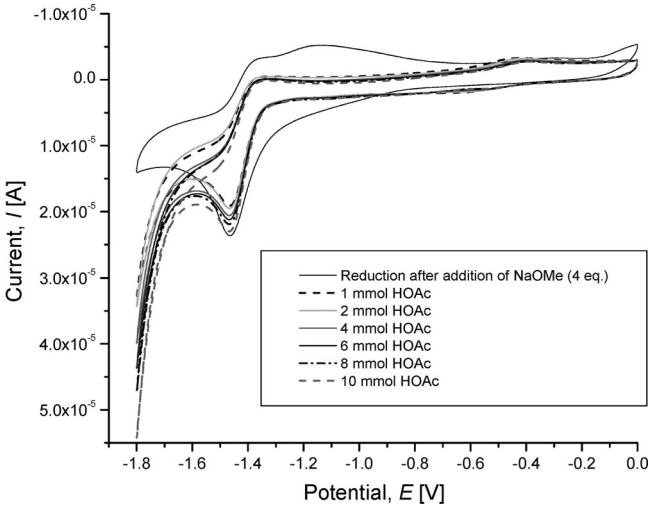

Figure 6. Cyclic voltammograms of the deprotected selenium complex (1 mmol) with HOAc (0–10 mmol) in acetonitrile (vs. Ag/Ag^+ reference electrode).

To investigate the electrochemical properties in water, a mixture of H_2O/ACN (5:1) was added to the deprotected selenium complex. With this, a large increase in the signal

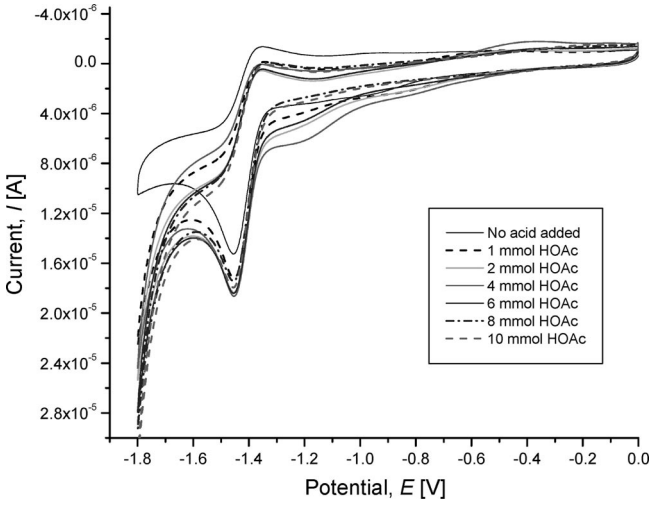

Figure 5. Cyclic voltammograms of **7** (1 mmol) with HOAc (0–10 mmol) in acetonitrile (vs. Ag/Ag^+ reference electrode).

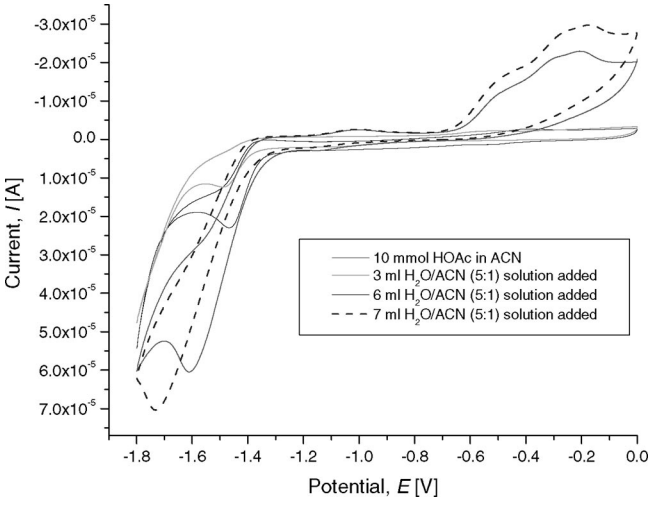

Figure 7. Cyclic voltammograms of the deprotected selenium complex detailing the effect of H_2O on the catalytic proton reduction.

intensity at –1.4 V and an intensive negative shift of this peak potential of approximately 250 mV (Figure 7) was observed.

Comparison of the Electrocatalytic Results

The oxidation potential of **7** for the $Fe^{I}Fe^{I} \rightarrow Fe^{II}Fe^{I}$ process experiences a cathodic shift of 120 mV relative to that of **4**. The iron centres in **7** are more easily reduced than those in **4**, as suggested by the positive shift of 40 mV for the first reduction process, $Fe^{I}Fe^{I} \rightarrow Fe^{0}Fe^{I}$, in the selenium analogue, whereas the second reduction occurs at a potential that is 130 mV more negative than the corresponding process in the sulfur compound (Table 2).

Table 2. Electrochemical data for **4** and **7** in acetonitrile (vs. Ag/Ag^{+} reference electrode).

	$E_{p(ox,irr)}$ [V] $Fe^{I}Fe^{I}/Fe^{II}Fe^{I}$	E_{pc}, E_{pa} [V] $Fe^{I}Fe^{I}/Fe^{0}Fe^{I}$	$E_{pc} - E_{pa}$ Separation [mV]	E_{pc}, E_{pa} [V] $Fe^{0}Fe^{I}/Fe^{0}Fe^{0}$
4	+1.09	–1.50 (E_{pc}) –1.39 (E_{pa})	110	–1.89 (E_{pc})
7	+0.97	–1.46 (E_{pc}) –1.36 (E_{pa})	100	–2.02 (E_{pc})

Deprotection of **4** and **7** with NaOMe leads to a new broad anodic wave, which disappears when adding acid. All complexes show a consequent increase in peak current for the $Fe^{I}Fe^{0} \rightarrow Fe^{0}Fe^{0}$ process with each aliquot of acetic acid, suggesting electrocatalytic hydrogen gas development.

In contrast to complex **5**, the deprotected Se compound was stable in solution even after adding 7 mL of a mixture of water/acetonitrile (5:1) to the acidic complex solution; a fact that must be ascribed by the influence of the selenium atoms. As a result of the more electropositive selenium, the iron atoms become more electron rich, leading to stronger π backbonding with the CO ligands. As a direct consequence, IR wavenumbers for the CO ligand slightly decrease.

Conclusions

Two new ligands based on tetra-*O*-acetyl-β-D-glucopyranosides **3** and **6** and the corresponding diiron complexes **4** and **7** were synthesized and characterized. No epimerization was observed. Complexes **4** and **7** show similar behaviour during electrochemical investigation and exhibit catalytic properties for H_2 formation. Deprotection of complexes **4** and **7** with NaOMe leads to the water-soluble complexes. It was thereby recognized that the deprotected selenium complex is more stable in aqueous solution than the sulfur compound. The presence of selenium offers higher activity towards H_2 development, but it occurs at lower potentials than the corresponding sulfur complexes. The sugar residue was found to have no notable influence on the catalytic cycle; instead, it changes the solubility properties of the complexes.

Experimental Section

General Procedures: Solvents for the syntheses were first dried with KOH and distilled from sodium/benzophenone. Chemicals were used as received from Fluka and Acros without further purification. 1,3-dibromo-2-propyl-β-D-glucopyranoside was synthesized by following literature procedures.[7] Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates (detection under UV light at 254 nm); flash chromatography (FC) was performed on Fluka silica gel 60. ^{1}H, ^{13}C and $^{77}Se\{^{1}H\}$ NMR spectra were recorded with a Bruker 400 MHz instrument. IR spectra were recorded with a Perkin–Elmer 2000 FTIR. Mass spectrometry was performed with an SSQ710 Finnagen MAT. All reactions were carried out under an argon atmosphere.

1,3-Dithioacetyl-2-propyltetra-*O*-acetyl-β-D-glucopyranoside (2): To a 50-mL round-bottomed flask containing 1,3-dibromo-2-propyltetra-*O*-acetyl-β-D-glucopyranoside (**1**; 500 mg, 0.836 mmol) dissolved in acetone (20 mL) was added potassium thioacetate (430 mg, 3.762 mmol). The solution was stirred for 1 week at room temperature, and the resulting precipitate was filtered off. The filtrate was evaporated to dryness and purified by FC (ethyl acetate/hexane, 1:1) to yield a white precipitate (220 mg, 49%). R_f = 0.63 (ethyl acetate/hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.19–5.14 (m, 1 H, 3-H), 5.05–5.00 (m, 1 H, 4-H), 4.95–4.90 (m, 1 H, 2-H), 4.63 (d, $^{3}J_{1,2}$ = 8 Hz, 1 H, 1-H), 4.23–4.12 (m, 2 H, 6-H, 6′-H), 3.75–3.70 [m, 2 H, 5-H and SCH_2-C*H*(O)-CH_2S], 3.15–2.87 [4 m, 4 H, S*C*H_2-CH(O)-C*H*$_2$S], 2.31/2.30 (2 s, 6 H, CH_3-S-acetyl), 2.05/2.03/1.99/1.97 (4 s, 12 H, CH_3-acetyl) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 195.1/194.8 (*C*O-S-acetyl), 170.6/170.2/169.4/169.2 (*C*O-acetyl), 101.0 (C-1), 79.3 (C-5), 72.8 (C-3), 71.9 [SCH_2-*C*H(O)-CH_2S], 71.2 (C-2), 68.4 (C-4), 61.9 (C-6), 32.9/32.3 [S*C*H_2-CH(O)-*C*H$_2$S], 30.5 (*C*H_3-S-acetyl), 20.7 (*C*H_3-acetyl) ppm. MS (Micro-ESI): *m*/*z* = 561.1 $[M + Na]^{+}$. IR (KBr): $\tilde{\nu}$ = 2954 (m), 2877 (m), 1747 (vs), 1690 (vs), 1431 (m), 1378 (s), 1232 (vs) cm^{-1}. $C_{22}H_{32}O_{11}S_2$ (538.12): calcd. C 46.83, H 5.61, S 11.91; found C 46.93, H 5.81, S 11.70.

1,3-Disulfanyl-2-propyltetra-*O*-acetyl-β-D-glucopyranoside (3): To a solution of **2** (1 g, 1.878 mmol) dissolved in dimethylformamide (40 mL) was added hydrazine dihydrate (0.329 g, 6.588 mmol). After stirring for 10 min, acetic acid (380 μL, 6.588 mmol) was added, and the resulting solution was stirred until TLC showed no remaining starting material (usually 4 d). Water was added, and the resulting precipitate was dissolved in ethyl acetate. The organic phase was separated, washed with water and dried with sodium sulfate. Evaporation of the solvent and recrystallization from ethyl acetate/pentane gave compound **3** (508 mg, 60%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.24–5.16 (m, 1 H, 3-H), 5.07–5.00 (m, 1 H, 4-H), 4.98–4.92 (m, 1 H, 2-H), 4.78 (m, 2 H, S*H*), 4.61 (d, $^{3}J_{1,2}$ = 8 Hz, 1 H, 1-H), 4.21–4.16 (m, 2 H, 6-H), 3.69 (m, 1 H, 5-H), 3.26–3.08 [m, 5 H, S*C*H_2-CH(O)-C*H*$_2$S and SCH_2-C*H*(O)-CH_2S], 2.07/2.02/2.01/1.98 (4 s, 12 H, CH_3-acetyl) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.6/170.3/169.3/169.2 (*C*O-acetyl), 101.9 (C-1), 83.5 (C-5), 72.5 (C-3), 72.1 [SCH_2-*C*H(O)-CH_2S], 71.0 (C-2), 68.3 (C-4), 62.1 (C-6), 44.82/44.83 [S*C*H_2-CH(O)-*C*H$_2$S], 20.7 (*C*H_3-acetyl) ppm. MS (FAB): *m*/*z* (%) = 452 $[M - 2H]^{+}$. IR (KBr): $\tilde{\nu}$ = 2925 (s), 2855 (m), 1755 (vs), 1654 (m), 1432 (m), 1369 (s), 1222 (vs), 1042 (vs) cm^{-1}. Elemental analysis was not obtained.

Hexacarbonyl(1,3-disulfanyl-2-propyltetra-*O*-acetyl-β-D-glucopyranoside)diiron (4): A solution of **3** (63 mg, 0.139 mmol) and $Fe_3(CO)_{12}$ (71 mg, 0.139 mmol) dissolved in thf (20 mL) was heated at reflux for 30 min. After cooling to room temperature, the solvent was evaporated, and crude complex **4** was purified by FC (ethyl acetate/hexane, 1:1) to yield of red solid (25 mg, 25%). Single crystals suitable for X-ray crystallography were obtained by diffusion of pentane into a solution of **4** in dichloromethane. R_f = 0.72 (ethyl acetate/hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.15–5.10

(m, 1 H, 3-H), 5.05–4.96 (m, 1 H, 4-H), 4.85–4.81 (m, 1 H, 2-H), 4.47 (d, $^3J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 4.21–4.09 (m, 2 H, 6-H), 3.65 (m, 1 H, 5-H), 3.04 [m, 1 H, SCH_2-C*H*(O)-CH_2S], 2.89/2.85, [d, ^3J = 8 Hz, 1 H, SCH_2-CH(O)-CH_2S] 2.69/2.65 [d, ^3J = 8 Hz, 1 H, SCH_2-CH(O)-C*H*$_2$S], 1.56–1.41 [m, 2 H, SCH_2-CH(O)-C*H*$_2$S], 2.15/1.99/1.96 (3 s, 12 H, CH_3-acetyl) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 207.4 (*C*O), 170.6/170.1/169.3/169.1 (*C*O-acetyl), 99.9 (C-1), 80.8 [SCH_2-*C*H(O)-CH_2S], 72.5 (C-3), 72.2 (C-5), 68.2 (C-4), 61.8 (C-6), 28.5/27.2 [S*C*H$_2$-CH(O)-*C*H$_2$S], 20.6 (*C*H$_3$-acetyl) ppm. MS (DEI): *m*/*z* = 648 [M – 3CO]$^+$, 620 [M – 4CO]$^+$, 592 [M – 5CO]$^+$, 452 [M – 2Fe – 6CO]$^+$. IR (KBr): $\tilde{\nu}$ = 2955 (m), 2925 (m), 2854 (m), 2077 (vs), 2036 (vs), 1995 (vs), 1757 (s), 1227 (s) cm^{-1}. $C_{23}H_{24}Fe_2O_{16}S_2$ (731.92): calcd. C 37.73, H 3.30, S 8.76; found C 37.71, H 3.25, S 8.17.

Hexacarbonyl(1,3-dithiolato-2-propyl-β-D-glucopyranoside)diiron (5)

Method A: To a solution of compound **4** (5 mg, 8.867 mmol) dissolved in methanol (1 mL) was added a catalytic amount of sodium methoxide, and the mixture was stirred for 2 h. The resulting solution was evaporated and used directly for NMR and MS analysis.

Method B: To a solution of **3** (41 mg, 0.091 mmol) dissolved in methanol (5 mL) and dichloromethane (1 mL) was added sodium methoxide (100 mg), and the mixture was stirred for 72 h. The solvent was evaporated, and the remaining solid was dissolved in thf (40 mL); $Fe_3(CO)_{12}$ (46 mg, 0.091 mmol) was then added. After 30 min under reflux, the formed precipitate was filtered off, and the solvent was evaporated to dryness. The remaining solid was dissolved in methanol, and the solution was separated from solid particles. After evaporation, **5** (22 mg, 53.2%) was obtained as a red solid. ^{1}HNMR (200 MHz, D_2O): δ = 5.03 (m, 1 H, 1-H), 3.80–3.25 [m, 11 H, 2-H, 3-H, 4-H, 5-H, 6-H, SC*H*$_2$-C*H*(O)-C*H*$_2$S] ppm. MS (FAB): *m*/*z* = 587 [M + Na]$^+$.

1,3-Diselenolan-2-propyltetra-*O*-acetyl-β-D-glucopyranoside (6): To sodium borohydride (88 mg, 2.3 mmol) and selenium (184 mg, 2.3 mmol) was added absolute ethanol (6 mL) whilst stirring. The resulting suspension was heated at reflux for 1 h and a red solution was obtained. The solution was then cooled to 0 °C and **1** (453 mg, 0.757 mmol) dissolved in absolute ethanol (20 mL) and thf (5 mL) was slowly added. The suspension was stirred for an additional 24 h. Water (15 mL) are added, and a red solid precipitated. After filtration, the separated solid was washed again with dichloromethane (2×). The solvent was evaporated, and crude product **6** was purified by FC (ethyl acetate/hexane, 1:1) to yield **6** (123 mg, 30%) as a slightly brown solid. R_f = 0.37 (ethyl acetate/hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.19–5.16 (m, 1 H, 3-H), 5.08–5.01 [m, 1 H, 4-H and $SeCH_2$-C*H*(O)-CH_2Se], 4.98–4.94 (m, 1 H, 2-H), 4.64 (d, $^3J_{1,2}$ = 8 Hz, 1 H, 1-H), 4.24–4.12 (m, 2 H, 6-H), 3.71–3.67 (m, 1 H, 5-H), 3.44–3.26 [m, 4 H, SeC*H*$_2$-CH(O)-C*H*$_2$Se], 2.07/2.04/2.01/1.99 (4 s, 12 H, CH_3-acetyl) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.6/170.2/169.3/169.2 (*C*O-acetyl), 99.2 (C-1), 85.5 [$SeCH_2$-*C*H(O)-CH_2Se], 72.5 (C-3), 72.1 (C-5), 71.2 (C-2), 68.3 (C-4), 61.9 (C-6), 35.3/33.2 [Se*C*H$_2$-CH(O)-*C*H$_2$Se], 20.7 (*C*H$_3$-acetyl) ppm. ^{77}Se{^{1}H} NMR (76 MHz, $CDCl_3$): δ = 261.7, 238.3 ppm. MS (ESI): *m*/*z* = 571 [M + Na]$^+$. IR (KBr): $\tilde{\nu}$ = 2940 (m), 1755 (vs), 1637 (m), 1431 (m), 1368 (s), 1230 (vs), 1041 (vs), 908 (m) cm^{-1}. $C_{17}H_{24}O_{10}Se_2$ (547.97): calcd. C 37.38, H 4.43; found C 37.88, H 4.43.

Hexacarbonyl(1,3-diselenolanolato-2-propyltetra-*O*-acetyl-β-D-glucopyranoside)diiron (7): Compound **6** (50 mg, 0.091 mmol) and $Fe_3(CO)_{12}$ (46 mg, 0.091 mmol) were dissolved in thf (20 mL) and stirred in a 50-mL Schlenk vessel. After 2 h under reflux, the solvent was evaporated, and the remaining solid was purified by FC (ethyl acetate/hexane, 1:1) to afford **7** (55 mg, 73%) as a red solid. R_f = 0.55 (ethyl acetate/hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.15–5.11 (m, 1 H, 3-H), 5.01–4.96 (m, 1 H, 4-H), 4.86–4.81 (m, 1 H, 2-H), 4.48 (d, $^3J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 4.20–4.08 (m, 2 H, 6-H), 3.65 (m, 1 H, 5-H), 2.95–2.71/1.61–1.44 [2 m, 5 H, SeC*H*$_2$-C*H*(O)-C*H*$_2$Se], 2.08/1.99/1.96 (3 s, 12 H, CH_3-acetyl) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.6 (CO), 170.5/170.1/169.3/169.1 (*C*O-acetyl), 99.5 (C-1), 80.6 [$SeCH_2$-*C*H(O)-CH_2Se], 72.5 (C-3), 72.2 (C-5), 71.1 (C-2), 68.2 (C-4), 61.8 (C-6), 20.6 (*C*H$_3$-acetyl), 17.9/16.4 [Se*C*H$_2$-CH(O)-*C*H$_2$Se] ppm. ^{77}Se{^{1}H} NMR (76 MHz, $CDCl_3$): δ = 209.3 (br.) ppm. MS (ESI): *m*/*z* = 850.6 [M + Na]$^+$. IR (KBr): $\tilde{\nu}$ = 2926 (m), 2855 (m), 2069 (vs), 2029 (vs), 1991 (vs), 1757 (vs), 1637 (m), 1436 (m), 1370 (s) cm^{-1}. $C_{23}H_{24}Fe_2O_{16}Se_2$ (827.81): calcd. C 33.44, H 2.93; found C 32.96, H, 2.42.

Electrochemical Procedure: Cyclic voltammograms were recorded against a nonaqueous Ag/Ag$^+$ reference electrode (0.1 M *n*Bu$_4$NPF$_6$ and 0.01 M $AgNO_3$ in CH_3CN). A glassy carbon (GC) macroelectrode and a platinum wire were used as the working and auxiliary electrodes, respectively. A solution of 0.05 M *n*Bu$_4$NPF$_6$ (Fluka, electrochemical grade) in acetonitrile (Aldrich, anhydrous, 99.8%) was used as the supporting electrolyte. Electrochemical experiments were carried out by using a CHI750C electrochemical bipotentiostat. Prior to each experiment, the electrochemical cell was degassed for at least 10 min by using argon and a blanket of argon was maintained throughout. The GC working electrode was prepared by successive polishing with 1.0 and 0.3 micron alumina pastes and sonicated in Millipore water for 5 min. All cyclic voltammograms were recorded at a scan rate of 100 mVs^{-1}.

Crystal Structure Determination: The intensity data for the compound were collected with a Nonius KappaCCD diffractometer by using graphite-monochromated Mo-K_α radiation. Data were not corrected for Lorentz and polarization effects, but for absorption effects.[18,19] The structure was solved by direct methods (SHELXS[20]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[21]). All hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 4: $C_{23}H_{24}Fe_2O_{16}S_2$, M_r = 732.24 g mol^{-1}, brown prism, size 0.04 × 0.04 × 0.03 mm^3, monoclinic, space group $P2_1$, a = 9.4890(4) Å, b = 6.8110(3) Å, c = 23.5479(9) Å, β = 93.422(2)°, V = 1519.18(11) Å^3, T = –90 °C, Z = 2, $\rho_{calcd.}$ = 1.601 g cm^{-3}, μ(Mo-K_α) = 11.64 cm^{-1}, F(000) = 748, 8761 reflections in h(–9/12), k(–8/7), l(–30/30), measured in the range 2.15° ≤ Θ ≤ 27.53°, completeness Θ_{max} = 97.4%, 5943 independent reflections, R_{int} = 0.0806, 4692 reflections with $F_o > 4\sigma(F_o)$, 392 parameters, 1 restraints, R_{1obs} = 0.0598, wR_{2obs} = 0.1323, R_{1all} = 0.0825, wR_{2all} = 0.1440, GOOF = 1.037, Flack parameter: –0.02(3), largest difference peak and hole: 0.697/–0.485 e Å^{-3}.

CCDC-683744 (for **4**) 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 footnote on the first page of this article): Additional cyclic voltammogram traces.

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