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Diiron Dichalcogenolato (Se and Te) Complexes: Models for the Active Site of [FeFe] Hydrogenase

**Mohammad K. Harb,[a] Ulf-Peter Apfel,[a] Takahiro Sakamoto,*[b]
Mohammad El-khateeb,*[c] and Wolfgang Weigand*[a]**

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday

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A short overview of diiron dichalcogenolato (Se and Te) model complexes related to the chemistry of the diiron subsite of [FeFe] hydrogenase is presented. These model complexes allow direct comparison with the diiron dithiolato compound analogues for their ability to catalyze the formation of H_2 from weak acids. Few detailed photoelectron spectroscopy (PES) investigations and density functional theory (DFT) calculations have been reported until now, and the results will be summarized here. On the basis of preliminary results, we propose targets for the synthesis of more efficient biomimetic diiron dichalcogenolato catalysts.

Introduction

Over 85% of the energy consumed worldwide is provided by non-renewable fuels because of their relatively cheap price and ease of access. These fuels, however, will be diminished in the coming few decades and cannot be replenished in a short period of time. Therefore, the search for renewable energy sources will be a major challenge for the scientific community. Ethanol, bio-diesel, and dihydrogen are among these renewable fuels that could provide an alternative to fossil fuels. Especially dihydrogen received enormous attention,[1–7] as it can be directly converted to electricity with high efficiency[7,8] and the only product of its combustion is water. Therefore, the effective production of dihydrogen becomes very important, and many researchers have reported studies on this process.[9–14]

In nature many organisms generate dihydrogen from water by using sunlight as the energy source and hydrogenase enzymes as catalyst.[15,16] Hydrogenases are proteins that possess solely iron or iron and nickel in their active sites, catalyzing the reversible, two-electron redox reaction between protons and molecular hydrogen [Equation (1)]. These enzymes are found in many microorganisms such as bacteria, archae, and eukarya, and they were first discovered in 1931 by Stephenson and Stickland in colon bacteria.[17]

$$2H^+ + 2e^- \xrightleftharpoons{\text{Hydrogenase}} H_2 \qquad (1)$$

Hydrogenases are classified, on the basis of the metal content in their active site, into three major families: [NiFe]-, [FeFe]- and [Fe] hydrogenases.[18–34] A characteristic feature of all hydrogenases is that the iron atoms are coordinated by biologically unusual ligands (CO, CN^-), which were first detected by FTIR spectroscopy.[35,36] [FeFe] and [NiFe] hydrogenases contain thiolato-bridged bimetallic centers, typically with a vacant coordination site on one iron atom. A subgroup of [NiFe] hydrogenase comprises [NiFeSe] hydrogenase, in which one of the terminal cysteine ligands of the nickel atom is replaced by selenocysteine.[37] This subfamily shows higher tolerance to O_2 exposure; studies on *Desulfomicrobium baculatum*, containing the [NiFeSe] unit, show that it retains partial activity for H_2 oxidation in the presence of O_2.[38]

The third class of enzymes, [Fe] hydrogenases, has long been thought to contain no metal. However, it was shown later that the active site includes a single iron atom with an unusual coordination sphere.[24,39–41]

Above all, [FeFe] hydrogenase has been considered to be mainly a H_2 producer and demonstrates considerably higher turnover numbers and frequencies for H_2 production relative to the other hydrogenases.[21,22,42] A representative example of these enzymes was isolated from *Desulfovibrio*

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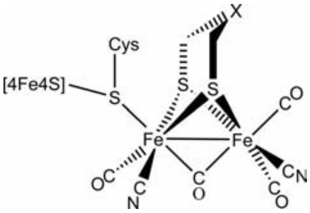
[a] Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena,
August-Bebel-Straße 2, 07743 Jena, Germany
E-mail: wolfgang.weigand@uni-jena.de
[b] Department of Chemistry and Biochemistry, The University of Arizona,
Tucson, AZ 85721, U.S.A
[c] Chemistry Department, Jordan University of Science and Technology,
22110 Irbid, Jordan

desulfuricans.[43] This enzyme can produce up to 9000 molecules of dihydrogen per second at 30 °C for each active site.[44]

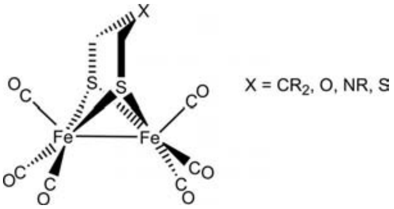
[FeFe] hydrogenase was first found in the gram positive bacterium *Clostridium pasteurianum* and solely possesses a diiron unit in the active site of its hydrogenase.[45] Spectroscopic and diffraction methods revealed a [4Fe4S] subsite, connected to a [2Fe2S] subsite. This unit is called the H-cluster (Scheme 1). Consecutive investigations revealed that the [2Fe2S] subsite is responsible for hydrogen production.[46]



Scheme 1. Basic structure of the H-cluster of [FeFe] hydrogenase, (X = CH_2, NH, or O, which remains crystallographically and analytically unresolved).

At the [2Fe2S] subsite, terminal carbon monoxide and cyanide ligands are bound to each iron atom. Moreover, the two iron atoms share a bridging carbon monoxide in the H_{ox}-state and a bridging (SCH_2XCH_2S) linker.[43,45] Currently, it is still an open question whether X is CH_2, NH, or O, and only one plausible mechanism for the biosynthesis of an S-to-S linker is described for an azadithiolato moiety.[47]

Several model complexes mimicking the active site of [FeFe] hydrogenase have been synthesized and their electrocatalytic activity towards dihydrogen formation is well documented. These complexes usually contain dithiolato-bridged diiron cores (Scheme 2).[48–51]



Scheme 2. Models of [FeFe] hydrogenases containing the dithiolato ligand.

This article briefly summarizes the chemistry related to the synthesis of structural and functional analogues of the active site of [FeFe] hydrogenase, containing the 3rd and 4th row chalcogen atoms, selenium and tellurium, instead of sulfur. Furthermore, this review presents the different properties of such model complexes, relative to those of the typical [2Fe2S] subsite units.

Synthetic Models

In contrast to the well-known [2Fe2S] compounds, the heavier analogues, containing Se and Te, are sparsely known. Recently, we and others paid attention to model complexes containing the heavier chalcogens such as Se or Te instead of sulfur.[52–60] Herein we highlight recent work on this topic, in order to give the reader an overview of the consequences of substituting selenium or tellurium in lieu of sulfur in dichalcogenolato [FeFe] hydrogenase model compounds.

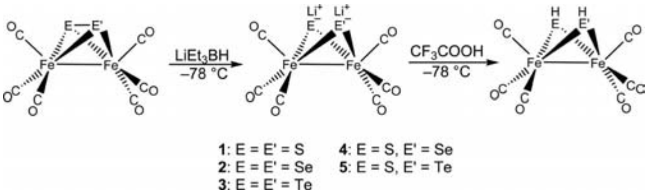
Mohammad K. Harb (left) received his B.Sc. and M.Sc. from the Jordan University of Science and Technology (Irbid) in 2006. He received his Ph.D. at the Friedrich-Schiller-Universität Jena (Germany) in 2010 for the investigation of diirondichalcogenolato complexes as models for the active site of [FeFe] hydrogenase, supported by a fellowship of the Deutscher Akademischer Austauschdienst (DAAD). He is currently a lecturer at Jordan University of Science and Technology (Irbid, Jordan).
Professor Mohammad El-khateeb (right) was born in Jordan in 1966. He got his B.Sc. and M.Sc. degrees in Chemistry from Yarmouk University, Irbid, Jordan. In 1996 he got his Ph.D. degree from McGill University, Montreal, Canada. Presently, he works as a full professor of inorganic chemistry at Jordan University of Science and Technology. His research interests include the synthesis, characterization, and application of organometallic chalcogenolato complexes.

Ulf-Peter Apfel (left) is a native German and received his Diploma and Ph.D. from the Friedrich-Schiller-Universität Jena in 2010 as a fellow of the Studienstiftung des deutschen Volkes. He is trained in bioorganometallic chemistry and electrochemistry and received his Ph.D. for investigating models for the active site of [FeFe] hydrogenase.
Wolfgang Weigand (right) is a native of Munich, Germany. He received his Ph.D. from the Ludwig-Maximilian-Universität München under the supervision of W. Beck in 1986. After a postdoctoral position with D. Seebach at the ETH Zürich in 1986/87, he returned to the Ludwig-Maximilian-Universität and received his habilitation in 1994. Since 1997 he is Professor of Inorganic Chemistry at the Friedrich-Schiller-Universität Jena. He is interested in the coordination chemistry of chalcogen-containing ligands, including models for [FeFe] hydrogenase as well as metal complexes for anticancer therapy and prebiotic chemistry (Synthetic Cells).

After receiving his Master of Science from Indiana University-Purdue University Indianapolis and a short internship in industry (Eli Lilly & Co, Indianapolis), Takahiro Sakamoto received his Ph.D. in 2010 from the University of Arizona (Tucson, USA) under the supervision of Prof. D. L. Lichtenberger. He is interested in the study of electronic structures and catalytic mechanisms of organometallic compounds using gas-phase photoelectron spectroscopy, electrochemistry, and DFT computations.

Structural Models

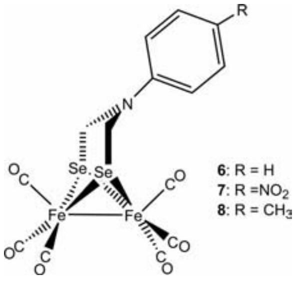
Reviewing the literature, one can find $(CO)_6Fe_2(\mu\text{-}EE')$ (E, E′ = S, Se, Te) complexes, which are readily available and easily functionalized.[61–75] These complexes are reduced by $LiEt_3BH$, leading to E–E′ bond cleavage and forming the dianionic species $[(\mu\text{-}EE')Fe_2(CO)_6]^{2-}$ (**1**–**5**), as shown in Scheme 3. Reaction of electrophiles such as organic halides with these dianions give complexes with general formulas $[(\mu\text{-}ER)(\mu\text{-}E'R)Fe_2(CO)_6]$ and $[(\mu\text{-}EE'R)Fe_2(CO)_6]$.[75–96]



Scheme 3. Preparation and protonation of dianion species $[(\mu\text{-}EE')Fe_2(CO)_6]^{2-}$.

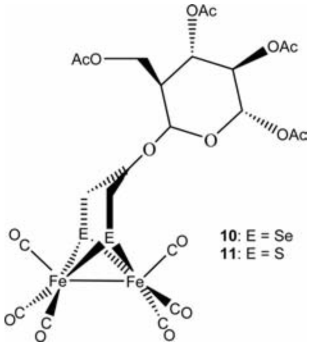
Numerous [FeFe] hydrogenase model complexes have been prepared by reaction of $[(CO)_6Fe_2(\mu\text{-}S_2)]^{2-}$ (**1**) and dibromoalkanes.[61,75] The analogous complexes $[(CO)_6Fe_2(\mu\text{-}Se_2)]^{2-}$ (**2**),[61–64] $[(CO)_6Fe_2(\mu\text{-}Te_2)]^{2-}$ (**3**),[67] $[(CO)_6Fe_2(\mu\text{-}SSe)]^{2-}$ (**4**), and $[(CO)_6Fe_2(\mu\text{-}STe)]^{2-}$ (**5**)[72,74] inspired scientists to synthesize model complexes containing heavier chalcogenolato ligands for structure mimics of the active sites, which leads to an increase of the electron density at the iron atoms. Probably, this should influence the reactivity and redox properties of the resulting model complexes. In addition, such studies might be able to provide more information for understanding the biological function of selenium in [NiFeSe] hydrogenase.

Peng and co-workers first described the synthesis of [FeFe] hydrogenase model complexes containing diselenolato ligands.[54] In their study, three diiron diselenolato complexes $[\{(\mu\text{-}SeCH_2)_2NC_6H_4R\}Fe_2(CO)_6]$ (R = H, **6**; R = 4-NO_2, **7**; R = 4-CH_3, **8**) were prepared (Scheme 4). The electrochemical reduction of protons catalyzed by **8** was investigated in the presence of *p*-toluenesulfonic acid (HOTs) as the proton source. Complex **8** has been proven to be a catalyst for electrochemical reduction of protons from *p*-toluenesulfonic acid to give dihydrogen. In order to evaluate the influence of the different bridging chalcogenolato atoms on the electrochemical properties as well as their electrocatalytic activity for proton reduction, IR spectroscopy and cyclic voltammetry were performed. For example, a small shift (ca. 9 cm^{-1}) of the IR bands to lower wavenumbers was observed upon selenium incorporation. However, no difference was observed in cyclic voltammetry, and both sulfur-containing $[\{(\mu\text{-}SCH_2)_2NC_6H_4(4\text{-}CH_3)\}Fe_2(CO)_6]$ (**9**) and selenium-containing compound **8** revealed reduction to the Fe^IFe^0 level at –1.50 V vs. the Ag/Ag^+ reference electrode.[54] In contrast, it was found that Se-containing compound **8** has a slightly higher electrocatalytic activity for proton reduction as compared to S-containing analogue complex **9**, when HOTs was used as proton source.



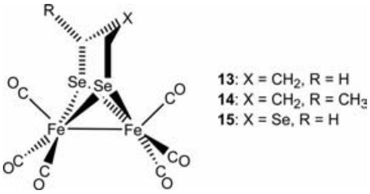
Scheme 4. Azadiirondiselenolato model complexes **6**–**8**.

Similar results were obtained for a water-soluble [FeFe] hydrogenase model containing a peripherally bound sugar residue with a [2Fe2E] core; $Fe_2(\mu\text{-}EC_3H_5RE)(CO)_6$ (R = tetra-*O*-acetyl-β-D-glucopyranoside) {E = Se **10**, S **11**}, (Scheme 5).[55] Both complexes revealed electrochemical H_2 production from acetic acid and water. The presence of selenium offers higher activity towards H_2 evolution, but at considerably more negative potentials than the corresponding sulfur complexes. In addition, compound **10** provided higher stability under reductive conditions upon addition of water. In accordance to the IR spectra, this was ascribed to the stronger electropositivity of selenium. Hence, the iron becomes more electron-rich, leading to a stronger π-backbonding of the CO ligands.



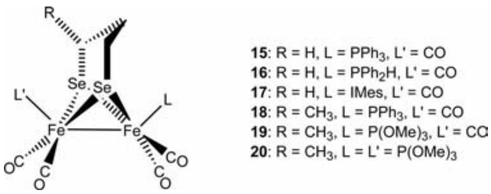
Scheme 5. Sugar-substituted diirondiselenolato model complex **10** and its dithiolato analogue **11**.

Following these initial experiments, more selenium-containing complexes based on the exhaustively investigated sulfur complex, $[Fe_2(\mu\text{-}SC_3H_6S)(CO)_6]$ (PDT) (**12**), were synthesized to obtain more detailed information on [2Fe2Se] cluster compounds. $[Fe_2(\mu\text{-}SeC_3H_6Se)(CO)_6]$ (PDSe) (**13**),[56,57] $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6]$ (**14**), and $[Fe_2\{(\mu\text{-}SeCH_2)_2Se\}(CO)_6]$ (**15**) (Scheme 6) were prepared subsequently. A lengthening of the Fe–Fe bond is notable for all these complexes. For example, whereas the Fe–Fe bond length is 2.5610(8) Å in **13**,[56] compound **12** displays a distance of 2.5103(11) Å.[97] As already described for complexes **6**–**8** and **10**, no distinct deviation of the peak potentials can be observed for **13** and **14**, relative to those of their sulfur-containing analogues. Once more, a comparative study on the catalytic activity of model **13** and its sulfur analogue **12** proved that Se-containing complex **13** provides higher activity for proton reduction to molecular H_2 under electrochemical conditions.[55] Moreover, the photoelectron spectrum of and theoretical calculations on **14** revealed that its reorganization energy is substantially lower than that for sulfur-analogue complexes.[54] This observation predicts faster electron transfer with complexes containing [2Fe2Se] rather than [2Fe2S] cores, which could explain the greater electrocatalytic activity toward H_2 production of Se-containing complexes.

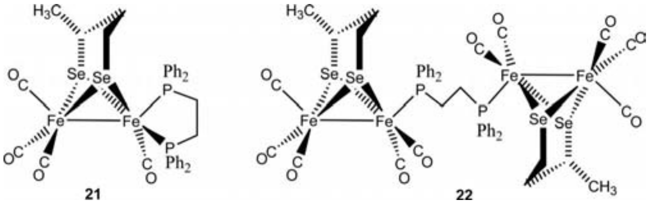


Scheme 6. Models of [FeFe] hydrogenases containing diselenolato ligands.

Replacement of CO ligands by strong donor ligands, according to procedures similar to those described for the sulfur analogues,[98] substantially increases the electron density on the iron atoms. It is well known that phosphanes and N-heterocyclic carbene ligands are good substitutes for the natural counterparts of CO and cyanide. Thus, similar donor properties are provided. Sun and co-workers prepared a series of monosubstituted diiron complexes [(μ-PDSe)-$Fe_2(CO)_5L$] {L = PPh_3 **15**, PPh_2H **16**, and 1,3-bis(mesityl)-imidazol-2-ylidene (I_{Mes}) **17**} (Scheme 8).[57] This investigation was followed by the work of Weigand and co-workers, in which a substitution study of the carbonyl groups of compound **14** by PPh_3 or $P(OMe)_3$ resulted in the monosubstituted complexes [(μ-$SeCH(CH_3)CH_2CH_2Se)Fe_2(CO)_5$-L] {L = PPh_3 **18**, $P(OMe)_3$ **19**} and the disubstituted compound [(μ-$SeCH(CH_3)CH_2CH_2Se)Fe_2(CO)_4\{P(OMe)_3\}_2$] (**20**) (Scheme 7).[58] Moreover, the replacement of carbonyl ligands of **14** by bis(diphenylphosphanyl)ethane (dppe) afforded the chelated diiron complex **21** and the bridged tetrairon complex **22** (Scheme 8).[58] In contrast to the numerous crystallographic data of such compounds, only little is known about substituted [2Fe2Se] complexes. Solely the electrochemical properties of complex **18** are described in the literature.[58] A significant shift of both the oxidation [+0.35 V (**18**)[58] < +0.76 V (**14**)[56]] and reduction potential [–2.00 V (**18**)[58] < –1.83 V (**14**)[56]] was observed. This trend is not unexpected, and similar shifts were already observed for sulfur-containing compounds.[99]

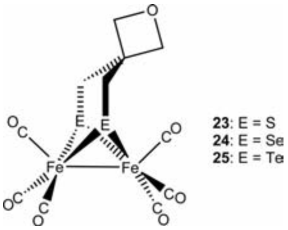


Scheme 7. Substituted diiron diselenide model complexes.



Scheme 8. Models of [FeFe] hydrogenases containing a chelating and bridging dppe ligand.

In order to compare S, Se, and Te analogues and to investigate the influence of the heavier atoms, it is important to provide the same substitution pattern in the E-to-E linker (E = S, Se, Te). In a recent study, Weigand and co-workers extended the current investigations on [FeFe] hydrogenase model complexes containing the higher homologues by using the concept of a fixed backbone and prepared complexes **23**, **24**, and **25** with dithiolato, diselenolato, and ditellurolato ligands, respectively (Scheme 9).[59]



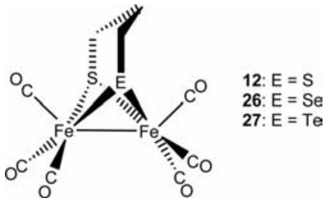
Scheme 9. Models of [FeFe] hydrogenases containing dichalcogenolato ligands.

The oxetane ring remarkably stabilizes diselenium and ditellurium precursor compounds. This provides the opportunity to synthesize the homologous S, Se, and Te series) (compounds **23**–**25**). The increasing donor ability of Se and Te atoms in these complexes is reflected by the decreasing carbonyl stretching frequencies (the average ν_{CO} values are 2019, 2013, and 2004 cm^{-1} for **23**, **24**, and **25**, respectively) and the decreasing vertical ionization energies. This trend is compensated by decreasing reorganization energies by which the adiabatic ionization energies and the electrochemical oxidation potentials of the [2Fe2S], [2Fe2Se], and [2Fe2Te] clusters appear within narrow ranges.[99]

Contrary to the above-mentioned results, the catalytic activity of the complexes towards proton reduction from weak acids is substantially diminished from **23** to **24** and even more to **25**. This trend was also reflected in DFT calculations, whereupon a disfavored ability to adopt the rotated structures and to provide a vacant coordination site was observed for anionic species. The increasing size of the chalcogen atoms and hence the increased distance between the iron atoms are likely reasons for this behavior.[99]

Recently, [FeFe] hydrogenase models utilizing mixed dichalcogenolato ligands were investigated. The mixed (S, Se) $Fe_2(\mu\text{-}SC_3H_6Se)(CO)_6$ (**26**) and (S, Te) $Fe_2(\mu\text{-}SC_3H_6Te)$-$(CO)_6$ (**27**) complexes were prepared by reaction of 1,2-thiaselenolane and 1,2-thiatellurolane with $Fe_3(CO)_{12}$ (Scheme 10).[60]

Cyclic voltammetry revealed no influence of the heavier chalcogens to the one-electron oxidation. In contrast, significant shifts of the reduction potentials to more positive values were observed [–1.652 V (**12**) > –1.618 V (**26**) > –1.585 V (**27**)].[60] It is remarkable that this trend was also



Scheme 10. Models of [FeFe] hydrogenases containing mixed dichalcogenolato ligands.

observed for compound **23**–**25**, where the dithiolato ligand was exchanged by a diselenolato and/or a ditellurolato ligand. However, no considerable improve of the catalysts properties for the H_2 generation was observed, compared to their sulfur counterparts.

Photoelectron Spectroscopy

Photoelectron spectroscopy provides an experimental measure of ionization and molecular reorganization energies, and it helps to quantify trends in electronic structure in this series of molecules. The ionization energies also are well-defined quantities used for validation of the electron energies from computational methods and provide a foundation for modeling the electrochemistry and chemical behavior.

The gas-phase photoelectron spectra of [FeFe] hydrogenase active site catalysts (**12**, **14**, **23**–**27**) were reported by Weigand and co-workers (Figure 1).[56,58–60] These active site catalysts typically exhibit extensive overlap of six Fe 3d orbitals and range up to about 9 eV with a weak shoulder on the low ionization energy side corresponding to ionization from the HOMO. The HOMO is calculated to be predominantly the Fe–Fe σ bond (vide infra), with an adiabatic ionization (IE_A) energy around 7.5 eV. The Fe-based metal ionizations visibly decreased with substitution from S to Se to Te, indicating increased electron richness of the diiron core. The second and third ionization bands, typically ranging from 9.0 to 9.5 eV, are chalcogen-based, and those from 10.0 eV and above are mixtures of Fe-, O-, C-, and chalcogen-based orbitals from the photoelectron spectra of the oxetane series of compounds (**23**–**25**). The orbital mixing of these catalysts can be observed from the combination of the relative intensity change between He I (21.2 eV) and He II (40.8 eV) photoelectron spectra and the theoretical partial photoionization cross-sections of the atoms.[100] The probability of ionization from a chalcogen p orbital falls by an average factor of 10 from He I to He II excitation, while the probability of O p orbital and Fe d orbital ionizations increases by almost a factor of two.[100]

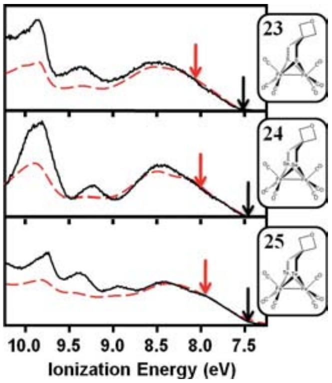


Figure 1. Photoelectron spectra of oxetane-containing compounds **23**–**25**. He I (solid line) and He II (dashed line). The black arrow indicates the calculated IE_A. The red arrow indicates the calculated IE_V.

Overall, the lower energy shift of the ionization energies observed in the photoelectron spectra reflects the greater donor ability of their chalcogen atom, from S to Se to Te, to the diiron core of the [FeFe] hydrogenase active site catalysts.

Density Functional Theory Calculations

DFT calculations can provide additional understanding of the electronic structure and chemical properties of a chemical system, provided the calculations are appropriately validated against experimental structures, spectroscopic observations, electrochemical measurements, and thermodynamic properties. The computational methodology utilized by Weigand and co-workers to investigate these catalysts (**12**, **13**, **23**–**27**) has previously been shown to give good quantitative agreement with the structures, CO stretching frequencies (νCO), oxidation and reduction potentials, bond energies, and pK_a values of a variety of catalysts inspired by [FeFe] hydrogenase active sites.[56,59,60,101–103] The optimized geometries and computed νCO values agree very well with the experimental values, suggesting that the computations are able to yield sufficiently reasonable electron distributions and energies for catalysts **12**, **14**, and **23**–**27**.

The calculations are also able to account for the onset energies of first ionization bands very well. The vertical ionization (IE_V) in these catalysts are difficult to define experimentally, because of the large number of broad overlapping ionizations in this region, but the IE_V energies, calculated by the ΔSCF method between the neutral molecule and the cation, were also able to properly account for the shifting of the primary ionization band intensity to lower energy with substitution of chalcogens from S to Se to Te. Furthermore, the calculated IE_A, for which the structures of the cations were optimized to their global minima, were close to the experimental onset energies of the first ionization bands. The agreement between the calculated ionization energies and the lower energy shifting trend of ionization band intensity illustrates the success of the computational model for these active site catalysts. The total cation reorganization energy (ΔE_r) for each catalyst was calculated as the energy difference between the IE_V and the IE_A. The trend in reduction of ΔE_r in these catalysts (**23**–**27**) is visually apparent in the photoelectron spectra, in which the energy separation between the IE_V and IE_A decreases down the series. The magnitude of reduction in ionization energies is influenced by the heavier chalcogens, reflecting their greater donor ability as well as the number of chalcogens substituted and variations of ligands attached to the diiron core of the molecule. Furthermore, smaller ΔE_r values may lead to smaller intramolecular (inner-sphere) and intermolecular (outer-sphere) reorganization of the diiron compounds, which could lead to faster electron-transfer rates,[104–106] according to Marcus theory,[107] and possibly to increased catalytic activities.

The computations were also able to reveal the Kohn–Sham orbitals (HOMO and LUMO). On the basis of the Fe–Fe bonding character in the HOMO of the neutral molecule, the primary geometry relaxation in the cation was expected to be a lengthening of the Fe–Fe distance, and indeed this was found when a computational search for the lowest-energy geometry of the cation started with the structure of the neutral molecule. The LUMOs for this family of catalysts consists mainly of the metal–metal antibonding interaction with some metal–chalcogen antibonding interaction. Similar to the removal of an electron from the HOMO, adding an electron into the Fe–Fe antibonding orbital (LUMO) promotes elongation of the Fe–Fe bond. However, a wider search on the potential energy surface found cations and anions with a bridging CO to be the global minimum (Figure 2). This general arrangement of the bridged CO "rotated" structure is analogous to the active site of [FeFe] hydrogenase.[108] This has been the subject of much attention[103,109–114] and thought to be critical for the H_2 production.[103]

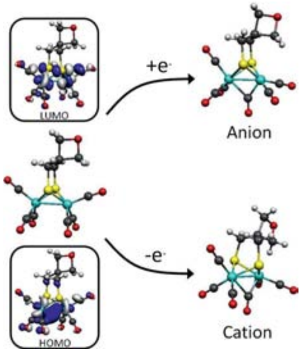


Figure 2. Gas-phase geometry-optimized structures of the neutral, anionic, and cationic forms of **23** with their HOMO and LUMO.

Concluding Remarks

As shown above, the replacement of S atoms of diiron dithiolato model complexes by more electropositive Se atoms leads to an enhancement of the catalytic activity of some [FeFe] hydrogenase models. This could be attributed to an increase of the electron density at the Fe atoms and faster electron transfer in complexes containing [2Fe2Se] rather than [2Fe2S] cores. Some limitation of this conclusion is found, due to disfavoring of the anions to adopt the rotated structures with complexes containing [2Fe2Se]. In order to overcome this limitation, we might expect further chemical studies on model systems containing high steric demands, which could force the basal CO ligand to form the rotated structure. This could be achieved either by replacing the apical CO with bulky ligands with good donor ability or by increasing the steric demand at the diselenolato ligands (e.g. $SeCR_2CH_2CH_2Se$, where R = Ph, *tert*-butyl). To the best of our knowledge, there are no known hydride diiron diselenolate model complexes. Enhancement of the electron density at the iron centers of diiron diselenolate systems could influence the ability to prepare and stabilize both bridging and terminal hydride model complexes. Therefore, we might anticipate further structural and electrochemical studies in this direction. Furthermore, it has been shown in the literature that the bridgehead CH_2 group of the PDT model complex could be formally replaced by NR, O, and S. To the best of our knowledge, only the Se and NR groups in bridgehead of PDSe analogues are known. We might expect studies pertaining to the preparation and characterization of heavier dichalcogenolato model complexes with different bridgehead moieties such as NH, S, and O. These model complexes could be compared with diiron dithiolato compound analogues for their ability to catalyze protons to molecular H_2 at moderate potential.

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[1] A. Melis, L. Zhang, M. Forestier, M. L. Ghirardi, M. Seibert, *Plant Physiol.* **2000**, *122*, 127–136.
[2] R. Cammack, M. Frey, R. Robson in *Hydrogen as a Fuel: Learning from Nature*, Taylor & Francis, London, **2001**.
[3] J. Woodward, M. Orr, K. Cordray, E. Greenbaum, *Nature* **2000**, *405*, 1014–1015.
[4] R. H. B. Coontz, *Science* **2004**, *305*, 957.
[5] M. Ball, M. Wietschel, *Int. J. Hydrogen Energy* **2009**, *34*, 615–627.
[6] T. Happe, A. Hemschemeier, M. Winkler, A. Kaminski, *Trends Plant Sci.* **2002**, *7*, 246–250.
[7] V. Ananthachar, J. J. Duffy, *Solar Energy* **2005**, *78*, 687–694.
[8] L. E. Macaskie, V. S. Baxter-Plant, N. J. Creamer, A. C. Humphries, I. P. Mikheenko, P. M. Mikheenko, D. W. Penfold, P. Yong, *Biochem. Soc. Trans.* **2005**, *33*, 76–79.
[9] M. J. Antal, S. G. Allen, D. Schulman, X. Xu, R. J. Divilio, *Ind. Eng. Chem. Res.* **2000**, *39*, 4040–4053.
[10] P. C. Hallenbeck, J. R. Benemann, *Int. J. Hydrogen Energy* **2002**, *27*, 1185–1193.
[11] R. D. Cortright, R. R. Davda, J. A. Dumesic, *Nature* **2002**, *418*, 964–967.
[12] G. W. Huber, J. W. Shabaker, J. A. Dumesic, *Science* **2003**, *300*, 2075–2077.
[13] G. A. Deluga, J. R. Salge, L. D. Schmidt, X. E. Verykios, *Science* **2004**, *303*, 993–997.
[14] M. W. W. Adams, E. I. Stiefel, *Science* **1998**, *282*, 1842–1843.

[15] M. Winkler, A. Hemschemeier, C. Gotor, A. Melis, T. Happe, *Int. J. Hydrogen Energy* **2002**, *27*, 1431–1439.
[16] A. Melis, T. Happe, *Plant Physiol.* **2001**, *127*, 740–748.
[17] M. Stephenson, L. H. Stickland, *Biochem. J.* **1931**, *25*, 205–214.
[18] P. M. Vignais, B. Billoud, *Chem. Rev.* **2007**, *107*, 4206–4272.
[19] A. L. De Lacey, V. M. Fernandez, M. Rousset, R. Cammack, *Chem. Rev.* **2007**, *107*, 4304–4330.
[20] E. C. Hatchikian, N. Forget, V. M. Fernandez, R. Williams, R. Cammack, *Eur. J. Biochem.* **1992**, *209*, 357–365.
[21] M. Y. Darensbourg, E. J. Lyon, J. J. Smee, *Coord. Chem. Rev.* **2000**, *206*, 533–561.
[22] D. J. Evans, C. J. Pickett, *Chem. Soc. Rev.* **2003**, *32*, 268–275.
[23] O. Pilak, B. Mamat, S. Vogt, C. H. Hagemeier, R. K. Thauer, S. Shima, C. Vonrhein, E. Warkentin, U. Ermler, *J. Mol. Biol.* **2006**, *358*, 798–809.
[24] W. Lubitz, E. Reijerse, M. van Gastel, *Chem. Rev.* **2007**, *107*, 4331–4365.
[25] P. E. M. Siegbahn, J. W. Tye, M. B. Hall, *Chem. Rev.* **2007**, *107*, 4414–4435.
[26] S. Shima, O. Pilak, S. Vogt, M. Schick, M. S. Stagni, W. Meyer-Klaucke, E. Warkentin, R. K. Thauer, U. Ermler, *Science* **2008**, *321*, 572–575.
[27] S. P. J. Albracht, *Biochim. Biophys. Acta Bioenerg.* **1994**, *1188*, 167–204.
[28] E. Graf, R. K. Thauer, *FEBS Lett.* **1981**, *136*, 165–169.
[29] R. Cammack, D. Patil, R. Aguirre, E. C. Hatchikian, *FEBS Lett.* **1982**, *142*, 289–292.
[30] G. Wang, M. Benecky, B. Huynh, J. Cline, M. Adams, L. Mortenson, B. Hoffman, E. Munck, *J. Biol. Chem.* **1984**, *259*, 14328–14331.
[31] M. W. W. Adams, L. E. Mortenson, *Biochim. Biophys. Acta Bioenerg.* **1984**, *766*, 51–61.
[32] C. Tard, C. J. Pickett, *Chem. Rev.* **2009**, *109*, 2245–2274.
[33] F. Gloaguen, T. B. Rauchfuss, *Chem. Soc. Rev.* **2009**, *38*, 100–108.
[34] D. M. Heinekey, *J. Organomet. Chem.* **2009**, *694*, 2671–2680.
[35] R. P. Happe, W. Roseboom, A. J. Pierik, S. P. Albracht, K. A. Bagley, *Nature* **1997**, *385*, 126.
[36] A. J. Pierik, W. Roseboom, R. P. Happe, K. A. Bagley, S. P. J. Albracht, *J. Biol. Chem.* **1999**, *274*, 3331–3337.
[37] E. Garcin, X. Vernede, E. Hatchikian, A. Volbeda, M. Frey, J. Fontecilla-Camps, *Structure* **1999**, *7*, 557–566.
[38] A. Parkin, G. Goldet, C. Cavazza, J. C. Fontecilla-Camps, F. A. Armstrong, *J. Am. Chem. Soc.* **2008**, *130*, 13410–13416.
[39] E. J. Lyon, S. Shima, R. Boecher, R. K. Thauer, F. Grevels, E. Bill, W. Roseboom, S. P. J. Albracht, *J. Am. Chem. Soc.* **2004**, *126*, 14239–14248.
[40] S. Shima, E. J. Lyon, M. Sordel-Klippert, M. Kauß, J. Kahnt, R. K. Thauer, K. Steinbach, X. Xie, L. Verdier, C. Griesinger, *Angew. Chem.* **2004**, *116*, 2601; *Angew. Chem. Int. Ed.* **2004**, *43*, 2547–2551.
[41] S. Shima, E. J. Lyon, R. K. Thauer, B. Mienert, E. Bill, *J. Am. Chem. Soc.* **2005**, *127*, 10430–10435.
[42] M. Frey, *ChemBioChem* **2002**, *3*, 153–160.
[43] Y. Nicolet, C. Piras, P. Legrand, C. E. Hatchikian, J. C. Fontecilla-Camps, *Structure* **1999**, *7*, 13–23.
[44] R. Cammack, *Nature* **1999**, *397*, 214–215.
[45] J. W. Peters, W. N. Lanzilotta, B. J. Lemon, L. C. Seefeldt, *Science* **1998**, *282*, 1853–1858.
[46] A. Silakov, E. J. Reijerse, S. P. J. Albracht, E. C. Hatchikian, W. Lubitz, *J. Am. Chem. Soc.* **2007**, *129*, 11447–11458.
[47] E. Pilet, Y. Nicolet, C. Mathevon, T. Douki, J. C. Fontecilla-Camps, M. Fontecave, *FEBS Lett.* **2009**, *583*, 506–511.
[48] J. Capon, F. Gloaguen, P. Schollhammer, J. Talarmin, *Coord. Chem. Rev.* **2005**, *249*, 1664–1676.
[49] X. Liu, S. K. Ibrahim, C. Tard, C. J. Pickett, *Coord. Chem. Rev.* **2005**, *249*, 1641–1652.
[50] L. C. Sun, B. Akermark, S. Ott, *Coord. Chem. Rev.* **2005**, *249*, 1653–1663.
[51] C. Tard, C. J. Pickett, *Chem. Rev.* **2009**, *109*, 2245–2274.
[52] L.-C. Song, W. Gao, C.-P. Feng, D.-F. Wang, Q.-M. Hu, *Organometallics* **2009**, *28*, 6121–6130.
[53] L.-C. Song, *Science China, Ser. B Chem.* **2009**, *52*, 1–14.
[54] S. Gao, J. Fan, S. Sun, X. Peng, X. Zhao, J. Hou, *Dalton Trans.* **2008**, 2128–2135.
[55] U.-P. Apfel, Y. Halpin, M. Gottschaldt, H. Görls, J. G. Vos, W. Weigand, *Eur. J. Inorg. Chem.* **2008**, 5112–5118.
[56] M. K. Harb, T. Niksch, J. Windhager, H. Görls, R. Holze, L. T. Lockett, N. Okumura, D. H. Evans, R. S. Glass, D. L. Lichtenberger, M. El-khateeb, W. Weigand, *Organometallics* **2009**, *28*, 1039–1048.
[57] L.-C. Song, B. Gai, H.-T. Wang, Q.-M. Hu, *J. Inorg. Biochem.* **2009**, *103*, 805–812.
[58] M. K. Harb, J. Windhager, A. Daraosheh, H. Görls, L. T. Lockett, N. Okumura, D. H. Evans, R. S. Glass, D. L. Lichtenberger, M. El-khateeb, W. Weigand, *Eur. J. Inorg. Chem.* **2009**, 3414–3420.
[59] M. K. Harb, U.-P. Apfel, J. Kübel, H. Görls, G. A. N. Felton, T. Sakamoto, D. H. Evans, R. S. Glass, D. L. Lichtenberger, M. El-khateeb, W. Weigand, *Organometallics* **2009**, *28*, 6666–6675.
[60] M. K. Harb, H. Görls, T. Sakamoto, G. A. N. Felton, D. H. Evans, R. S. Glass, D. L. Lichtenberger, M. El-khateeb, W. Weigand, *Eur. J. Inorg. Chem.* **2010**, *25*, 3976–3985; M. K. Harb, H. Görls, T. Sakamoto, G. A. N. Felton, D. H. Evans, R. S. Glass, D. L. Lichtenberger, M. El-khateeb, W. Weigand, *Eur. J. Inorg. Chem.* **2010**, *28*, 4561.
[61] W. Hieber, J. Gruber, *Z. Anorg. Allg. Chem.* **1958**, *296*, 91–103.
[62] C. F. Campana, F. Lo, L. F. Dahl, *Inorg. Chem.* **1979**, *18*, 3060–3064.
[63] W. Hieber, W. Beck, *Z. Anorg. Allg. Chem.* **1960**, *305*, 265–273.
[64] P. Mathur, D. Chakrabarty, M. M. Hossain, R. S. Rashid, V. Rugmini, A. L. Rheingold, *Inorg. Chem.* **1992**, *31*, 1106–1108.
[65] D. Seyferth, R. S. Henderson, L.-C. Song, *Organometallics* **1982**, *1*, 125–133.
[66] N. S. Nametkin, V. D. Tyurin, M. A. Kukina, *J. Organomet. Chem.* **1978**, *149*, 355–370.
[67] L. E. Bogan, D. A. Lesch, T. B. Rauchfuss, *J. Organomet. Chem.* **1983**, *250*, 429–438.
[68] P. Mathur, D. Chakrabarty, M. M. Hossain, *J. Organomet. Chem.* **1991**, *418*, 415–420.
[69] D. A. Lesch, T. B. Rauchfuss, *Inorg. Chem.* **1981**, *20*, 3583–3585.
[70] D. Seyferth, R. S. Henderson, *J. Organomet. Chem.* **1980**, *204*, 333–343.
[71] V. W. Day, D. A. Lesch, T. B. Rauchfuss, *J. Am. Chem. Soc.* **1982**, *104*, 1290–1295.
[72] P. Mathur, M. M. Hossain, S. N. Datta, R. Kondru, M. M. Bhadbhade, *Organometallics* **1994**, *13*,2532–2535.
[73] P. Mathur, D. Chakrabarty, M. M. Hossain, *J. Organomet. Chem.* **1991**, *401*, 167–172.
[74] D. Chakrabarty, M. M. Hossain, R. K. Kumar, P. Mathur, *J. Organomet. Chem.* **1991**, *410*, 143–148.
[75] D. Seyferth, L.-C. Song, R. S. Henderson, *J. Am. Chem. Soc.* **1981**, *103*, 5103–5107.
[76] P. Mathur, A. K. Dash, M. M. Hossain, S. B. Umbarkar, C. V. V. Satyanarayana, Y. Chen, E. M. Holt, S. N. Rao, M. Soriano, *Organometallics* **1996**, *15*, 1356–1361.
[77] P. Mathur, M. M. Hossain, *Organometallics* **1993**, *12*, 2398–2400.
[78] P. Mathur, M. M. Hossain, S. Umbarkar, C. V. V. Satyanarayana, S. S. Tavale, V. G. Puranik, *Organometallics* **1995**, *14*, 959–963.
[79] P. Mathur, A. K. Dash, M. Munkir Hossain, C. V. V. Satyanarayana, *J. Organomet. Chem.* **1995**, *493*, 257–260.
[80] D. Seyferth, R. S. Henderson, *J. Am. Chem. Soc.* **1979**, *101*, 508–509.
[81] D. Seyferth, R. S. Henderson, *J. Organomet. Chem.* **1979**, *182*, C39–C42.

[82] D. Seyferth, R. S. Henderson, L.-C. Song, *J. Organomet. Chem.* **1980**, *192*, C1–C5.
[83] D. Seyferth, R. S. Henderson, M. K. Gallagher, *J. Organomet. Chem.* **1980**, *193*, C75–C78.
[84] A. Shaver, P. J. Fitzpatrick, K. Steliou, I. S. Butler, *J. Am. Chem. Soc.* **1979**, *101*, 1313–1315.
[85] P. Mathur, B. Manimaran, R. Trivedi, M. M. Hossain, M. Arabatti, *J. Organomet. Chem.* **1996**, *515*, 155–162.
[86] P. Mathur, B. Manimaran, M. M. Hossain, R. Shanbag, J. Murthy, I. S. Saranathan, C. V. V. Satyanarayana, M. M. Bhadbhade, *J. Organomet. Chem.* **1995**, *490*, 173–178.
[87] P. Mathur, B. Manimaran, C. V. V. Satyanarayana, B. Varghese, *J. Organomet. Chem.* **1997**, *527*, 83–91.
[88] P. Mathur, P. Sekar, C. V. V. Satyanarayana, M. F. Mahon, *Organometallics* **1995**, *14*, 2115–2118.
[89] D. Seyferth, G. B. Womack, *Organometallics* **1986**, *5*, 2360–2370.
[90] D. Seyferth, G. B. Womack, R. S. Henderson, M. Cowie, B. W. Hames, *Organometallics* **1986**, *5*, 1568–1575.
[91] D. Seyferth, R. S. Henderson, L.-C. Song, G. B. Womack, *J. Organomet. Chem.* **1985**, *292*, 9–17.
[92] J. A. De Beer, R. J. Haines, *J. Organomet. Chem.* **1970**, *24*, 757–767.
[93] E. D. Schermer, W. H. Baddley, *J. Organomet. Chem.* **1971**, *30*, 67–73.
[94] L. Maresca, F. Greggio, G. Sbrignadello, G. Bor, *Inorg. Chim. Acta* **1971**, *5*, 667–674.
[95] J. A. de Beer, R. J. Haines, *J. Organomet. Chem.* **1972**, *36*, 297–312.
[96] M. Basato, *J. Chem. Soc., Dalton Trans.* **1975**, 911–917.
[97] E. J. Lyon, I. P. Georgakaki, J. H. Reibenspies, M. Y. Darensbourg, *Angew. Chem.* **1999**, *111*, 3373; *Angew. Chem. Int. Ed.* **1999**, *38*, 3178–3180.
[98] J. Windhager, U.-P. Apfel, T. Yoshino, N. Nakata, H. Görls, M. Rudolph, A. Ishii, W. Weigand, *Chem. Asian J.* **2010**, *5*, 1600–1610.
[99] P. Li, M. Wang, C. He, G. Li, X. Liu, C. Chen, B. Akermark, L. Sun, *Eur. J. Inorg. Chem.* **2005**, 2506–2513.
[100] J. J. Yeh, I. Lindau, *At. Data Nucl. Data Tables* **1985**, *32*, 1–155.
[101] G. A. N. Felton, A. K. Vannucci, N. Okumura, L. T. Lockett, D. H. Evans, R. S. Glass, D. L. Lichtenberger, *Organometallics* **2008**, *27*, 4671–4679.
[102] B. J. Petro, A. K. Vannucci, L. T. Lockett, C. Mebi, R. Kottani, N. E. Gruhn, G. S. Nichol, P. A. J. Goodyer, D. H. Evans, R. S. Glass, D. L. Lichtenberger, *J. Mol. Struct.* **2008**, *890*, 281–288.
[103] G. A. N. Felton, A. K. Vannucci, J. Chen, L. T. Lockett, N. Okumura, B. J. Petro, U. I. Zakai, D. H. Evans, R. S. Glass, D. L. Lichtenberger, *J. Am. Chem. Soc.* **2007**, *129*, 12521–12530.
[104] F. E. Inscore, R. McNaughton, B. Westcott, M. E. Helton, R. Jones, I. K. Dhawan, J. H. Enemark, M. L. Kirk, *Inorg. Chem.* **1999**, *38*, 1401–1410.
[105] P. Kennepohl, E. I. Solomon, *Inorg. Chem.* **2003**, *42*, 679–688.
[106] O. L. Griffith, N. E. Gruhn, J. E. Anthony, B. Purushothaman, D. L. Lichtenberger, *J. Phys. Chem. C* **2008**, *112*, 20518–20524.
[107] R. A. Marcus, *J. Chem. Phys.* **1956**, *24*, 966–978.
[108] J. W. Peters, *Curr. Opin. Struct. Biol.* **1999**, *9*, 670–676.
[109] A. K. Justice, G. Zampella, L. D. Gioia, T. B. Rauchfuss, *Chem. Commun.* **2007**, 2019–2021.
[110] J. I. van der Vlugt, T. B. Rauchfuss, C. M. Whaley, S. R. Wilson, *J. Am. Chem. Soc.* **2005**, *127*, 16012–16013.
[111] A. K. Justice, G. Zampella, L. DeGioia, T. B. Rauchfuss, J. I. van der Vlugt, S. R. Wilson, *Inorg. Chem.* **2007**, *46*, 1655–1664.
[112] A. K. Justice, T. B. Rauchfuss, S. R. Wilson, *Angew. Chem.* **2007**, *119*, 6264; *Angew. Chem. Int. Ed.* **2007**, *46*, 6152–6154.
[113] T. Liu, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2007**, *129*, 7008–7009.
[114] C. M. Thomas, M. Y. Darensbourg, M. B. Hall, *J. Inorg. Biochem.* **2007**, *101*, 1752–1757.

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