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Synthesis, structural characterization and electrochemical studies of $[Fe_2(\mu\text{-}L)(CO)_6]$ and $[Fe_2(\mu\text{-}L)(CO)_5(PPh_3)]$ (L = pyrazine-2,3-dithiolate, quinoxaline-2,3-dithiolate and pyrido[2,3-*b*]pyrazine-2,3-dithiolate): Towards modeling the active site of [FeFe]–Hydrogenase

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ABSTRACT

The reaction of heterocyclic 1,2-ene-dithiol ligands, namely, pyrazine-2,3-dithiol (H_2pydt), quinoxaline-2,3-dithiol (H_2qdt) and pyrido[2,3-*b*]pyrazine-2,3-dithiol (H_2ppdt) with $Fe_2(CO)_9$ yields the '[FeFe]–hydrogenase' model complexes $[Fe_2\{\mu\text{-pydt}\}(CO)_6]$ **(1)**, $[Fe_2\{\mu\text{-qdt}\}(CO)_6]$ **(2)** and $[Fe_2\{\mu\text{-ppdt}\}(CO)_6]$ **(3)**, respectively. A further reaction of complexes **1**, **2** and **3** with PPh_3 in the presence of equimolar amount of decarbonylating agent Me_3NO in CH_3CN at room temperature resulted in the formation of unsymmetrical mono-PPh_3-substituted model complexes $[Fe_2\{\mu\text{-pydt}\}(CO)_5PPh_3]$ **(4)**, $[Fe_2\{\mu\text{-qdt}\}(CO)_5PPh_3]$ **(5)** and $[Fe_2\{\mu\text{-ppdt}\}(CO)_5PPh_3]$ **(6)**, respectively. The complexes **1**–**6** were well characterized by routine elemental analysis, IR, ^{1}H NMR, ^{13}C NMR spectroscopy and unambiguously characterized by X–ray crystallographic analysis. IR spectroscopy and electrochemical analysis show that an increase of the electron– withdrawing character of the bridging ligands (where electron–withdrawing character is in the order of $\text{pydt}^{2-} > \text{ppdt}^{2-} \geq \text{qdt}^{2-}$) leads to a decreased electron density at the iron centers, which yield a milder reduction potential and higher CO stretching frequencies. All the compounds **1**–**6** are further characterized by electrochemical studies.

1. Introduction

Recent research has significantly advanced our understanding the nature's most efficient catalysts for hydrogen production, the [FeFe]-hydrogenases (Fig. 1) [1–3]. [FeFe]–hydrogenase ([FeFe] H_2ase), that catalyses the reductive generation of hydrogen (shown in eq. (1)), has attracted intensive attention because the molecular hydrogen (H_2) is a clean and a highly efficient fuel [4–13].

$$2H^+ + 2e^- \xrightleftharpoons{[FeFe]-\text{hydrogenases}} H_2 \qquad (1)$$

The high resolution X-ray crystallographic structures have established that [FeFe]H_2ase, isolated from *Desulfovibrio desulfuricans* and *Clostridium pasteurianum*, features a butterfly 2Fe2S subunit as their active site (also called H–cluster) as shown in Fig. 1 [14–19]. In the active site, the iron centers are coordinated by carbon monoxide, cyanide ligands and by a dithiolate bridging ligand between the two iron centers; one of the iron centers (Fe_p) is coordinated by a cysteinyl–linked Fe_4S_4 cluster (Fig. 1). The well-defined/established structure of active site (H–cluster) and its remarkable hydrogen–producing ability provoked chemists to design and synthesize a range of model compounds. Several review articles, on the topic of [FeFe]–hydrogenase model complexes and their catalytic activity, have been published [20–24].

Numerous model diiron complexes, that are analogous to the active site of the iron only enzyme, have been shown as **A**–**F** representations in Scheme 1. Rauchfuss and co-workers reported the electrocatalytic reduction of strong acids like H_2SO_4, HCl etc. using a derivative of **A** (one CO of one iron is replaced by PMe_3 and one CO of other iron is replaced by CN^-) [25–28]. It was shown by Darensbourg and co–workers that **A** can electrocatalyze the dihydrogen production from acetic acid (a weak acid) [29–32]. Borg et al. described detailed electrochemistry and spectroelectrochemical investigation on compound **A** in the context of number of electrons involved in the initial reduction of **A** [33–35]. Song and co-workers demonstrated ADT type model complex **B** [36,37] and also have described that the model compound **C** catalyzes the reduction of Et_3NHCl [38]. Ott, Sun, Akermark and their groups

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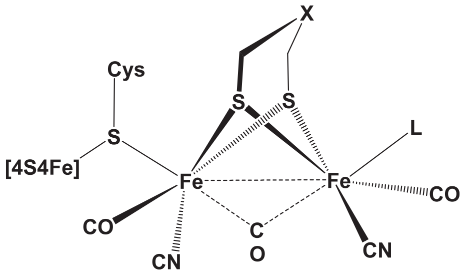
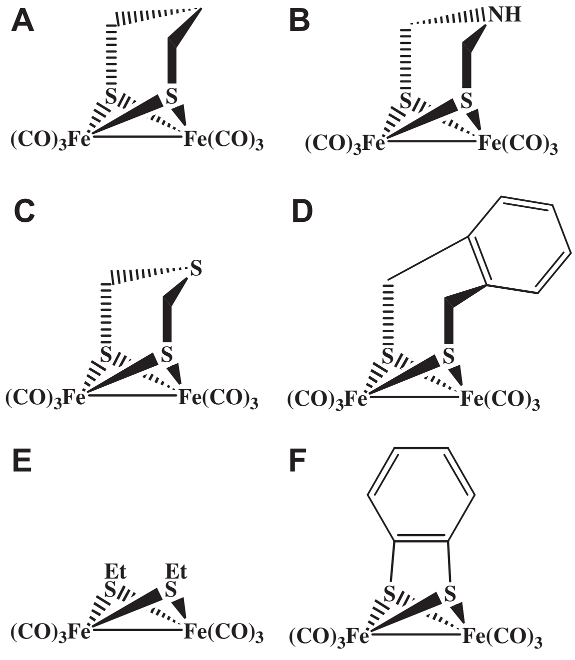


L = H_2O, H or Vacant X= C, N, O or S.

Fig. 1. The active site of [FeFe]–hydrogenase.

described the syntheses and characterizations of nitro- and amino-functionalized diiron azadithiolate complexes (**B** in Scheme 1) and they have shown the electrocatalytic formation of hydrogen from acetic acid and $HClO_4$ proposing a CECE (chemical electrochemical chemical electrochemical) mechanism [39–41]. Electrocatalytic dihydrogen production has been demonstrated using systems **D** and **E** (Scheme 1) as the electrocatalysts [42].

Capon and co-workers first reported the compound **F** as [FeFe]-hydrogenase active site model [43] and it has been further used by Lichtenberger, Evans, Glass and their co-workers to demonstrate electrocatalytic hydrogen generation from weak acids [44,45]. They have described a novel mechanism deduced from both electrochemical and theoretical studies on compound **F**. For the system **F**, the ene-1,2-dithiolate (bdt^{2-}) ligand coordination is able to modulate the potentials between oxidation states drastically in favor of electrochemical proton reduction [46]. Likewise, the coordination of the bdt^{2-} ligand to the $\{Fe_2S_2\}$ core has a special ability to facilitate the electrocatalytic hydrogen production by lowering the potential difference between successive metal oxidation states in the catalytic cycle [43,44,46]. This has been explained by an interaction of the iron orbitals with a combination of the filled sulfur p orbitals and the arene p orbitals, which act to shield the change in electron density at the iron center as the oxidation state is changed, thus minimizing the changes in electron energies upon reduction. It is worth mentioning that the ene-1,2-dithiolate type ligand has been known to serve as an effective electron transfer pathway. Moreover, '*Nature*' uses this type of ligand in the active sites of Mo/W metalloenzymes that catalyze range oxidation/reduction reactions with a variety of substrates (for example, sulfite, xanthine, formate, trimethylamine etc.) [47–52]. It is obvious from the above discussion that the coordination of "ene-1,2-dithiolate" type of ligand (Scheme 2) with $\{Fe_2S_2\}$ core should afford potential model systems for the active sites of [FeFe]H_2ases as far as structural analogies are concerned. We wish to report herein the synthesis, detailed characterization and electrochemical reduction properties of a series of heterocyclic ene-1,2-dithiolate ligands (see in Scheme 3) based diiron complexes $[Fe_2\{\mu\text{-pydt}\}(CO)_6]$ ($pydt^{2-}$ = pyrazine-2,3-dithiolate) (**1**), $[Fe_2\{\mu\text{-qdt}\}(CO)_6]$ (qdt^{2-} = quinoxaline-2,3-dithiolate) (**2**), $[Fe_2\{\mu\text{-ppdt}\}(CO)_6]$ ($ppdt^{2-}$ = pyrido[2,3-*b*]pyrazine-2,3-dithiolate) (**3**) and their triphenylphosphine derivatives $[(CO)_3Fe\{\mu\text{-pydt}\}Fe(CO)_2(PPh_3)]$ (**4**), $[(CO)_3Fe\{\mu\text{-qdt}\}Fe(CO)_2(PPh_3)]$ (**5**) and $[(CO)_3Fe\{\mu\text{-ppdt}\}Fe(CO)_2(PPh_3)]$ (**6**). Out of these, Sascha Ott and co-workers have already reported qdt-complex **2** in terms of synthesis and electrochemistry [53]. Here we have described the crystal structure of this compound for comparative studies.



Scheme 1. [FeFe]–hydrogenase active site model complexes.

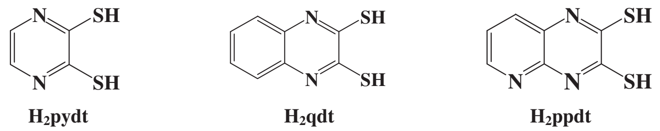
The novelty of the present work lies in the fact that the present system offers relatively low reduction potentials, which is important in terms of proton reduction. In particular, compound **1** exhibits reduction potential at −1.08 V *vs* $Fe^{+/0}$, the lowest reduction potential as far as "ene-1,2-dithiolate" associated model systems are concerned.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization of model complexes *1*–*6*

Based on aforementioned considerations, we have synthesized and structurally characterized three relevant $\{Fe^IFe^I\}$ carbonyl complexes bridging with 1,2-ethylene dithiolate ligands. As shown in Scheme 3, the treatment of heterocyclic 1,2-ethylene dithiolene ligands H_2pydt, H_2qdt and H_2ppdt with $Fe_2(CO)_9$ in THF at −10 °C to 20 °C, afford the complexes **1**, **2** and **3** respectively. Further treatment of complexes **1**, **2** and **3** in presence of equimolar amount of decarbonylating agent Me_3NO with Ph_3P in CH_3CN at room temperature produced the unsymmetrical sole mono Ph_3P-substituted model complexes **4**, **5** and **6** respectively, in moderate yields [54,55].

The complexes **1**–**6** were purified by column chromatography and characterized by IR, ^1H NMR, ^{13}C NMR spectroscopy and satisfactory elemental analysis. The APCI positive mode LC–MS spectra show the parent ion peak $[M + H]^+$ values at *m*/*z* 422.85, 472.85 and 474.35 for compounds **1**, **2** and **3**, respectively. The IR spectra of complexes **1**, **2** and **3** in KBr exhibit strong absorption band frequencies in the region of 1950–2100 cm^{-1}, corresponding to the terminally coordinated carbonyl (CO) groups. The differences



Scheme 2. *N*–heterocyclic 1,2-dithiolene ligands.