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Terminal pyridine-N ligation at [FeFe] hydrogenase active-site mimic

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ABSTRACT

Diiron model complexes (μ-pdt)$Fe_2(CO)_5$L with L = pyridine ligands, *e.g.* py (**A**), etpy (**B**), btpy (**C**), were synthesized as active site analogues of [FeFe] hydrogenase, and characterized by X-ray crystallography and electrochemistry. Pyridine-N ligation was found to be able to tune the redox properties of the diiron centers of model complexes.

1. Introduction

[FeFe] hydrogenase has sparked chemical mimic research interest due to the capability of producing hydrogen efficiently. The active site has been called “H-cluster”, which comprises a dithiolate-bridged diiron subsite and a cuboidal Fe_4S_4(S-Cys)$_4$ cluster, linked up through a cysteine sulfur atom. Chemical model studies have shown that classical Reihlen diiron dithiolate complexes (μ-SR)$_2$$Fe_2(CO)_6$ share several structural features with the diiron subsite, *e.g.* short Fe–Fe distance (*ca.* 2.6 Å), bidentated dithiolate bridge and diatomic CO ligands [1–3].

To obtain better structural and functional diiron model complexes, good donor ligands, such as carbene [4–7], cyanide [8–12], phosphine [13–18], thioether or sulfoxide [19,20], have been introduced into diiron model complexes by the method of CO-displacement of (μ-pdt)$Fe_2(CO)_6$ (**1**). While the structural models of the active site of [FeFe] Hydrogenase have matured considerably over recent years [21–25], little attention has been devoted to the influence of the N-ligation at diiron models, for it is difficult to isolate the labile coordination of the amine to iron atom, for instance in (μ-pdt)$Fe_2(CO)_5(NH_2Pr)$ (**2**) which is unstable [26].

But the electron-donating capability of the nitrogen atom is expected in N-ligation of nitrogen-hetercycles, which are abundant in nature and play important role in organometallic chemistry. We thought it would be interesting to evaluate the role of N-ligation in diiron model complexes with the introduction of pyridine or other heterocyclic-N ligands [27], which was expected to extend new promising models for structural or functional modification for 2Fe2S model complexes. Herein, we report the preparation of a series of active site analogues of [FeFe] hydrogenase with the substitution of pyridine ligands, and their characterization and electrochemistry.

2. Experimental

2.1. Reagents and measurements

All manipulations and reactions were carried out under dry oxygen-free N_2 using standard Schlenk techniques. All chemicals were analytical reagents and used without further purification. The compounds etpy, btpy (Supplementary) and (μ-pdt)$Fe_2(CO)_6$ (**1**) [28,29] were prepared according to the literature. All solvents were dried and distilled prior to use according to the standard methods. Infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer using KBr pellets. ^{1}H NMR spectra were collected on a Varian Unity 500NMR spectrometer. Mass spectra were recorded on an DECAX-3000 LCQ Deca XP instrument. Elemental analysis was carried out on a Vario EL III Elemental Analyser.

2.2. Preparations

2.2.1. Preparation of (μ-pdt)$Fe_2(CO)_5$Py (A)

(μ-pdt)$Fe_2(CO)_6$ (3 mmol, 1.158 g) (**1**) reacted with $Me_3NO \cdot 2H_2O$ (3 mmol, 0.333 g) under the ice bath condition in 30 mL of CH_3CN, and then pyridine (3 mmol, 0.237 g) was added. The colour turned from red into black. After 24 h the solvent was filtered and evaporated under vacuum. The remaining residue was extracted with 30 mL of freshly distilled *n*-hexane and filtered. Dark

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crystals were obtained after several days in the refrigerator at −20 °C. Yield: 70% (0.92 g). Anal. Calcd for $Fe_2S_2C_{13}O_5H_{11}N$: C, 35.73; H, 2.54; N, 3.21. Found: C, 35.54; H, 2.59; N, 3.14%. IR (cm^{-1}, KBr pellet): (ν_{co}) 2029 (s), 1980 (vs), 1939 (m), 1918 (m). ^1H NMR (CD_3CN): δ 8.36 (2H, Py), 7.33 (1H, Py), 7.20 (2H, Py), 2.15 (4H, $SCH_2CH_2CH_2S$), 1.85 (2H, $SCH_2CH_2CH_2S$). *m/z* 437.7 $[M+H]^+$.

2.2.2. Preparation of (μ-pdt)$Fe_2(CO)_5$(etpy) (**B**)

The reaction steps were similar to those of **A**, but 4-(ethylthio)pyridine (3 mmol, 0.418 g) was used to replace pyridine. Yield: 60% (0.89 g). Anal. Calcd for $Fe_2S_3C_{15}O_5H_{15}N$: C, 36.24; H, 3.04; N, 2.82. Found: C, 37.19; H, 3.11; N, 2.97%. IR (cm^{-1}, KBr pellet): (ν_{co}) 2033 (s), 1978 (vs), 1918 (m). ^1H NMR (CD_3CN): δ 8.36 (2H, Py), 7.19 (2H, Py), 2.16 (4H, $SCH_2CH_2CH_2S$), 2.13 (2H, SCH_2CH_3), 1.85 (2H, $SCH_2CH_2CH_2S$), 1.36 (3H, SCH_2CH_3). *m/z:* 498.7 $[M+H]^+$, 414.9 $[M+H-3CO]^+$.

2.2.3. Preparation of [(μ-pdt)$Fe_2(CO)_5$(btpy)] (**C**)

The reaction steps were similar to those of **A**, but 4-(*n*-butylthio)pyridine (3 mmol, 0.501 g) was used to replace pyridine. Yield: 64% (1.01 g). Anal. Calcd for $Fe_2S_3C_{17}H_{19}O_5N$: C, 38.88; H, 3.65; N, 2.67. Found: C, 38.84; H, 3.78; N, 2.53%. IR (cm^{-1}, KBr pellet): (ν_{co}) 2038 (s), 1969 (vs), 1953 (s), 1920 (m). ^1H NMR (CD_3CN): δ 8.37 (2H, Py), 7.21 (2H, Py), 2.46 (2H, $SCH_2CH_2CH_2CH_3$), 2.15 (4H, $SCH_2CH_2CH_2S$), 1.86 (2H, $SCH_2CH_2CH_2S$), 1.69 (2H, $SCH_2CH_2CH_2CH_3$), 1.35 (2H, CH_2CH_3), 0.95 (3H, CH_2CH_3). *m/z:* 525.9 $[M+H]^+$.

2.3. X-ray crystallography

Diffraction measurements of single crystals of complexes **A** and **B** were made on a Rigaku Mercury diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), while single crystal of complex **C** was performed on a Rigaku Saturn70 diffractometer. Crystal data collection, refinement and reduction were accomplished with the CRYSTALCLEAR processing program. The structure was solved by direct methods with SHELXS-97 [30] and refined by using the SHELXL-97 crystallographic software package [31]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added in a riding model, while the pdt bridge in **C** was refined with "envelope-flap" disorder. Crystallographic data of **A**, **B** and **C** are summarized in Table 1.

Table 1
Crystallographic data summary for complexes **A**, **B** and **C**.

	A	**B**	**C**
Empirical formula	$Fe_2S_2C_{13}O_5H_{11}N$	$Fe_2S_3C_{15}O_5H_{15}N$	$Fe_2S_3C_{17}O_5H_{19}N$
Formula weight	437.07	497.19	525.24
Space group	*P*2(1)/*n*	*P*2(1)/*n*	$P\bar{1}$
a (Å)	8.200(3)	8.899(5)	9.342(6)
b (Å)	12.661(5)	22.291(10)	11.528(7)
c (Å)	16.094(7)	10.382(6)	11.564(7)
α (°)	90.00	90.00	66.769(17)
β (°)	90.717(5)	106.380(8)	79.15(3)
γ (°)	90.00	90.00	77.62(2)
V ($Å^3$)	1670.6(12)	1975.9(17)	1110.3(12)
Z	4	4	2
ρ_{calc} ($g\ cm^{-3}$)	1.738	1.671	1.571
Absorption coefficient (mm^{-1})	2.007	1.810	1.615
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0359$ $\omega R_2 = 0.0929$	$R_1 = 0.0499$ $\omega R_2 = 0.0931$	$R_1 = 0.0591$ $\omega R_2 = 0.1295$
R indices (all data)	$R_1 = 0.0518$ $\omega R_2 = 0.1023$	$R_1 = 0.0913$ $\omega R_2 = 0.1098$	$R_1 = 0.1170$ $\omega R_2 = 0.1734$

2.4. Electrochemistry

Electrochemical measurements were made using a CH instrument Model 630A Electrochemical Workstation. Cyclic voltammograms were obtained in a conventional and gastight three-electrode cell under Ar and at room temperature. The working electrode was a glassy carbon electrode (3 mm in diameter), the reference electrode a Ag|AgCl electrode (*ca.* −0.43 V vs. Fc/Fc^+), and the counter electrode a platinum wire. The supporting electrolyte is 0.1 M Bu_4NPF_6 in CH_3CN.

3. Results and discussion

3.1. Synthesis and characterization

(μ-pdt)$Fe_2(CO)_6$ (**1**) was treated with $Me_3NO \cdot 2H_2O$ under the ice bath condition in CH_3CN in the atmosphere of N_2 [10], and then pyridine ligands (py, etpy or btpy) were added. Considerable yields of all the model complexes and their moderate stability in air as solid were ensured to research their properties.

The IR data of the CO bands for **A**, **B** and **C** show *ca.* 50 cm^{-1} shift to lower frequency compared to that of the all-carbonyl complex **1** (Table 2), and similar average $\nu_{(CO)}$ and the frequency range of the CO bands to those of different mono-subsituated complexes, *e.g.* (μ-pdt)$Fe_2(CO)_5$(CN) (**3**) [10], (μ-pdt)$Fe_2(CO)_5(PPhMe_2)$ (**4**) [15], (μ-pdt)$Fe_2(CO)_5(SEt_2)$ (**5**) [19], which prove the considerable electron-donating capabilities of pyridine ligands. The ^1H NMR spectra of **A**, **B** and **C** each show typical signals for μ-$SCH_2CH_2CH_2S$ at 2.15–2.16 and 1.85–1.86 ppm in spite of the introduction of pyridine groups. As shown in Table 3, it is interesting to observe that the chemical shifts for α- and β-H in pyridine groups are upfield-shifted as compared to those in non-coordinated pyridine complexes, indicating π-backdonation capability from diiron center to the pyridine ring.

3.2. X-ray crystallographic structures of complexes **A**, **B** and **C**

The structures of complexes **A**, **B** and **C** were determined by X-ray diffraction. Their molecular diagrams are depicted in Fig. 1, and the selected bond lengths and bond angles are given in Table 3. Complexes **A** and **B** crystallize in monoclinic $P2_1/n$ space group,

Table 2
Listing of ν_{CO} infrared and electrochemical parameters for the model complexes **1**–**5**, **A**, **B** and **C**.

Complex	Ligand	ν_{CO} (KBr)/cm^{-1}	Average value of ν_{CO}/cm^{-1}	E_{pc1}/V vs. Ag|AgCl (Fe^IFe^I/Fe^IFe^0)	Reference
1	All-CO	2071, 2026, 1989, 1972	2015	−1.24	[29]
2	NH_2Pr	1980, 1943, 1907, 1892[a]	1931[a]	−1.36	[26]
3	CN^-	2029, 1974, 1955, 1941, 1917	1963	−1.73	[10]
4	$PPhMe_2$	2040, 1980, 1921	1980	−1.88	[15]
5	SEt_2	2045, 1976, 1960, 1919	1975	−1.29	[19]
A	py	2029, 1980, 1939, 1918	1967	−1.21	This work
B	etpy	2033, 1978, 1918	1976	−1.25	This work
C	btpy	2038, 1969, 1953, 1920	1970	−1.23	This work

[a] ν_{CO} in THF.