Modeling the active site of [FeFe]-hydrogenase: Electro-catalytic hydrogen evolution from acetic acid catalysed by [Fe₂(μ-L)(CO)₆] and [Fe₂(μ-L)(CO)₅(PPh₃)] (L=pyrazine-2,3-dithiolate, quinoxaline-2,3-dithiolate and pyrido[2,3-*b*]pyrazine-2,3-dithiolate)

GUMMADI DURGAPRASAD and SAMAR K DAS*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India
e-mail: skdsc@uohyd.ernet.in.

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Abstract. Compounds [Fe₂{μ-pydt}(CO)₆] (pydt = pyrazine-2,3-dithiolate) (**1**), [Fe₂{μ-qdt}(CO)₆] (qdt = quinoxaline-2,3-dithiolate) (**2**), [Fe₂{μ-ppdt}(CO)₆] (ppdt = pyrido[2,3-*b*]pyrazine-2,3-dithiolate) (**3**), [Fe₂{μ-pydt}(CO)₅PPh₃] (**4**), [Fe₂{μ-qdt}(CO)₅PPh₃] (**5**) and [Fe₂{μ-ppdt}(CO)₅PPh₃] (**6**) have been synthesized in order to model the active sites of '[FeFe]-hydrogenase'. Compounds **1–6** have been characterized by routine spectral studies and unambiguously by single crystal X-ray crystallography. Supramolecular chemistry of compounds **1–6** have been described in terms of intermolecular interactions, observed in their respective crystal structures. Electro-catalytic hydrogen evolution studies (from acetic acid) have been performed using compounds **1–6** as electro-catalysts. The mechanistic aspects of relevant electro-catalytic proton reductions have been discussed in detail.

Keywords. Modeling the active site; [FeFe]-hydrogenase; spectroscopy; electrocatalytic hydrogen evaluation.

1. Introduction

[FeFe]-hydrogenase ([FeFe] H₂ase), that catalyses the reductive generation of hydrogen (equation 1) has attracted much attention because the molecular hydrogen (H₂) is a clean and a highly efficient fuel.¹

The relevant crystal structure has shown that the active site of [FeFe]-hydrogenase consists of a butterfly Fe₂S₂ subunit (also called H cluster) as shown in scheme 1.² The active site of this enzyme has been described by two iron centres that are bridged by dithiolate ligand and additionally coordinated by carbon monoxide and cyanide ligands. In the active site, one of the iron centres is coordinated by a cysteinyl-linked Fe₄S₄ cluster as shown in scheme 1. Numerous model di-iron complexes that are analogous to the active site of the [FeFe] H₂ase enzyme have been reported.³ In this regard, we have recently reported⁴ six model complexes [Fe₂{μ-pydt}(CO)₆] (pydt = pyrazine-2,3-dithiolate) (**1**), [Fe₂{μ-qdt}(CO)₆] (qdt = quinoxaline-2,3-dithiolate) (**2**), [Fe₂{μ-ppdt}(CO)₆] (ppdt = pyrido[2,3-*b*]pyrazine-2,3-dithiolate) (**3**) and their triphenylphosphine derivatives [(CO)₃Fe{μ-pydt}

Fe(CO)₂(PPh₃)] (**4**), [(CO)₃Fe{μ-qdt} Fe(CO)₂(PPh₃)] (**5**) and [(CO)₃Fe{μ-ppdt} Fe(CO)₂(PPh₃)] (**6**) in terms of their syntheses and molecular structures (single crystal X-ray crystallography), including electrocatalytic hydrogen production mediated by compound **1**. In the present study, we have described the supramolecular aspects in the crystal structures of compounds **1–6**. Electrochemical studies on compounds **1–6** indicate that all these complexes undergo protonation in the presence of a weak acid.⁴ This prompted us to investigate whether this system results in the isolation of any protonated compounds in the presence of an acid in its {Fe^IFe^I} form. We have chosen a relatively stronger acid (for example, triflic acid CF₃SO₃H) for protonation, because weaker acids do not form precipitates of protonated compounds so easily. When the protonation of compounds **1**, **2** and **5** takes place under the treatment with an excess of CF₃SO₃H (HOTf, triflic acid) in CHCl₃, precipitate was found to be formed with a change in colour of the solution from wine red to dark red, resulting in the formation of protonated compounds **1a**, **2a** and **5a**, respectively. Based on these protonations, we have discussed the mechanistic aspects of electro-catalytic proton reductions (hydrogen evaluations from acetic acid), mediated by compounds **1–6** as electro-catalysts.

*For correspondence

Scheme 1. Active site of [FeFe]-hydrogenase.

2. Experimental

2.1 General consideration

All the reactions were performed using standard Schlenk line and vacuum-line technique in an atmosphere of nitrogen. Microanalytical (C, H, N) data were obtained with a FLASH EA 1112 Series CHNS Analyzer. The IR spectra were recorded in the range of 400–4000 cm⁻¹ (KBr pellets) on a JASCO FT/IR-5300 spectrometer. Electronic absorption spectra were obtained on a Cary 100 Bio UV-Visible spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on Bruker DRX-400 spectrometer using Si(CH₃)₄ (TMS) as an internal standard. Solution mass spectra (LCMS) were obtained on a LCMS-2010A Shimadzu spectrometer.

2.2 Electrochemistry

Acetonitrile (Finar, HPLC grade) used for the performance of electrochemical studies was dried with molecular sieve (4 Å) and then freshly distilled with CaH₂ under N₂ atmosphere. A solution of 0.1 M [nBu₄N][ClO₄] (TBAP) (Across, electrochemical grade) in CH₃CN was used as supporting electrolyte. Electrochemical measurements were recorded by using a Cypress model CS-1090/CS-1087 electrochemical potentiostat. The electrolyte solution was degassed by bubbling with dry nitrogen for 10 min before measurement. Cyclic voltammograms were obtained in a three-electrode cell under nitrogen. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 0.3-μm alumina paste and sonicated in iron-free water for 10 min. The reference electrode was an Ag/AgCl and the auxiliary electrode was a platinum wire. The potentials, reported here, are uncorrected for junction contributions.

2.3 Syntheses of compounds 1–6

Compounds [Fe₂{μ-pydt}(CO)₆] (1), [Fe₂{μ-qdt}(CO)₆] (2), [Fe₂{μ-ppdt}(CO)₆] (3) [Fe₂{μ-pydt}(CO)₅PPh₃] (4), [Fe₂{μ-qdt}(CO)₅PPh₃] (5) and [Fe₂{μ-ppdt}(CO)₅PPh₃] (6) have been synthesized using procedures described in our earlier report.⁴

A general synthetic procedure for protonated complexes [Fe₂{μ-Hpydt}(CO)₆][CF₃SO₃] (1a), [Fe₂{μ-Hqdt}(CO)₆][CF₃SO₃] (2a), and [Fe₂{μ-Hqdt}(CO)₅PPh₃][CF₃SO₃] (5a) of 1, 2 and 5, respectively is as follows.

100 μL of HOTf was added to a solution of complexes 1, 2 and 5 (50 mg) in CHCl₃ (4 mL) in separate experiments. The solution was stirred for 10 min. The red solution turned into dark red, which was precipitated out. The solvent was decanted and the solid was washed four times with hexane and diethylether and filtered, dried *in vacuo*. Respective N-protonated products 1a, 2a and 5a were obtained with moderate yield. The characterization data of 1a, 2a and 5a are described below.

Complex 1a. Yield: 30 mg (60%). LC-MS: *m/z* = 424.0 [M + H]⁺. IR (KBr pellet, cm⁻¹): 3425 ν_(N-H), 2087, 2058, 2019 ν_(CO), 1604, 1249 ν_(C-F), 1174, 1035 ν_(S=O), 748, 644, 580. Anal. calcd for C₁₁H₃N₂O₉S₃Fe₂F₃: C, 23.09; H, 0.53; N 4.89%. Found: C, 23.15; H, 0.58; N, 4.86%.

Complex 2a. Yield: 30 mg (60%). LC-MS: *m/z* = 474.3 [M + H]⁺. IR (KBr pellet, cm⁻¹): 3402 ν_(N-H), 2116, 2064, 2011 ν_(CO), 1631, 1530, 1421, 1371, 1249 ν_(C-F), 1180, 1100, 1032 ν_(S=O), 893, 760, 640, 601, 570, 518. ¹H NMR (400 MHz, CD₃CN) δ: 7.91 (d, *J* = 3.3 Hz, 2H), 7.76 (d, *J* = 3.4 Hz, 2H) ppm. Anal. calcd for C₁₅H₅N₂O₉S₃Fe₂F₃: C, 28.96; H, 0.81; N, 4.50%. Found: C, 28.76; H, 0.95; N, 4.61%.

Complex 5a. Yield: 25 mg (50%). IR (KBr pellet, cm⁻¹): 3450 ν_(N-H), 2060, 2006 ν_(CO), 1618, 1506, 1369, 1251 ν_(C-F), 1186, 1147, 1032 ν_(S=O), 756, 640, 596, 518. ¹H NMR (400 MHz, CD₃CN) δ: 7.72–7.70 (m, 11H), 7.69–7.60 (m, 8H) ppm. Anal. calcd for C₃₂H₂₀Fe₂N₂O₈PS₃F₃: C, 44.88; H, 2.35; N, 3.27%. Found: C, 44.75; H, 2.39; N, 3.35%.

3. X-ray crystallographic studies

3.1 Single crystal structure determination

The single crystal data were measured at room temperature for compounds 1–6 on a Bruker SMART APEX CCD, area detector system (λ (Mo Kα) = 0.7103 Å) with graphite monochromator. A total of 2400 frames was recorded with an ω scan width of 0.3°, each for 8 s.

crystal–detector distance is 60 mm with collimator distance 0.5 mm. Data were reduced by SAINTPLUS;⁵ absorption correction was performed using an empirical method SADABS.⁶ Structure solution was done using SHELXS-97⁷ and refined using SHELXL-97.⁸ All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the aromatic rings were introduced at calculated positions and included in the refinement riding on their respective parent atoms. The crystallographic parameters, data collection and structure refinement of the compounds **1–6** were summarized in our earlier relevant publication.⁴ Selected bond lengths and angles for compounds **1–3** and **4–6** are also reported in tabular forms.⁴ Relevant hydrogen bonding parameters in the crystal structures of compounds **1–6** are described in table 1.

4. Results and Discussion

4.1 Syntheses

Acid forms of the dithiolato ligands, pydt^{2−}, qdt^{2−} and ppdt^{2−}, that have been used to synthesize compounds [Fe₂{μ-pydt}(CO)₆] (**1**), [Fe₂{μ-qdt}(CO)₆] (**2**), [Fe₂{μ-ppdt}(CO)₆] (**3**) [Fe₂{μ-pydt}(CO)₅PPh₃] (**4**), [Fe₂{μ-qdt}(CO)₅PPh₃] (**5**) and [Fe₂{μ-ppdt}(CO)₅PPh₃] (**6**) are schematically shown in scheme 2.

The synthetic details of compounds **1–6** have been reported earlier by us.⁴ In this study, we have synthesized [Fe₂{μ-Hpydt}(CO)₆][CF₃SO₃] (**1a**), [Fe₂{μ-Hqdt}(CO)₆][CF₃SO₃] (**2a**), and [Fe₂{μ-Hqdt}(CO)₅PPh₃][CF₃SO₃] (**5a**) by protonating their parent compounds **1, 2** and **5**, respectively using a considerably stronger acid CF₃SO₃H. The protonated compounds **1a**, **2a** and **5a** are shown in scheme 3.

The protonated products **1a**, **2a** and **5a**, as shown in scheme 3, were characterized by IR and ¹H NMR spectral studies and elemental analyses. No signal was perceived at δ < 0 ppm, indicating that the protonation on N atom of the diazine ring of heterocyclic dithiolate ligand takes place rather than on the Fe(I)–Fe(I) bond to give μ–H species. Resonances in the ¹H NMR spectra (CD₃CN) of protonated species are generally shifted to lower magnetic field strengths than those in parent compound.⁹ For compound **2**, aromatic protons appear at δ = 7.70 and 7.66 ppm. These chemical shift values shift to 7.91 and 7.76 ppm, respectively on protonation of compound **2** with the formation of mono-protonated compound **2a**. Similar trend is followed for the protonation of other compounds (e.g., compounds **1**, **5**, etc.). We could not succeed in observing the corresponding N–H peak at room temperature in its ¹H NMR spectrum. Proton directly bonded to a nitrogen atom differs from protons on a carbon atom because they are exchangeable (fluxional behaviour)

Table 1. Hydrogen bonding parameters (Å, deg) of complexes **1–6**.

D–H...A	d(D...H)	d(H...A)	d(D...A)	<(DHA)
Complex 1				
C(9)–H(9)...O(6) ⁱ	0.93	2.79	3.587(3)	145.0
Complex 2				
C(12)–H(12)...O(7) ⁱⁱ	0.93	2.63	3.361(7)	136.2
C(26)–H(26)...O(1) ⁱⁱⁱ	0.93	2.63	3.376(7)	137.4
Complex 3				
C(13)–H(13)...O(2) ^{iv}	0.93	2.46	3.274(3)	146.3
Complex 4				
C(44)–H(44)...O(8) ^v	0.93	2.61	3.403(6)	143.7
C(26)–H(26)...O(7) ^{vi}	0.93	2.70	3.492(6)	143.4
C(19)–H(19)...O(10) ^{vii}	0.93	2.60	3.454(5)	152.3
C(17)–H(17)...O(3) ^{viii}	0.93	2.44	3.280(5)	150.5
Complex 5				
C(15)–H(15)...O(3) ^{ix}	0.93	2.54	3.253(5)	133.3
C(13)–H(13)...O(2) ^x	0.93	2.58	3.456(5)	157.5
Complex 6				
C(18)–H(18)...O(2) ^{xi}	0.93	2.54	3.253(4)	133.5
C(15)–H(15)...N(2) ^{xii}	0.93	2.70	3.396(4)	132.5

Symmetry transformations used to generate equivalent atoms: (i) $x, -y+5/2, z-1/2$; (ii) $x, -y+1, z-1/2$; (iii) $x, -y, z+1/2$; (iv) $-x+3/2, y+1/2, -z+3/2$; (v) $-x+1, y+1/2, -z+3/2$; (vi) $x, y, z-1$; (vii) $x, -y+3/2, z-1/2$; (viii) $-x+2, y-1/2, -z+1/2$; (ix) $x, y+1, z$; (x) $-x+2, y+1/2, -z+1/2$; (xi) $1\ x, y-1, z$; (xii) $x, -y+1/2, z-1/2$.

Scheme 2. Acid forms of the ligands, pydt²⁻, qdt²⁻ and ppdt²⁻.

and are subject to partial or complete decoupling by the electrical quadrupole moment of the nitrogen nucleus. Thus, we performed the variable temperature ¹H NMR spectral studies on protonated compounds **2a** and **5a** ranging from room temperature to low temperature (−30°C) in acetonitrile-*d*₃ solvent. N–H exchange rate is low; thus the relevant protons (for compounds **2a** and **5a**) respond to low temperature ¹H NMR studies by exhibiting characteristic broad signals at 3.40 and 2.56 ppm, respectively as shown in figure 1. The spectral data further indicate that protonation occurs on the N–atom of the diazine ring. As expected, the IR (KBr pellet) spectra exhibited significant changes in the carbonyl region. When protonation occurs, there is a significant shift of the CO bands to higher frequencies of 3–30 cm^{−1}.^{9,10} This is consistent with our observation on the IR spectra of protonated compounds (**1a**, **2a** and **5a**) and respective parent compounds (**1**, **2** and **5**). The IR peaks at 2084, 2054, 2017 cm^{−1} (compound **1**) shift to 2087, 2058, 2019 cm^{−1} (compound **1a**), respectively on protonation as shown in figures 2a and c, respectively. Similarly, for compounds **2** and **5**, the IR bands 2085, 2037, 1983 cm^{−1} and 2050, 1988 cm^{−1} shift to 2116, 2064, 2011 cm^{−1} (**2a**) and 2060, 2006 cm^{−1} (**5a**) respectively on protonation as shown in figures 2b, h and e, i, respectively. The N–H bond, formed on protonation, displays strong and broad absorption band in the 3450–3400 cm^{−1} region because of N–H stretching vibrations. The other strong band in the range of 1530–1500 cm^{−1} is observed due to the N–H bending motions (see supplementary information). Appearance of a broad vibrational band centred at 1250 cm^{−1} in the IR spectra of the compounds **1a**, **2a** and **5a** suggests the C–F stretching modes and a strong absorption in the 1030 cm^{−1} region for S=O stretching, indicating the existence of triflate anion in the complexes.

4.2 Electronic absorption spectra

The UV/Vis spectra of the dinuclear iron complexes **1–3** are characterized by two major absorptions: one of the absorptions is around 270 nm and the other one is in the range of 330 to 350 nm as presented in figure 3. The electronic absorption spectra for compounds **4–6** show similar features but the second peak is shifted to 375 nm on derivative formation (coordination of triphenylphosphine to iron centre) with triphenylphosphine (figure 3). A similar trend in electronic absorption spectra was also found in related dinuclear iron complexes,¹⁰ relevant to the active site of [FeFe]-hydrogenase.

4.3 Supramolecular aspects in the crystal structures of compounds [Fe₂{μ-pydt}(CO)₆] (**1**), [Fe₂{μ-qdt}(CO)₆] (**2**), [Fe₂{μ-ppdt}(CO)₆] (**3**), [Fe₂{μ-pydt}(CO)₅PPh₃] (**4**), [Fe₂{μ-qdt}(CO)₅PPh₃] (**5**) and [Fe₂{μ-ppdt}(CO)₅PPh₃] (**6**)

Molecular structures of compounds **1–6** in their respective crystals have been reported earlier.⁴ Here, we have described the supramolecular chemistry of compounds **1–6** in terms of weak intermolecular interactions. The crystal structures of the complexes **1–3** are characterized by C–H···O hydrogen bonding interactions. The relevant hydrogen bonding geometrical parameters of the complexes **1–3** are listed in table 1. In the crystal structure of each of the complexes **1–3**, one of the hydrogen atoms of heterocyclic ring is involved in weak hydrogen bonding interaction with carbonyl oxygen of another molecule resulting in one-dimensional supramolecular structures of the types step-wise/staircase (compound **1**), helical (compound **2**), and zigzag (compound **3**) as shown in figure 4a, b and c, respectively.

Scheme 3. One of the ring nitrogen atoms in **1a**, **2a** and **5a** is protonated. Protonation is not shown in this scheme.

Figure 1. Variable-temperature ^1H NMR spectra of (a) compound **2a** and (b) compound **5a** in acetonitrile- d_3 .

Crystal structures of the complexes **4–6** also show weak $\text{C–H}\cdots\text{O}$ -type hydrogen bonding interactions. The hydrogen bonding building units for the formation of supramolecular architectures in the crystal structures of complexes **4**, **5** and **6** are depicted in figure 5a, b and c, respectively. The relevant hydrogen bonding geometrical parameters of the complexes **4–6** are listed in table 1.

In complex **4**, three hydrogen atoms of triphenylphosphine ligand are involved in weak hydrogen bonding interaction with carbonyl oxygens of another

three different adjacent Fe_2S_2 moieties (figure 5a). In the crystal structure of the complex **5**, in addition to the hydrogen atom of the PPh_3 ligand, one of the H-atoms of the quinoxaline dithiolate ring is involved in $\text{C–H}\cdots\text{O}$ hydrogen bonding interactions (figure 5b). The crystal structure of the complex **6** is well-characterized by both $\text{C–H}\cdots\text{O}$ and $\text{C–H}\cdots\text{N}$ hydrogen bonding interactions (figure 5c). In this case, H-atom of PPh_3 ligand is involved in $\text{C–H}\cdots\text{N}$ [$\text{C}\cdots\text{N}$ bond distance $3.396(4)$ Å] interactions with N atom of the ppdt ring of the adjacent molecule, positioned at $x, -y+1/2, z-1/2$.

Figure 2. Comparison of the terminal carbonyl IR spectra of parent complexes (a) **1**, (b) **2** and (c) **3**, and its derivatives (d) **4**, (e) **5** and (f) **6** and protonated complexes (g) **1a** (h) **2a** and (i) **5a**.

4.4 Electrochemistry

The active site of the native enzyme ($[\text{FeFe}]$ -hydrogenase) is well-characterized by the presence of iron dimer core (scheme 1) and this iron core is known to undergo proton-coupled red-ox reaction through the formation of Fe–H hydride followed by hydrogen

Figure 3. Electronic absorption spectra for the complexes **1–6** in DCM ($1 \times 10^{-4}\text{M}$).

Figure 4. One-dimensional supramolecular chains of (a) complex **1**; (b) complex **2** and (c) complex **3**, characterized by C–H $\cdots$ O weak interaction.

Figure 5. View of the molecular structures of (a) complex **4**, (b) complex **5** and (c) complex **6** (solid lines) (some hydrogen atoms are removed for clarity) showing possible H-bonding intermolecular contacts with other surrounding moieties (dotted lines).

production. Thus, electrochemical studies were performed on model compounds **1**–**6** to ascertain their red–ox properties for understanding the mechanism of enzymatic function better. This study (compounds **1**–**6**) deals with ene-1,2-dithiolate-bridged di-iron complexes and has been realized that ‘Nature’ exploits this type of ligand in the active sites of Mo/W metalloenzymes catalysing a range of red–ox reactions (*vide supra*). Thus, some ene-1,2-dithiolate-bridged di-iron complexes have been investigated in modelling the active sites of [FeFe]-H₂ases. However, the reports of electrochemical data on ene-1,2-dithiolate-bridged-{Fe₂S₂} complexes are scarce. In this study, compound [Fe₂{μ-pydt}(CO)₆] (**1**) exhibits a quasi-reversible reduction (E) at –0.74 V vs Ag/AgCl in acetonitrile as shown in figure 6a. This reduction has already been established as two-electron process.^{4,11} The behaviour of catalytic proton reduction by compounds **1**–**6** has been investigated by CV studies in the presence of a weak acid, CH₃COOH in CH₃CN. As shown in figure 6a, for compound **1**, the first reduction peak (E) at –0.74 V apparently shifts to –0.84 V with an appearance of a new peak at –1.20 V along with an electro-catalytic response at –1.80 V. The reduction at –1.80 V with an increased current height can be described as electro-catalytic proton reduction because the current intensity of the peak at –1.80 V gradually increases further with increasing acetic acid concentration, as shown in figure 6b. The peak at –0.84 V slowly disappears and the current intensity of the shifted peak at –1.20 V does not increase further with sequential increments of the acid concentration. Only the height of reduction peak at –1.80 V continuously increased with increased acid concentration, which is characteristic of an

electrochemical catalytic process. Compounds **2** and **3** (figures 7a and b, respectively) also exhibit similar behaviour of catalytic proton reduction as shown by compound **1**.

Thus for all-CO complexes **1**–**3**, electro-catalysis (proton reduction from acetic acid) occurs at at –1.80 V vs Ag/AgCl for compound **1** (figure 6) and electro-catalysis (proton reduction from acetic acid) occurs at –1.90 V vs Ag/AgCl for compounds **2** and **3** (figure 7a and b respectively).

For compound **1**, we have assigned the reductive event at –0.84 V vs Ag/AgCl (after adding acetic acid to the compound **1** solution) to the process [(Fe^IFe^I)(NNH)]¹⁺ + e[–] → [(Fe^IFe⁰)(NNH)]⁰ because the reductive response of compound **1** at –0.74 V vs Ag/AgCl (without adding an acid) shifts to the first reductive response at –0.84 V vs Ag/AgCl and second reductive response at –1.20 V vs Ag/AgCl after the addition of acetic acid. This cathodic shift is possible if the inductive effect of the diazine ring is lost due to the protonation of the ring nitrogen(s).

The one-electron reduced species [(Fe^IFe⁰)(NNH)]⁰ undergo further protonation to form [(Fe^IFe⁰)(HNNH)]¹⁺ showing the second reductive response at –1.20 V vs Ag/AgCl, which can be described as [(Fe^IFe⁰)(HNNH)]¹⁺ + e[–] → [(Fe⁰Fe⁰)(HNNH)]⁰. Finally, the electro-catalytic proton reduction from acetic acid, catalysed by compound [Fe₂{μ-pydt}(CO)₆] (**1**) occurs at –1.80 V vs Ag/AgCl. The E_{AcOH}⁰ for AcOH is –1.46 V vs. Fe⁺/Fe⁰ in acetonitrile; and thus, the E_{AcOH}⁰ for AcOH is –1.04 V vs. Ag/AgCl in acetonitrile. The least negative potential of the catalyst, that will allow reduction of AcOH to dihydrogen should be more negative than –1.04 V vs. Ag/AgCl. Thus, compound

Figure 6. (a) Red: cyclic voltammogram of complex **1** (1.0 mM) in MeCN; blue: cyclic voltammogram of complex **1** (1.0 mM) in MeCN with 0.08 mM acetic acid. (b) Cyclic voltammograms of complex **1** (1.0 mM) and 0–28 mM acetic acid in MeCN (0.1 M n-Bu₄NClO₄ at a scan rate of 100 mV/s).

Figure 7. (a) Cyclic voltammograms of complex **2** (1.0 mM) and 0–100 mM acetic acid in MeCN; (b) cyclic voltammograms of complex **3** (1.0 mM) and 0–60 mM acetic acid in MeCN; (0.1 M *n*-Bu₄NClO₄ at a scan rate of 100 mV/s).

[Fe₂{μ-pydt}(CO)₆] (**1**), in principle, will not be able to reduce AcOH to dihydrogen thermodynamically, because it has a first reduction potential of -0.74 V vs Ag/AgCl in acetonitrile. However, practically we have seen the electro-catalytic proton reduction to dihydrogen (from acetic acid), catalysed by compound [Fe₂{μ-pydt}(CO)₆] (**1**) as shown in figure 6. This, electro-catalytic proton reduction to dihydrogen (from acetic acid) can be explained by protonation of compound **1** resulting in a final protonated species that exhibits reductive response at -1.20 V vs Ag/AgCl. This protonated species, in principle, would be able to reduce AcOH to dihydrogen thermodynamically, because -1.20 V vs Ag/AgCl is more negative than -1.04 V vs. Ag/AgCl. Compounds [Fe₂{μ-qdt}(CO)₆] (**2**) and [Fe₂{μ-ppdt}(CO)₆] (**3**) exhibit similar electrochemical behaviour in terms of protonation and electro-catalytic proton reduction as shown by compound [Fe₂{μ-pydt}(CO)₆] (**1**) in the presence of acetic acid (AcOH).

Scheme 4. Plausible CECE mechanism for electrocatalytic proton reduction in the presence of HOAc for compounds **1–3** (as electro-catalysts).

Overall results of cyclic voltammetric studies suggest a CECE (chemical–electrochemical–chemical–electrochemical) mechanism for the electrochemical catalysis of proton reduction by all CO complexes **1–3** as shown in scheme 4. Protonation of the ring nitrogens in the proposed mechanism (scheme 3) is supported by the isolation of mono-protonated salt [Fe₂{μ-Hpydt}(CO)₆][CF₃SO₃] (**1a**), [Fe₂{μ-Hqdt}(CO)₆][CF₃SO₃] (**2a**) of compounds **1** and **2**, respectively (see experimental section, *vide supra*). We performed the protonation experiments using triflic acid (CF₃SO₃H) instead of acetic acid, because triflate salts are easily isolable. We could isolate only mono-protonated salt of {Fe^IFe^I} form that corresponds to one of the protonated species, described in scheme 4. In the same scheme, we have proposed a diprotonated species of {Fe^IFe⁰} form, which could not be isolated. The mono-protonated salts **1a** and **2a** have been characterized by temperature-dependent ¹H NMR spectroscopy (*vide supra*, see also Supplementary Information for the relevant spectra) including elemental analysis.

The PPh₃-derivatives [Fe₂{μ-pydt}(CO)₅PPh₃] (**4**), [Fe₂{μ-qdt}(CO)₅PPh₃] (**5**) and [Fe₂{μ-ppdt}(CO)₅PPh₃] (**6**) show the major reduction event at ca. 2.0 V vs Ag/AgCl, more specifically, 2.22, 2.33 and 2.08 V vs Ag/AgCl for **4**, **5** and **6**, respectively (figure 8). This reduction event is assigned to the one-electron reduction based on the assignment of a similar reported system (μ-SRS)[Fe(CO)₂L]₂ (R = *o*-CH₂C₆H₄CH₂(μ-*o*-xyldt); L = PMe₃).¹²

Darensbourg and co-workers have explained, in this context that the appearance of the reduction waves for PMe₃-derivatives at more negative potentials than corresponding all-CO complexes is consistent with the better donor character of the PMe₃ ligand relative to CO ligand.¹² The same explanation can be offered for the

Figure 8. (a) Cyclic voltammograms of complex **4** (1.0 mM) and 0–40 mM acetic acid in MeCN; (b) cyclic voltammograms of complex **5** (1.0 mM) and 0–100 mM acetic acid in MeCN and (c) cyclic voltammograms of complex **6** (1.0 mM) and 0–80 mM acetic acid in MeCN (0.1 M *n*-Bu₄NClO₄ at a scan rate of 100 mV/s).

appearance of the reduction waves at more negative potentials for compounds **4–6** (compared to that for compounds **1–3**), because PPh₃ ligand is a far better donor than the CO donor.

A chemical–electrochemical (CE) mechanism, as shown in scheme 5, can be proposed on the basis of the bimolecular reaction for two mono-protonated species. A similar but EC (electrochemical–chemical)

Scheme 5. Plausible CE (chemical–electrochemical) mechanism for the electro-catalytic proton reduction in the presence of HOAc for compounds **4–6**.

mechanism was proposed for $(\mu-SRS)[Fe(CO)_2L]_2$ ($R = o-CH_2C_6H_4CH_2(\mu-o-xyldt)$; $L = PMe_3$), in which

Figure 9. Plots of current heights of electro-catalytic events vs. concentration of HOAc in CH₃CN for complexes **1–6**.

hydrogen adduct was formed by oxidative addition reaction resulting in $(\eta^2\text{-H}_2)(\text{Fe}^{\text{II}}\text{Fe}^{\text{I}})$ species.¹² The proposed mechanism (scheme 5) in this study can be corroborated by the isolation of monoprotonated species $\text{Fe}_2\{\mu\text{-Hqdt}\}(\text{CO})_5\text{PPh}_3$ [CF_3SO_3] (**5a**) of compound **5** (see experimental section for its characterization through temperature-dependent ^1H NMR spectroscopy in addition to its elemental analysis).

Figure 9 presents a good linear dependence of the current height of the reductive responses on the concentrations of HOAc for complexes **1–3** and their PPh_3 derivatives **4–6**, providing a comparison of electrocatalytic activities of the model complexes in this study. Similar plots were reported in the context of electrochemical reduction of protons by $2\text{Fe}_2\text{S}$ hydrogenase model complexes.^{11,13} As shown in figure 9, complex **2** (steepest slope) has relatively high electrocatalytic activity for reduction of protons from HOAc as compared to the catalytic activity shown by complexes **1**, **3**, and **4–6** under similar conditions. Complexes **4–6** (triphenylphosphine derivatives) show fewer electrocatalytic activities compared to their respective parent complexes **1–3**.

5. Conclusion

Since ‘Nature’ has used ‘ene-1,2-dithiolate’ type ligands in the active sites of molybdenum and tungsten containing metalloenzymes that catalyse a range of substrates (e.g., sulphite, xanthine, etc.) and the active site of iron only hydrogenase is characterized by two iron centres, bridged by a dithiolate bridging ligand, we anticipate that the coordination of ‘ene-1,2-dithiolate’ type of ligand with $\{\text{Fe}_2\text{S}_2\}$ core should afford potential model systems for the active sites of $[\text{FeFe}]\text{-H}_2$ ases. In this regard, we have synthesized three ene-1,2-dithiolate type ligands pyrazine-2,3-dithiol (H_2pydt), quinoxaline-2,3-dithiol (H_2qdt) and pyrido[2,3-*b*]pyrazine-2,3-dithiol (H_2ppdt) and synthesized a series of heterocyclic 1,2-ethylene dithiolate ligand based di-iron complexes $[\text{Fe}_2\{\mu\text{-pydt}\}(\text{CO})_6]$ (**1**), $[\text{Fe}_2\{\mu\text{-qdt}\}(\text{CO})_6]$ (**2**), $[\text{Fe}_2\{\mu\text{-ppdt}\}(\text{CO})_6]$ (**3**) and their triphenylphosphine derivatives $[(\text{CO})_3\text{Fe}\{\mu\text{-pydt}\}\text{Fe}(\text{CO})_2(\text{PPh}_3)]$ (**4**), $[(\text{CO})_3\text{Fe}\{\mu\text{-qdt}\}\text{Fe}(\text{CO})_2(\text{PPh}_3)]$ (**5**) and $[(\text{CO})_3\text{Fe}\{\mu\text{-ppdt}\}\text{Fe}(\text{CO})_2(\text{PPh}_3)]$ (**6**). We have characterized compounds **1–6** not only by single crystal X-ray structure determinations, but also by extensive spectroscopic analyses. The crystal structures show interesting supramolecular features. We have demonstrated that electrochemical generation of dihydrogen from an weak acid (acetic acid) by model complexes **1–3** and **4–6** which occurs by CECE and CE

mechanisms, respectively that are deduced from electrochemical studies, which are supported by protonation experiments.

Supplementary information

The electronic supporting information can be seen at www.ias.ac.in/chemsci.

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References

- Fontecilla-Camps J C, Volbeda A, Cavazza C and Nicolet Y 2007 *Chem. Rev.* **107** 4273; Siegbahn P E M, Tye J W and Hall M B 2007 *Chem. Rev.* **107** 4414; Vignais P M and Billoud B 2007 *Chem. Rev.* **107** 4206; Adams M W W 1990 *Biochim. Biophys. Acta* **1020** 115; Cammack R 1999 *Nature* **397** 214; Nicolet Y, Lemon B J, Fontecilla-Camps J C and Peters J W 2000 *Trends Biochem. Sci.* **25** 138; Darensbourg M Y, Lyon E J, Zhao X and Georgakaki I P 2003 *Proc. Natl. Acad. Sci. U.S.A.* **100** 3683; Evans D J and Pickett C J 2003 *Chem. Soc. Rev.* **32** 268; Alper J 2003 *Science* **299** 1686; Song L C 2005 *Acc. Chem. Res.* **38** 21; Adams M W W and Stiefel E I 1998 *Science* **282** 1842; Vincent K A, Parkin A and Armstrong F A 2007 *Chem. Rev.* **107** 4366; Frey M 2002 *ChemBioChem.* **3** 153
- Nicolet Y, de Lacey A L, Vernede X, Fernandez V M, Hatchikian E C and Fontecilla-Camps J C 2001 *J. Am. Chem. Soc.* **123** 1596; Lemon B J and Peters J W 2000 *J. Am. Chem. Soc.* **122** 3793; Lemon B J and Peters J W 1999 *Biochemistry* **38** 12969; Nicolet Y, Piras C, Legrand P, Hatchikian E C and Fontecilla-Camps J C 1999 *Structure* **7** 13; Bennett B, Lemon B J and Peters J W 2000 *Biochemistry* **39** 7455; Peters, J W, Lanzilotta W N, Lemon B J and Seefeldt L C 1998 *Science* **282** 1853
- Durgaprasad G, Bolligarla R and Das S K 2012 *J. Organomet. Chem.* **706** 37; Durgaprasad G and Das S K 2012 *J. Organomet. Chem.* **717** 29; Heinekey D M 2009 *J. Organomet. Chem.* **694** 2671; Tard C and Pickett C J 2009 *Chem. Rev.* **109** 2245; Capon J –F, Gloaguen F, Petillon F Y, Schollhammer P and Talarmin J 2009 *Chem. Rev.* **253** 1476; Felton G A N, Mebi C A, Petro B J, Vannucci A K, Evans D H, Glass R S and

- Lichtenberger D L 2009 *J. Organomet. Chem.* **694** 2681; Capon J -F, Gloaguen F, Petillon F Y, Schollhammer P and Talarmin J 2008 *C. R. Chim.* **11** 842; Boyke A C, Rauchfuss T B, Wilson S R, Rohmer M -M and Benard M 2004 *J. Am. Chem. Soc.* **126** 15151; Justice K A, Linck R C, Rauchfuss T B and Wilson S R 2004 *J. Am. Chem. Soc.* **126** 13214; Gloaguen F, Lawrence J D and Rauchfuss T B 2001 *J. Am. Chem. Soc.* **123** 9476; Gloaguen F, Lawrence J D, Rauchfuss T B and Rohmer M -M 2002 *Inorg. Chem.* **41** 6573; Borg S J, Behrsing T, Best S P, Razavet M, Liu X and Pickett C J 2004 *J. Am. Chem. Soc.* **126** 16988; Zhao X, Chiang C -Y, Miller M L, Rampersad M V and Darensbourg M Y 2003 *J. Am. Chem. Soc.* **125** 518; Mejia-Rodriguez R, Chong D, Reibenspies J H, Soriaga M P and Darensbourg M Y 2004 *J. Am. Chem. Soc.* **126** 12004; Zhao X, Georgakaki I P, Miller M L, Mejia-Rodriguez R, Chiang C -Y and Darensbourg M Y 2002 *Inorg. Chem.* **41** 3917; Cheah M H, Borg S J and Best S P 2007 *Inorg. Chem.* **46** 1741; Borg S J, Tye J W, Hall M B and Best S P 2007 *Inorg. Chem.* **46** 384; Ott S, Kritikos M, Akermark B and Sun L 2003 *Angew. Chem. Int. Ed.* **42** 3285; Song L -C, Wang L -X, Tang M -Y, Li C -G, Song H -B and Hu Q -M 2009 *Organometallics* **28** 3834; Song L -C, Tang M -Y, Mei S -Z, Huang J -H and Hu Q -M 2007 *Organometallics* **26** 1575; Song L -C, Yang, Z Y, Hua Y J, Wang H T, Liu Y and Hu Q -M 2007 *Organometallics* **26** 2106; Capon J -F, Gloaguen F, Schollhammer P and Talarmin J 2004 *J. Electroanal. Chem.* **566** 241; Ott S, Kritikos M, Akermark B, Sun L and Lomoth R 2004 *Angew. Chem. Int. Ed.* **43** 1006; Liu T, Wang M, Shi Z, Cui H, Dong W, Chen J, Akermark B and Sun L 2004 *Chem.-Eur. J.* **10** 4474; Capon J -F, Gloaguen F, Schollhammer P and Talarmin J 2006 *J. Electroanal. Chem.* **595** 47; Felton G A N, Vannucci A K, Okumura N, Lockett L T, Evans D H, Glass R S and Lichtenberger D L 2008 *Organometallics* **27** 4671
4. Durgaprasad G, Bolligarla R and Das S K 2011 *J. Organomet. Chem.* **696** 3097
 5. *Software for the CCD Detector System*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1998
 6. Sheldrick G M, SADABS, *Program for Absorption Correction with the Siemens SMART Area-Detector System*; University of Göttingen: Göttingen, Germany, 1996
 7. Sheldrick G M, SHELXS-97, *Program for Solution of Crystal Structures*. University of Göttingen: Göttingen, Germany, 1997
 8. Sheldrick G M, SHELXL-97, *Program for Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997
 9. Zhao X, Georgakaki I P, Miller M L, Yarbrough J C and Darensbourg M Y 2001 *J. Am. Chem. Soc.* **123** 9710
 10. Ott S, Borgstrom M, Kritikos M, Lomoth R, Bergquist J, Akermark B, Hammarstrom L and Sun L 2004 *Inorg. Chem.* **43** 4683; Jiang S, Liu J, Shi Y, Wang Z, Akermark B and Sun L 2007 *Dalton Trans.* 896; Dong W, Wang M, Liu X, Jin K, Li G, Wang F and Sun L 2006 *Chem. Commun.* 305
 11. Felton G A N, Vannucci A K, Chen J, Lockett L T, Okumura N, Petro B J, Zakai U I, Evans D H, Glass R S and Lichtenberger D L 2007 *J. Am. Chem. Soc.* **129** 12521
 12. Chong D, Georgakaki I P, Mejia-Rodriguez R, Sanabria-Chinchilla J, Soriaga M P and Darensbourg M Y 2003 *Dalton Trans.* 4158
 13. Duan L, Wang M, Li P, Na Y, Wang N and Sun L 2007 *Dalton Trans.* 1277