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Electrochemical Proton Reduction Catalyzed by $[Fe_2(CO)_6{\mu-(TeCH_2Te)}]$ Model that Mimics the Structure of the Active Site of [FeFe]-Hydrogense

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Abstract

In this report we discuss the synthesis of $[Fe_2(CO)_6{\mu-(TeCH_2Te)}]$ (2) using $Fe_3(CO)_{12}$ and $Me_2Sn(CH_2I)_2$ in the presence of potassium tellurocyanate, freshly prepared. The resulting complex was characterized by different spectroscopic methods $({}^{1}H, {}^{13}C{}^{1}H$ and ${}^{125}Te{}^{1}H$ NMR) as well as X-ray diffraction analysis. Moreover, we investigate the redox properties and the catalytic behaviour of **2** in the presence of weak and moderate acids, Acetic acid (AcOH) and trifluoracetic acid (TFA), respectively, as a source of protons.



Introduction

The development of hydrogen as an energy resource is of significance for a competitively sustainable economy.^[1a] Nature has developed highly effective enzyme called [FeFe]-hydrogenase that catalyze the reversible reduction of protons to molecular hydrogen at an organometallic active site called the H-cluster (Figure 1).^[1b] The latter consists of an [Fe₄S₄] cubane attached through a cysteinyl residue to a butterfly [Fe₂S₂] subcluster. The [Fe₂S₂] unit features a bridging azadithiolato ligand as well as biologically unusual CO and CN⁻ ligands.^[2-5] Several model complexes mimicking the active site of the [FeFe]-hydrogenase have been synthesized, characterized and their catalytic applications have been studied in detail.^[6-13] In two recent papers we described the influence of the presence of the Sn atom in μ -(XCH₂)₂SnMe₂ (X = S or Se) linker of the synthetic H-cluster mimics (Figure 1).^[14,15]



Figure 1. The active H-cluster site of [FeFe]-hydrogenase (left) and synthetic model of the active site of [FeFe]-hydrogenase (right).

As a result, it has been found that the electron density of the μ -S atoms (and hence that of Fe-Fe bond) is increased and that protonation of the Fe-Fe bond using the moderately strong acid CF₃CO₂H can be accomplished in the case of X = Se. In continuation of our efforts in this field, the present work aims to synthesize [Fe₂(CO)₆{ μ -(TeCH₂)₂SnMe₂}] (1), through the reaction of in situ generated Me₂Sn(CH₂TeCN)₂ with Fe₃(CO)₁₂. Unfortunately, complex **1** is not obtained in this reaction and instead we got [Fe₂(CO)₆{ μ -(TeCH₂Te)}] (2) as the main product. Indeed, complex **2** was previously reported by Mathur and co-workers, which they could obtain complex **2** via the reaction of [Fe₂(CO)₆{ μ -(Te₂)}] and diazomethane.^[16] However, the electrochemistry of complex **2** and its reactivity toward protons have not yet been reported. In this contribution, we herein characterize complex 2 by employing a variety of analytical techniques (NMR spectroscopy, elemental analysis, IR spectroscopy, mass spectrometry and X-ray structure determination). Furthermore, a detailed electrochemical study of complex 2 in the absence and presence of a weak acid (AcOH) as well as a moderately stronger acid (TFA) as proton sources has been reported.

Results and Discussion

Synthesis and Characterization

The in situ prepared dimethylbis(tellurocyanatometyl)stannane was obtained via the reaction of Me₂Sn(CH₂I)₂^[17] with twofold excess of potassium tellurocyanate, freshly prepared by heating of tellurium and potassium cyanide in refluxing dimethyl sulfoxide. The latter solution was then added to a solution of Fe₃(CO)₁₂ dissolved in THF and refluxed for two hours followed by subsequent column chromatography to afford complex **2** as a major product instead of complex **1** as shown in Scheme 1. In fact, the reason of not obtaining complex **1** could be explained due to the bigger size of Te atoms compared to that of S and Se atoms in their corresponding analogues.^[14,15] Furthermore, the steric hindrance or the tension of forming the moiety that contains a Sn atom together with two Te atoms could avoid the formation of complex **1**. Complex **2** was characterized by spectroscopic methods (¹H NMR, ¹³C{¹H} NMR, ¹²⁵Te{¹H} NMR and IR), mass spectrometry, elemental analysis, and X-ray structure determination. The mass spectrum of complex **2** shows the parent ion peak at *m/z* 549 and the consecutive loss of six CO ligands.



Scheme 1. Synthetic pathway to complex 2.

In order to understand the influence of the bridging chalcogen atoms on the electronic properties of complex **2** and its Se/S analogues, we have made comparisons with some of their spectral as shown in Table 1. As can be seen in Table 1, The IR spectra of complex **2** and its Se/S analogues exhibited five absorption bands in the ranges of 2054-1960, 2071-1980 and 2079-1988 cm⁻¹, respectively. The increase of these CO stretching frequencies from complex **2** to its Se/S analogues is obviously due to the decreased π back-bonding between their Fe atoms and the attached CO groups, caused by the decreasing donor ability from Te to Se/S. The ¹H NMR spectra of complex **2** and its Se/S analogues showed one singlet peak at $\delta = 2.20$ ppm with ¹²⁵Te satellites (²*J*_(TeH) = 20 Hz) for complex **2**, while those for Se/S analogues at $\delta = 4.02$ and 4.90 ppm, respectively, which are assigned to protons of the methylene moiety. Moreover, the ¹³C{¹H} NMR spectrum of complex **2** displays a signal at $\delta = 211.8$ ppm for the CO ligands in the Fe(CO)₃ moiety as well as a signal at $\delta = 22.5$ ppm which is assigned to the methylene carbon atom. The ¹²⁵Te{¹H} NMR spectrum shows one signal for the chemically equivalent Te atoms at $\delta = 337.9$ ppm.

[Fe2(CO)6{µ-(XCH2X)}]	IR (cm ⁻¹)	¹ H NMR (ppm)
	<mark>(νс≡о)</mark>	(CH ₂)
	2054(s), 2025(m),	
<mark>X = Te</mark>	<mark>1998(m), 1986(m),</mark>	<mark>2.20</mark>
	<mark>1960(w)</mark>	
	2071(m), 2032(vs),	
$\mathbf{X} = \mathbf{S}\mathbf{e}^{19}$	<mark>1999(vs), 1992(s),</mark>	<mark>4.02</mark>
	<mark>1980(w)</mark>	
$\mathbf{X} = \mathbf{S}^{18}$	2079(m), 2039(s),	<mark>4 90</mark>
	2008(s), 1999(s), 1988(w)	

Table 1. Some spectral data of 2 and its Se/S analogues.

Molecular structure

Single crystal suitable for X-ray diffraction study was obtained from a saturation solution of **2** in pentane at -20 °C. The molecular structure of complex **2** is shown in Figure 2.



Figure 2. Molecular structure (50% probability) of complex 2.

In agreement with the previously reported diiron dithiolato and diselenolato analogues complexes,^[18,19] complex **2** exhibited the [Fe₂S₂] core with butterfly conformation. The geometry around each iron atom can be best described as distorted octahedron in which the central atom is Fe surrounded by three CO ligands in a facial fashion as well as two chalcogen atoms that bridge both iron centres. The Fe-Fe bond length in complex **2**, (2.5921(6) Å), is slightly longer than those of diiron dithiolato and diselenolato analogues complexes.^[18,19] This is attributed to the larger van der Waals radii of Te compared to S and Se atoms. The average Fe-CO bond length in **2**, (1.7915 Å), is comparable to those observed in the corresponding S and Se analogues. The torsion angle, τ , formed from the intersection between (O)C-Fe-Fe-C(O) of complex **2** is ca. 33.15°, which is larger than those of corresponding S and Se analogues (9.19° and 6.23°, respectively).^[18,19]

Electrochemical Investigation

The electrochemical behaviour of complex 2 was investigated by cyclic voltammetry (CVs). Figure 3 shows the cyclic voltammetric reduction of 2 in CH₂Cl₂-[*n*Bu₄N][BF₄] at various scan rates (0.05 V s⁻¹ \ge *v* \ge 10 V s⁻¹).



Figure 3. Cyclic voltammetry of 1.0 mM solution of complex **2** in CH₂Cl₂-[*n*Bu₄N][BF₄] at (a) 0.05 V s⁻¹ $\ge v \ge 1.0$ V s⁻¹ and (b) 1.0 V s⁻¹ $\ge v \ge 10.0$ V s⁻¹. Glassy carbon disk (*d* = 1.6 mm). The potential *E* are given in V and referenced to Fc⁺/Fc couple. The arrows indicate the scan direction.

On initiating the electrochemical scan in the cathodic direction at a scan rate of 0.2 V s⁻¹, a quasi-reversible reduction event at $E_{1/2} = -1.67$ V was observed. Increasing the scan rate of 2 up to 10 V s⁻¹ results in no wave-splitting for the reduction peak of 2 (Figure 3). This reduction peak of complex 2 is due to two-electron reduction in a single step based on the study of the current function, $[I_p/c \cdot v^{1/2} = (2.69 \times 10^5) \cdot A \cdot D^{1/2} \cdot n^{3/2},$ where I_p = peak current, c = complex concentration, v = scan rate, A = electrode area, D = diffusion coefficient and n = number of transferred electron] of 2. It is well established that the dependence of the current function on the scan rate provides mechanistic information on the electron transfer chemistry and the number of electrons *n* at a given potential.^[20-26] In general, when the reduction process does not have any chemical route (simple E mechanism (E = electron transfere), n = 1), the current function of this reduction process should remain constant at all scan rates since 2.69 x 10^5)·A·D^{1/2}·n^{3/2} is constant. In contrast, when an ECE mechanism (C = chemical process) (n = 2) in which a chemical process takes place, the current function of this reduction process decreases significantly toward that expected for a one electron as the scan rates increase. This means, at higher scan rates there is no enough time for such a chemical process to occur and thus the second electron transfer will not take place (i.e. conversion of the mechanism from ECE to simple E process). Based on that, the value of the $I_p/c \cdot v^{1/2}$ of the reduction of 2 decreases with increasing v towards a value predicted for a one-electron reduction (Figure 4), suggesting an intervening chemical process in an ECE reduction mechanism.



Figure 4. The scan rate dependence of the current function of the reduction peak of **2** in 0.1 M CH₂Cl₂-[*n*Bu₄N][BF₄] solution. Glassy carbon electrode ($A = 0.0206 \text{ cm}^2$). The dashed line represents the current function expected for a one-electron process assuming $D = 9 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, a value calculated for various [FeFe]-hydrogenase models.

Catalytic reduction of protons

We have probed by cyclic voltammetry the plausible catalytic behaviour of complex 2 toward proton reduction using weak and moderate acids, AcOH and TFA, respectively.



Figure 5. Cyclic voltammetry of 1.0 mM solution of complex **2** in CH₂Cl₂-[*n*Bu₄N][BF₄] at 0.2 V s⁻¹ in the presence of a) various equivalents of AcOH and b) various equivalents of TFA. Glassy carbon disk (d = 1.6 mm). The potential *E* are given in V and referenced to Fc⁺/Fc couple. The arrows indicate the scan direction.

Figure 5a shows the cyclic voltammetry of complex **2** in CH₂Cl₂-[nBu₄N][BF₄] in the presence of various equivalents of AcOH. The presence of one equiv. AcOH shifts the primary reduction peak of **2** to less negative potential (ca. 32 mV), which is typical observation when protonation of a reduced species takes place.^[15,27,28] However, when

the acid concentration was increased, the current of this process remains unaffected. At more reducing potentials in the area of the vicinity of -1.80 V to -2.10 V for complex 2, the voltammetric profile of 2 shows a reduction peak ($E_{pc} = -1.98$ V) with a current that increases in response to the systematic increase in the acid concentration, indicating a catalytic proton reduction.

On the other hand, the addition of a moderate acid, TFA, to a solution of **2** in CH₂Cl₂-[*n*Bu₄N][BF₄], shifts the primary reduction peak of **2** to less negative potential (ca. 60 mV) and the current of this process evidently grew with the sequential addition of TFA (Figure 5b). This observation could be explained as arising from a catalytic cycle that evolved H₂ (process I, Figure 5b). Additionally, another reduction peak was also observed at more negative potential ($E_{pc} = -1.96$ V) and its current significantly increases with consecutive addition of TFA indicating that a catalysis process is also occurring at this potential (process II. Figure 5b).

Conclusion

In this paper we have reported the synthesis of $[Fe_2(CO)_6{\mu-(TeCH_2Te)}]$ (2) by the reaction of in situ generated dimethylbis(tellurocyanatometyl)stannane with Fe₃(CO)₁₂ under reflux conditions. The resulting complex was fully characterized by use of ¹H, ¹³C{¹H} and ¹²⁵Te{¹H} NMR as well as IR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography. Moreover, the proton reduction catalyzed by complex **2** was also investigated by cyclic voltammetry using weak and moderate acids such as AcOH and TFA, respectively. As a result, complex **2** shows a catalytic behaviour via an EECC electrocatalysis mechanism for H₂ production in the case of AcOH, while in the case of TFA shows a catalytic behaviour though two processes via an EECCC mechanism (process I) and EECC mechanism (process II) for H₂ production.

Experimental Section

All reactions were performed using standard Schlenk and vacuum-line techniques under an inert gas (nitrogen). The ¹H, ¹³C{¹H} and ¹²⁵Te{¹H} NMR spectra were recorded with a Bruker Avance 400 MHz spectrometer. Chemical shifts are given in parts per million with references to internal SiMe₄ (¹H, ¹³C) or CHCl₃. The ¹²⁵Te chemical shift was measured vs. external PhTeTePh and converted to that of Me₂Te. The mass spectrum was recorded with Finnigan MAT SSQ 710 instrument. The IR spectra were recorded with a Bruker Equinox 55 spectrometer equipped with an ATR unit. Elemental analysis was performed with a Leco CHNS-932 apparatus. TLC was performed by using Merck TLC aluminum sheets (Silica gel 60 F254). Solvents from Fisher Scientific and other chemicals from Acros and Aldrich were used without further purification. All solvents were dried and distilled prior to use according to standard methods. Me₂Sn(CH₂I)₂ was synthesized according to the known literature methods.¹⁷

Electrochemistry: Corrections for the iR drop were performed for all experiments. Cyclic voltammetric measurements were conducted in three-electrode technique [glassy carbon disk (diameter d = 1.6 mm) as working electrode, Ag/Ag⁺ in MeCN as reference electrode, Pt wire as counter electrode] using a Reference 600 Potentiostat (Gamry Instruments). All experiments were performed in CH₂Cl₂ solutions (concentration of the complex 1.0 mM) containing 0.1 M [*n*-Bu₄N][BF₄] at room temperature. Solutions were deaerated by N₂ purge for 5-10 min, and a blanket of N₂ was maintained over the solutions during the measurements. The vitreous carbon disk was polished on a felt tissue with alumina before each measurement. All potential values reported in this paper are referenced to the potential of the ferrocenium/ferrocene (Fc⁺/Fc) couple.

Crystal structure determination of complex 2:

The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_{α} radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.^[29-31] The structure was solved by direct methods (SHELXS)^[32] and refined by full-matrix least squares techniques against Fo² (SHELXL-97).^[32] Both hydrogen atoms were located by difference Fourier synthesis and refined isotropically. MERCURY^[33] was used for structure representations.

Crystal Data for 2: C₇H₂Fe₂O₆Te₂, Mr = 548.99 gmol⁻¹, red-brown prism, size 0.088 x 0.082 x 0.078 mm³, monoclinic, space group P 2₁/c, a = 6.8003(1), b = 13.7428(3), c = 14.0199(4) Å, β = 104.035(1)°, V = 1271.12(5) Å³, T= -140 °C, Z = 4, $\rho_{calcd.}$ = 2.869 gcm⁻³, μ (Mo-K_α) = 67.9 cm⁻¹, multi-scan, transmin: 0.5704, transmax: 0.7456, F(000) = 992, 16724 reflections in h(-8/8), k(-17/17), l(-18/18), measured in the range 3.09° ≤ $\Theta \le 27.47^{\circ}$, completeness Θ max = 99.6%, 2900 independent reflections, R_{int} = 0.0348, 2693 reflections with F₀ > 4 σ (F₀), 162 parameters, 0 restraints, R1_{obs} = 0.0206, wR²_{obs}

= 0.0422, $R1_{all}$ = 0.0233, wR^2_{all} = 0.0434, GOOF = 1.070, largest difference peak and hole: 0.554 / -0.655 e Å⁻³.

General Procedure for the Synthesis of Complex 2: A mixture of Te (1.86 mmol) and KCN (1.86 mmol) was dissolved in dimethyl sulfoxide (10 mL) and refluxed for one hour. The resulting deep-red solution was cooled down to room temperature before the addition of Me₂Sn(CH₂I)₂ (0.93 mmol) and then stirred overnight. Subsequently, a solution of Fe₃(CO)₁₂ (1.90 mmol) in THF (25 mL) was added and the mixture was stirred under reflux for two hours. The resulting reddish solution was cooled down and the solvent removed by rotary evaporator. The residue was introduced into column chromatography using 100% hexane as eluent. Complex 2 was collected from the first band as red powder.

[Fe₂(CO)₆{ μ -(TeCH₂Te)}], **2**: Yield 33%. ¹**H** NMR (400 MHz, CHCl₃, ppm): δ = 2.20 (s, with ¹²⁵Te satellites, (²*J*_(TeH) = 20 Hz, 2H, C*H*₂). ¹³C{¹**H**} NMR (100.6 MHz, CHCl₃, ppm): δ = 22.5 (s, *C*H₂), 211.8 (s, CO). ¹²⁵T{¹**H**} NMR (126 MHz, CHCl₃, ppm): δ = 337.9. **IR** (*v*_{CO}, cm⁻¹): 2054 (s), 2025 (m), 1998 (m), 1986 (m) and 1960 (w). **DEI-MS**: m/z = 549 [M]⁺. C₇H₂Fe₂O₆Te₂: C 15.61 (calcd. 15.32), H 0.60 (0.37), S 13.45 (13.70).

Supporting Information Available: Crystallographic data deposited at the Cambridge Crystallographic Data Centre under CCDC-1825815 for **2** contain the supplementary crystallographic data excluding structure factors; this data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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