Electrochemical catalysis investigation into the dynamic coordination properties of a pyridine–substituted [2Fe2S] model complex

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Abstract: A pyridine-substituted diiron dithiolate complex (μ -dmedt)Fe₂(CO)₅Py **1** was prepared as a biomimetic model for the active site of [FeFe]-hydrogenase by CO-substitution of all-carbonyl complex (μ -dmedt)Fe₂(CO)₆ [dmedt = SCH(CH₃)CH(CH₃)S] with pyridine, which has been determined by IR, ¹HNMR, elemental analysis and X-ray crystallography analysis. Electrochemical and IR investigation of the complex **1** in MeCN-[NBu₄][PF₆] under N₂ and under CO has demonstrated that the reversible transformation reaction between the complex **1** and the acetonitrile-substituted species (μ -dmedt)Fe₂(CO)₅(NCCH₃) **2**. As in reverse transformation, a

pyridine ligand is coordinated to a Fe^{I} centre, and can be replaced by a solvent molecule under appropriate conditions, which could mimic the function of the flexible coordination site in the H_2 ase enzymes. Electrochemical studies also show complex **1** can catalyze hydrogen evolution from HOAc and aqueous media at -1.26 V.

1. Introduction

Hydrogenase enzymes, which were found in a variety of microorganisms and can efficiently catalyze the reduction of protons to hydrogen, can be classified into $[\text{Fe}]$ - H_2 ases (Hmd- H_2 ases), $[\text{NiFe}]$ - H_2 ases and $[\text{FeFe}]$ - H_2 ases (H-Cluster). $[\text{FeFe}]$ -Hydrogenase is the most important hydrogenases which can reversibly catalyze the reduction of proton to hydrogen with a high efficiency. Inspired by hydrogenase, chemists are interested in studying the biomimetic chemistry of $[\text{Fe-Fe}]$ - H_2 ases due to its highest and fastest catalytic capability for production of hydrogen among all. To obtain better structural and functional diiron model complexes, good donor ligands, such as [1], cyanide [2], phosphine [3-4], thioether or sulfoxide [5], have been introduced into diiron model complexes. Unfortunately, the potentials for catalytic proton reduction of the corresponding phosphine-substituted model complexes fall in the range of ca.-1.76 to -2.42 V [5], which is significantly higher than that found for the natural $[\text{FeFe}]$ -hydrogenase (ca.-0.4 V vs. NHE) [6]. Some weak σ -donating ligands, in particular those with N-donor sites, could greatly reduce the potential gap between the $[\text{FeFe}]$ -hydrogenase active site and biomimetic complexes. But synthetic diiron complexes of type $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_5(\text{L})]$ (L = ligand, pdt = propyldithiolate) with loosely bound ligands are inherently unstable [7]. The dynamic exchange between the ligand and donor solvent molecule may on one hand limit their functional studies for proton reduction but on the other hand provide a model that can mimic the function of the flexible coordination site in the H_2 ase enzymes.

Herein, $(\mu\text{-dmedt})[\text{Fe}(\text{CO})_3]_2$ (dmedt = 2,3-butanedithiol) [8] was chosen as the parent complex to synthesize a pyridine mono-substituted $[\text{2Fe}_2\text{S}]$ model complex **1**, as shown in Scheme 1. The complex **1** was expected to extend new promising models for structural or functional modification with stability and lower reduction potential. The electrochemical catalytic behavior and dynamic coordination of pyridine in CH_3CN of complex **1** was investigated. Electrochemical and IR investigation of the complex **1** in MeCN - $[\text{NBu}_4][\text{PF}_6]$ under N_2 and under CO has demonstrated that the reversible transformation reaction between the complex **1** and the acetonitrile-substituted species $(\mu\text{-dmedt})\text{Fe}_2(\text{CO})_5(\text{NCCH}_3)$ **2**. As in reverse transformation, a pyridine ligand is coordinated to a Fe^{I} centre, and can be replaced by a solvent molecule under appropriate conditions, which could mimic the function of the flexible coordination site in the H_2 ase enzymes. The complex **1** catalyzed H_2 formation from HOAc and aqueous media at -1.26 V and greatly improved stability under such conditions.

[Scheme 1 inserted here]

2. Experiment

2.1. Materials and instruments: Solvents were dried and distilled prior to use according to the standard methods. Other chemicals were of reagent grade and used without further purification. The compound $[(\mu\text{-dmedt})\{\text{Fe}(\text{CO})_3\}_2]$ was prepared according to the literature [8]. Cyclic voltammograms were obtained on a CHI-760E electrochemical analyzer using a three-electrode cell in which a glassy carbon (diameter 3 mm) electrode was the working electrode, a saturated Ag/AgNO_3 electrode was the reference electrode, and a platinum wire was the auxiliary electrode. The NMR spectra were measured on a Bruker AVANCE III 400 MHz NMR spectrometer. Solution IR spectra were recorded on a Shimadzu FTIR-8400 spectrometer using 0.1 mm KBr sealed cells. Elemental analysis was carried out on a Heraeus CHN-Rapid, fully automatic elemental analyzer with TCD detection, type: TMT CHN, BESTELL-NR 2215001. The single-crystal X-ray diffraction

data were collected with a Rigaku MM-007 diffractometer equipped with a Saturn 724CCD. Data were collected at 293 K or 113 K using a confocal monochromator with Mo-K α radiation ($\lambda=0.71073$ Å). Data collection, reduction and absorption correction were performed with the CRYSTALCLEAR program [9]. Structure was solved by direct methods using the SHELXS-97 program [9] and refined by full-matrix least-squares techniques (SHELXL-97) on F^2 . Details of crystal data, data collections and structure refinements are summarized in Table S1 and Fig. S1-S2.

2.2. The synthesis of (μ -dmedt) Fe₂(CO)₅Py (complex 1):

The reaction of [(μ -dmedt){Fe(CO)₃}₂] 298 mg (0.74 mmol) [6] with Me₃NO 58 mg(0.76 mmol) in 5 mL CH₃CN was carried out at 0°C for 30 min under an atmosphere of nitrogen, the color turned into black from red. The IR spectrum in CH₃CN shows CO absorption bands at 2050, 2041, 1986, 1962 and 1932 cm⁻¹, suggesting the formation of acetonitrile mono-substituted species (μ -dmedt)Fe₂(CO)₅(NCCH₃) [8]. And then pyridine 59 mg (0.74 mmol) was added. After stirring for 6 h at room temperature under an atmosphere of nitrogen, the solvent was filtered and evaporated under vacuum. The remaining residue was purified by column chromatography on neutral alumina with petroleum ether as elute to give complex 1 as a black solid. Dark-red crystals of complex 1 were collected by volatilized from hexane at -5°C. Yield: 178 mg(56.1%). Anal. Calcd. (%) for C₁₄H₁₃Fe₂NO₅S₂: C, 37.28; H, 2.91; N, 3.11 Found(%): C, 37.02; H, 2.87; N, 3.02. IR(MeCN, cm⁻¹): ν (CO)2046(s), 2037(m), 1983(s), 1961(w), 1921(m). ¹HNMR(400 MHz, CD₃CN): 8.58(d, Py), 7.62(s, Py), 7.23(d, Py), 2.18(s, SCH(CH₃)CH(CH₃)S), 1.88(m, SCH(CH₃)CH(CH₃)S), 1.47(d, SCH(CH₃)CH(CH₃)S), 1.28 (d, SCH(CH₃)CH(CH₃)S) .

3. Results and discussion

3.1. Crystal structure of complex 1

The crystallographic structure of complex 1 is depicted in Fig. 1. Selected bond lengths and bond angles are tabulated in Table S2. Single-crystal X-ray analysis reveals that the [Fe₂S₂] skeleton of

complex **1** shares the well-known butterfly conformation in which each iron center adopts distorted square-pyramidal coordination geometry. The distinction of bridgehead group on mono-substituted diiron complex model has a slight influence on the Fe–Fe distance in comparison with that in (μ -pdt)Fe₂(CO)₅Py [10]. The Fe-Fe bond distance (2.5326(7) Å) is shorter than that of the same pyridine substituted model complex (μ -pdt)Fe₂(CO)₅Py(2.5342(8) Å) [10]. The ligand lies in the apical position rather than the basal position as the pyridine ligand in (μ -pdt)Fe₂(CO)₅Py [9]. The Fe-N bond distance (2.0212(18) Å) is shorter than that of complex (μ -pdt)Fe₂(CO)₅Py(2.029(2) Å). The mean Fe-S distance is 2.236 Å and the average angles of Fe-S-Fe and S-Fe-S are 69.07 ° and 79.855 °, respectively. Furthermore, the mean Fe-C distance (1.7842 Å) of the substituted iron atom is shorter than that of the unsubstituted iron atom, revealing the increased strength of back-bonding from Fe to CO caused by coordination of the ligand. The angle of Fe(1)-Fe(2)-N(1) in complex **1** is much higher than that complex (μ -pdt)Fe₂(CO)₅Py [7]. Accordingly, the basal coordination environment of pyridine on the Fe atoms is different from the complex (μ -pdt)Fe₂(CO)₅Py and indicates the stronger π -back-donation from the Fe center to the N [11].

[Fig. 1 inserted here]

3.2. Electrochemistry and IR investigation of reversible CO binding of complexes **1-2**

The electrochemical properties of complex **1** were investigated by cyclic voltammogram(CV) in coordinating solvent CH₃CN in the presence of Bu₄NPF₆ as supporting electrolyte. The current response of the redox events at -1.26 V and -1.76 V versus Ag/AgNO₃ show a linear dependence on the square root of the scan rate, which is an indicative of a diffusion-controlled process, with the electrochemically active species freely diffusing in the CH₃CN solution under N₂ (Fig. S3). For further examination of the electrochemistry of the complex **1** under CO atmosphere, the reactivity of complex **1** with CO has been considered [12-13]. The FTIR-spectrum of complex **1** in CH₂Cl₂ solution under CO atmosphere and under N₂ atmosphere showed complex **1** is stable, Fig. S4. On

the other hand, compared the CV of complex **1** and corresponding all-carbonyl complex $[(\mu\text{-dmedt})\{\text{Fe}(\text{CO})_3\}_2]$ in CH_3CN solution under CO atmosphere, the CV of all-carbonyl complex $[(\mu\text{-dmedt})\{\text{Fe}(\text{CO})_3\}_2]$ in CH_3CN solution under CO atmosphere displayed a quasi-reversible reduction event at -1.72 V (Fig. S5) and the CV of complex **1** showed a reduction peak at -1.26 V (Fig. 2A). In summary, complex **1** showed no reactivity with CO under CO atmosphere. Furthermore the study of complex **1** under N_2 and CO atmosphere is shown in Fig. 2, reversible transformation between complex **1** and **2** can be observed by CV. In CH_3CN solution (under CO atmosphere) a reduction peak was observed at -1.26 V (Fig. 2A), which belongs to complex **1**. The deductive potentials of the complex **2** are 400-500 mV more positive than $(\mu\text{-pdt})\text{Fe}_2(\text{CO})_6$ [7] and $[(\mu\text{-dmedt})\{\text{Fe}(\text{CO})_3\}_2]$, and close to the complex $(\mu\text{-pdt})\text{Fe}_2(\text{CO})_5\text{Py}$ [10]. The electrochemical behavior conveys a message that, although the average electron density of the diiron centers of complex **1** is comparable to $(\mu\text{-pdt})\text{Fe}_2(\text{CO})_6$ [10] and $[(\mu\text{-dmedt})\{\text{Fe}(\text{CO})_3\}_2]$, the π -orbits of the pyridine ring can render the uneven electron density of the two iron atoms through an electron delocalization. The strong-accepting capability, also reported in the complex $(\mu\text{-pdt})\text{Fe}_2(\text{CO})_5\text{Py}$ [10], suggests pyridine rings has the potential candidates to tune the electron properties of the diiron centers. This can be supported by another evidence that the carbene disubstituted complex $((\mu\text{-dmedt})[\text{Fe}_2(\text{CO})_5]\text{Ime})$, $\text{Ime} = 1,3\text{-dimethylimidazol-2-ylidene}$) displays similar reductive behaviors to those of the mono-substituents [14]. Then, CO was removed by continuously N_2 for 5 min, a new reduction peak was observed at -1.76 V (Fig. 2B) in CH_3CN solution with the presence of N_2 , which implied the formation of $(\mu\text{-dmedt})\text{Fe}_2(\text{CO})_5(\text{NCCH}_3)$ by replacement of CH_3CN molecules. After continuous ventilation with nitrogen for two hours, only a reduction peak can be observed at -1.76 V (Fig. 2C), which implied the complex **1** was disappeared and generation of $(\mu\text{-dmedt})\text{Fe}_2(\text{CO})_5(\text{NCCH}_3)$ [8]. Next, removing N_2 by CO and addition of excess pyridine, the peak of complex **1** at -1.26 V was recovered and the peak at -1.76 V disappeared (Fig. 2D), which implied the generation of complex

1 by immediate replacement of CH₃CN molecules by pyridine molecules. According to the relevant literatures [15-16], CH₂Cl₂ solution is used as a non-coordinate solvent for the most [Fe-Fe]-H₂ases mimics. Hence, we studied the electrochemistry of complex **1** in CH₂Cl₂ under CO atmosphere and under N₂ atmosphere. As shown in Fig. S6, by switching the atmosphere from N₂ to CO, complex **1** both showed a reductive event at -1.28 V in CH₂Cl₂ either under CO atmosphere or under N₂ atmosphere, coincident with the FTIR-spectrum of complex **1** in CH₂Cl₂ solution. This suggests that introduction of a pyridine ligand by CO-substitution of parent complex [(μ-dmedt){Fe(CO)₃}₂] can diminish the overpotential for proton reduction, which would have higher electrocatalytic efficiency for proton reduction than parent complex (μ-pdt)Fe₂(CO)₆ [7], [(μ-dmedt){Fe(CO)₃}₂] and other hydrogenase mimics complexes [15-16].

[Fig. 2 inserted here]

Further proofs of this hypothesis as well as structural information on the reduced species were sought from FTIR-spectrum. The spectral changes are consistent with the formation of the respective complex **1** and **2**. Reversible transformation between complex **1** and **2** can also be observed. As shown in Fig. 3A, complex **1** was really stable under CO atmosphere in CH₃CN solution. When exposed to N₂, complex **1** slowly rearranges to (μ-dmedt)Fe₂(CO)₅(NCCH₃) [8] by replacement one CO ligand with CH₃CN molecules, complex **1** was completely converted to complex **2** after two hours of exposure to N₂ in CH₃CN solution (Fig. 3B and 3C). Next, removing N₂ by CO and addition of excess pyridine, (μ-dmedt)Fe₂(CO)₅(NCCH₃) [8] was readily converted into complex **1** within 5 min in the presence of CO (Fig. 3D).

[Fig. 3 inserted here]

Noteworthy is that in CH₃CN under CO atmosphere, the conversion from complex **1** to (μ-dmedt)Fe₂(CO)₅(NCCH₃) [8] could not happen, which proved the complex **1** is more stable than the previous complex (μ-pdt)Fe₂(CO)₅(NH₂Pr) [8]. When the complex **1** exposed to N₂ atmosphere in

CH₃CN solution, the conversion from complex **1** to **2** went to completion within 2 h, which was considerably slower than the previous reports [8]. These experiments show that reversible carbonylation of model complexes is affected not only by the nature of pendant ligated ligand but also the type of bridging thiolate ligand. The [2Fe₂S] model complexes of type [(μ-dmedt)Fe₂(CO)₅(L)] (L = ligand, pdt = 2,3-butanedithiol) are more stable and require lower reduction potential than previous reports [8].

3.3. Electrochemical proton reduction investigation

To determine possible electrocatalytic activity of complex **1**, the electrocatalytic property towards H₂ development of complex **1** was carried out in the presence of HOAc in MeCN. The electrochemical behavior of complex **1** was analyzed in details in the presence of HOAc (0–8 mmol) as a source of protons (Fig. 4). Upon addition of 1 mmol of HOAc to the complex **1**, the first reductive peak for complex **1** at -1.26 V did not shift and the current height showed a minor growing, indicating that H⁺ did not incorporate to the model complex **1**. Interestingly, with the upon addition of HOAc (0–8 mmol), an increase in the current of this second cathodes wave was observed, with these shifts continuing with each increment of acid added thereafter, the second peak at -1.76 V (which belongs to the complex **2**) was shifted towards a more negative potential at -1.81 V when detected under N₂ [17-20]. It is tentatively proposed that any hydrogen evolution occurs from the Fe⁰Fe⁰ redox state. The electrochemical behavior features a proton relative process. This suggests that both complex **1** and complex **2** species can combine with protons and be active toward electrocatalytic H₂ production, but the reactivity of the later is stronger than the former.

[Fig. 4 inserted here]

Inspired by DuBois group's work [21,22,23], we also tried to explore the catalytic hydrogen evolution in aqueous media, a much more attractive medium for the sustainable generation of hydrogen. Cyclic voltammetry was carried out in the presence of water in CH₃CN. As shown in Fig.

5, following the addition of water to the solution, an increase in the peak current at -1.26 V was observed and no positive or negative shift, typical for the reduction of $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ to Fe^0Fe^0 , indicating complex **1** displayed the catalytic function in water for H_2 formation. The new ligand motif that a pyridine ligand is coordinated to a Fe^{I} centre, and can be related to water-soluble hydrogenases complexes for further functional studies, with an emphasis on efficient and clean energy utilization way.

[Fig. 5 inserted here]

4. Conclusions

In summary, we successfully prepared a new pyridine substituted $[\text{2Fe}_2\text{S}]$ model complex **1** fully characterized by spectroscopic methods and single-crystal structure analysis. During the investigation of the electrochemical properties in CH_3CN , complex **1** is more stable than the previously amine-coordinated iron hydrogenase active site model complex and replacement of pyridine ligand with solvent molecule is slower. Complex **1** was observed to catalyze hydrogen evolution from HOAc and aqueous media at -1.26 V. The results reported in this work further demonstrate that the low binding strength of a ligand how to affect the stability of a $[\text{2Fe}_2\text{S}]$ model complex, which could mimic the function of the flexible coordination site in the H_2 ase enzymes. Those will be of relevance to the natural system. Comparison of the data could help us to develop more efficient catalyst systems by using earth abundant metal ions in the future.

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Appendix A. Supplementary data

CCDC 1410968 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>. Supplementary data related to this article can be found at <http://>

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Captions to Scheme and Figures

Scheme 1 The synthesis of the complexes **1** and **2**

Fig. 1 X-ray crystal structure of complex **1**(ellipsoids at 30% probability level). The hydrogen atoms are omitted for clarity.

Fig. 2 Cyclic voltammogram of complex **1**(1.0 mM) in 0.1 M *n*-Bu₄NPF₆/MeCN. Under CO atmosphere(A), under N₂ 5 min(B), under N₂ 2 h(C), in the presence of excess pyridine under CO

atmosphere(D) ; scan rate, 100 mV/s.

Fig. 3 IR spectral changes for complex **1** following various conditions and time in 0.1 M *n*-Bu₄NPF₆/MeCN. A(under CO atmosphere), B(under N₂ 5 min), C(under N₂ 2 h), D(in the presence of excess pyridine under CO atmosphere), respectively.

Fig. 4 Cyclic voltammograms of the complex **1** (1 mM) and with HOAc(0, 1, 2, 4, 6 and 8 mmol) in CH₃CN solution(0.1 M *n*-Bu₄NPF₆) under N₂ at room temperature; scan rate, 100 mV/s.

Fig. 5 Cyclic voltammograms of complex **1** (1 mM) detailing the effect of H₂O on the catalytic proton reduction in CH₃CN solution(0.1 M *n*-Bu₄NPF₆) under N₂ at room temperature; scan rate, 100 mV/s.

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