# A Novel Biomimetic Catalyst for Electrochemical Hydrogen Production

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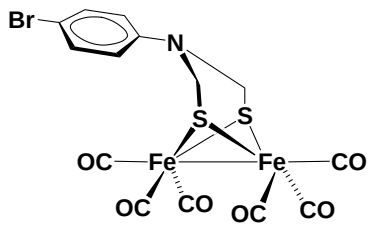
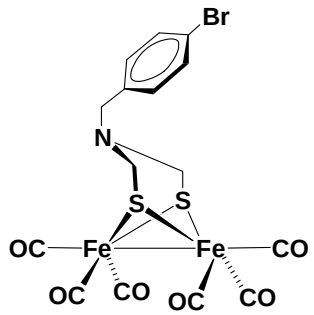
## Introduction

To totally solve the problems of pollution and green house effects, the ultimate mean is to use renewable energy source such as solar energy which has been used by nature through photosynthesis for billion years. Hydrogenases are a class of natural enzymes which catalyse the metabolism of hydrogen in cyanobacteria and other microorganisms. They can thereby function either as sinks for energy-rich electrons or provide the organisms with reducing power from hydrogen oxidation.[1-3] Hydrogenases are generally divided into two families, the nickel-iron (Ni-Fe) hydrogenases and the iron only(Fe-Fe) hydrogenases, reflecting the different base metals present in the active site. Biologically, the two families differ from each other. The Ni-Fe hydrogenases seem to be more involved in hydrogen oxidation, whereas the iron only hydrogenases tend to catalyse preferentially the production of hydrogen.[4-5] It is this remarkable ability of the iron only hydrogenases which has inspired chemists of the bioinorganic community to synthesize close mimics to the active site of the natural system in the search for active hydrogen production catalysts.[6-8] From crystallographic as well as theoretical studies of the enzyme, the active site is known to consist of two iron nuclei, which are in bonding distance.[9,10] They are linked by a dithiolate bridge, recently suggested to possess the structure S-$CH_2$-NH-$CH_2$-S (azadithiolate = ADT).[11,12] Apart from a cysteine-linked [$Fe_4S_4$] cluster which is part of the electron transfer chain to and from the active site, diatomic ligands carbonyl and cyanide occupy the remaining coordination sites around the iron nuclei.

As biomimetic models for the active sites of Fe-only Hydrogenases, numerous reports have emerged in the bioinorganic literature.[13-22] We have recently described the concept of light-driven proton reduction, using a ruthenium polypyridine complex as the light-harvesting component and a biomimetic model of the iron hydrogenase as proton activation catalyst.[23-24] This projected process commences with the absorption of a photon by the ruthenium photosensitizer. The photo-excited ruthenium complex is oxidatively quenched by the dinuclear iron site, giving rise to a reduced iron species. After regeneration of the photosensitizer (by an external electron donor), this process is repeated to afford a doubly reduced diiron species which could then drive the reduction of protons.




**1**



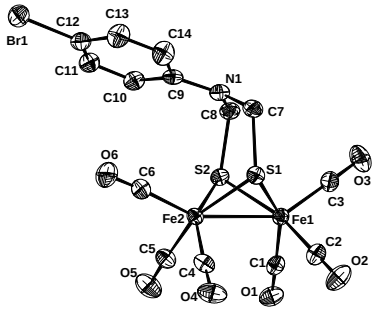

**2**

In this paper two biomimetic systems **1** and **2** where a 2-aza-1,3-dithiol bridged Fe-dimer complexes have been synthesized and characterized. The catalytic electrochemical hydrogen evolution of these two complexes have been investigated.

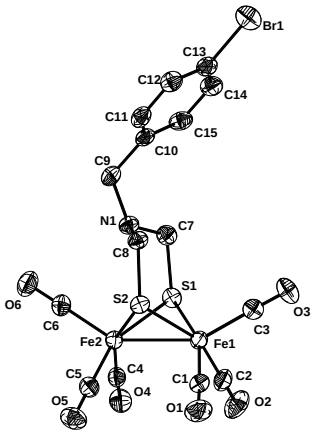
## Results and discussion

The bromo-substituted iron complexes **1** and **2** were synthesized by applying a recently published procedure for the preparation of some related complexes.[25] Thus, the lithium salt of diironhexacarbonyldisulfide was reacted with the respective *N,N*-di(chloromethyl)-4-bromoaniline and *N,N*-di(chloromethyl)-4-bromobenzylamine, which in

turn were synthesized from the *p*-bromoaniline and *p*-bromobenzylamine in two steps.

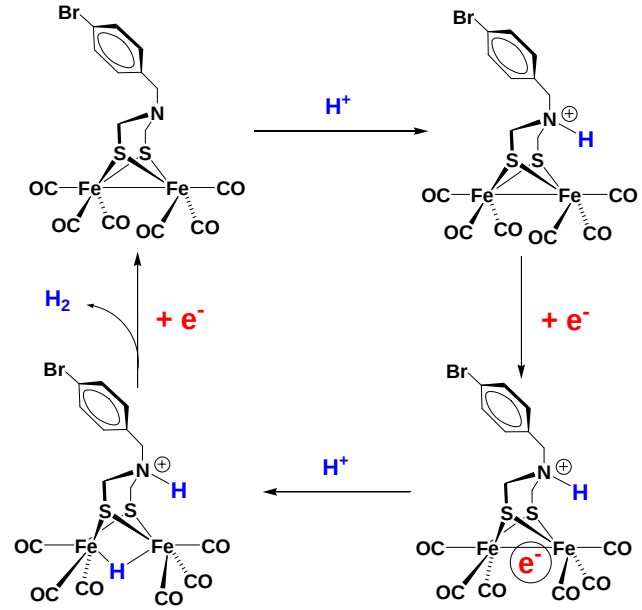



From the X-ray crystal structure it is shown that the $[(\mu\text{-S})_2Fe_2(CO)_6]$ unit of **1** is very similar to those found in other $[(\mu\text{-S})_2Fe_2(CO)_6]$ structures reported.[26] In the central $[(\mu\text{-SR})_2Fe_2(CO)_6]$ unit the two Fe atoms and the two S atoms form a butterfly conformation in which the metal




atoms are connected to each other through a Fe-Fe single bond (2.494 Å). In contrast to the Fe-Fe distances the S···S contacts vary slightly more, 3.075 Å. The Fe-C and C-O distances and Fe-C-O angles are all normal with one exception. The Fe-C-O angles for the carbonyls closest to the amine functionality (i e trans to the Fe-Fe bond) in **1** deviate significantly from the expected 180° linear arrangements with value of 175.6(7)°. The non-bonding C···N distance between the amine and the closest carbonyl carbon atom in **1** is 3.578 Å. Moreover, the nitrogen atom deviates from the plane defined by C7, C8 and C9 by 0.174(5) Å. This non-planarity ruptures the potential π -conjugation between the phenyl ring and the nitrogen p-orbital.

In contrast to the structure features of **1**, the benzyl moiety in complex **2** resides in a pseudo-equatorial position of the mettaloheterocycle with the nitrogen lone-pair pointing towards an iron nucleus. In the crystal structure, the non-bonding C···N distance between the amine nitrogen and the nearest carbonyl carbon atom in **2** is significantly shorter than that in 1 (3.0 Å vs. 3.5 Å). After protonation of **2**, a close proximity of the proton to the diiron active site can therefore be anticipated. In acetonitrile solution of **2** in the presence of $HClO_4$, an acidic form $\mathbf{2}H^+$ has been observed by $^1$HNMR. The UV-Vis absorption maximum is shifted from 328 nm to 332 nm. Two isobestic points at 325 and 362 nm are preserved during the titration, indicating the formation of a single protonation product. Electrochemical hydrogen evolution has been observed in case of **2** at the reduction potential of -1.5 V vs. $Fc^0/Fc^+$. The turnover numbers of this catalysis have been determined as 25. No hydrogen production was found without the complex **2** at the same condition. The catalytic mechanism for this process is proposed as shown in




Scheme-1. This is the first example of electrochemical hydrogen production catalysed by a novel biomimetic model of hydrogenase active site, where a 2-aza-1,3-dithiol bridged Fe-dimer complex has been used.

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