



Synthesis and Characterization of Iron(II) Carbonyl Complexes Related to Cluster-Free Hydrogenase

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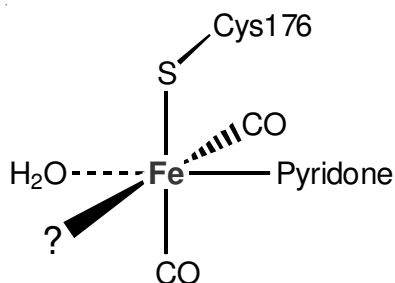
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Reactions of $[\text{Fe}(\text{CO})_4\text{I}_2]$ with one equivalent of $\text{PyCH}_2\text{NHC}_2\text{H}_4\text{SNa}$ ($\text{L}_1^- \text{Na}^+$) and PyCH_2NH_2 (L_2) in THF separately gave rise to complexes $[\text{Fe}(\text{CO})_2(\text{L}_1)\text{I}]$ (**1**) and $[\text{Fe}(\text{CO})_2(\text{L}_2)\text{I}_2]$ (**2**). Both the complexes show two strong carbonyl absorptions at 2027, 1974 cm^{-1} (**1**) and 2036, 1989 cm^{-1} (**2**), which are very close to that of cluster-free hydrogenase (Hmd).

Key Words: [Fe]-Hydrogenase, Iron carbonyl, 2-Aminomethylpyridine, N-(2-Mercaptoethyl)picolyamine.

INTRODUCTION

H_2 -Forming methylenetetrahydromethanopterin dehydrogenase (Hmd) is an unusual hydrogenase which present in many methanogenic archaea. It can catalyze the reversible reduction of methenyltetrahydromethanopterin (methenyl- H_4MPT^+) with H_2 to methylene- H_4MPT and H^+ ($\Delta G^\circ = -5.5 \text{ kJ mol}^{-1}$)^{1,2}. The active site iron atom of the [Fe]-hydrogenase takes an octahedral coordination, in which it is connected with two *cis*-CO, a S atom of Cys176, a sp^2 -hybridized N atom of the pyridone derivative, a H_2O molecule and an unknown ligand³ (**Scheme-I**). The two CO, S atom of Cys176 and the unknown ligand form a square, the sp^2 -hybridized N of the pyridone derivative perpendicular to the square, the H_2O *trans* to the pyridone⁴.



Scheme-I: Mode for Hmd active site

Obrist *et al.*⁵ had synthesized a model complex of [Fe]-hydrogenase using $[\text{Fe}(\text{CO})_3(\text{PPh}_3)\text{I}_2]$ reaction with sodium 6-methyl-2-pyridonate. Royer *et al.*⁶ had used the thioester $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-C(O)SPh}$ to react with $[\text{Fe}_2(\text{CO})_9]$ to give com-

plex $[\text{Ph}_2\text{PC}_6\text{H}_4\text{C(O)Fe}(\text{SPh})(\text{CO})_3]$, a model for the CO-inhibited active site of the methylenetetrahydromethanopterin dehydrogenase. Both complexes have acyl ligand. Li *et al.*⁷ had synthesized 12 model complexes of [Fe]-hydrogenase using $[\text{Fe}(\text{CO})_4\text{I}_2]$ as a starting compound. Recently, our group had synthesized a mono-iron complex $[\text{Fe}(\text{cis-CO})_2\text{L}]$ by reaction of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with tridentate ligand HL (HL = 2,2'-(pyridin-2-ylmethylazanediy)diethanethiol)⁸. This complex possesses two *cis*-CO, N-pyridine and thiolate ligation which has some structural relevance to the methylenetetrahydromethanopterin dehydrogenase. Infrared data and Mossbauer data for mono-iron complex possessing two *cis*-CO and a model complex revealed the iron centre of the cluster-free hydrogenase Hmd is low-spin Fe(II). On the other hand, $[\text{Fe}(\text{CO})_4\text{I}_2]$ has been intensively used as a precursor to synthesis Hmd due to its good reactivity through halogen elimination. The oxidation state of iron centre of the $[\text{Fe}(\text{CO})_4\text{I}_2]$ is Fe(II). The substituted reactions of CO and I atoms on $[\text{Fe}(\text{CO})_4\text{I}_2]$ are fast and complete at room temperature⁹. For example the xanthate, dithiocarbamate *etc.* ligands were chosen to substitute the I atoms of precursor $[\text{Fe}(\text{CO})_4\text{I}_2]$. Herein, we report our investigation on Hmd by reactions of $[\text{Fe}(\text{CO})_4\text{I}_2]$ with tridentate $\text{PyCH}_2\text{NHC}_2\text{H}_4\text{SNa}$ ($\text{L}_1\text{-Na}^+$) and bidentate PyCH_2NH_2 (L_2) ligands that containing N-pyridine, nitrogen and sulfur atoms.

EXPERIMENTAL

Unless otherwise stated, all operations were carried out under Ar using standard Schlenk techniques. The reaction vessels were oven dried at 150 °C prior to use. Solvents were distilled under nitrogen from appropriate drying agents

(tetrahydrofuran from sodium-benzophenone, toluene from sodium). $\text{Fe}(\text{CO})_5$, I_2 , NaH, 2-aminomethyl pyridine (L_2) and propane sulfur heterocyclic were commercially available used without further purification. Infrared spectra were recorded on Varian FTS 2000 spectrometer. ^1H NMR spectra were collected on a Varian INOVA 400 NMR spectrometer.

Preparation of $[\text{Fe}(\text{CO})_4\text{I}_2]^{\ominus}$: I_2 (19.439 g, 76.5 mmol) in THF (100.0 mL) was slowly added in to $\text{Fe}(\text{CO})_5$ (10.0 mL, 76.5 mmol) in THF (50.0 mL) solution. After being stirred for 4 h at room temperature, the mixture turned into a black solution. The solution was removed by vacuum pump to give a black solid. Quickly crystallization of this black solid from THF/*n*-hexane at $-24\text{ }^\circ\text{C}$ gave product $[\text{Fe}(\text{CO})_4\text{I}_2]$. Yield: 89.5 %, IR (THF, ν_{max} , cm^{-1}): 2136 (s), 2087 (s), 2074 (s).

Preparation of ligand $\text{PyCH}_2\text{NHC}_2\text{H}_4\text{SH}$ (HL_1)¹⁰⁻¹³: A colourless mixture of 2-aminomethyl pyridine (L_2) (4.0 mL, 38.7 mmol) and propane sulfur heterocyclic (2.0 mL, 49.7 mmol) in dry toluene (20.0 mL) was heated in a sealed ampoule at $115\text{ }^\circ\text{C}$ for 56 h. After being cooled at room temperature, the pale yellow mixture was formed. This yellow precipitation was filtered and loaded onto a silica gel column, eluted with ethyl acetate/petroleum ether/triethylamine (4:1:0.1). The third band was collected and concentrated with a rotary evaporator to give a yellow liquid HL_1 . Yield: 57.0 %. ^1H NMR (CD_3Cl): δ 8.567 (d, $J = 3.96$ Hz, 1H, PyH), 7.657 (m, 1H, PyH), 7.325 (d, $J = 7.72$ Hz, 1H, PyH), 7.182 (m, 1H, PyH), 3.946 (d, $J = 3.6$ Hz, 2H, PyCH_2), 3.879 (t, $J = 6.36$ Hz, 2H, NCH_2CH_2), 2.727 (m, 2H, NCH_2CH_2).

Preparation of $[\text{Fe}(\text{CO})_2(\text{L}_1)\text{I}]$ (1**):** HL_1 (0.100 g, 0.60 mmol) in THF (10.0 mL) was slowly added in to NaH (17.20 mg, 0.72 mmol) in THF (5.0 mL) solution. A white solid produced immediately during the addition. After being stirred for 3 h at room temperature, $[\text{Fe}(\text{CO})_4\text{I}_2]$ (0.235 g, 0.56 mmol) in THF (3.0 mL) was slowly added into the above solution. After being stirred for 20 min at $0\text{ }^\circ\text{C}$, the solution was filtered. Treatment of the filtrate with CO for 0.5 h formed a black solid at the bottom of the solution, which was filtered and dried in vacum. Yield: 13.9 %. IR (THF, ν_{max} , cm^{-1}): 2027(s), 1974(s). ^1H NMR (CD_3CN): δ 9.009 (s, 1H, PyH), 7.774 (s, 1H, PyH), 7.420 (s, 1H, PyH), 7.385 (s, 1H, PyH), 4.213 (d, $J = 16.8\text{ Hz}$, 2H, PyCH_2), 2.249 (s, 4H, NCH_2CH_2).

Preparation of $[\text{Fe}(\text{CO})_2(\text{L}_2)\text{I}_2]$ (2**):** L_2 (0.20 mL, 19.4 mmol) was added in to a solution of $[\text{Fe}(\text{CO})_4\text{I}_2]$ (0.820 g, 19.4 mmol) in THF (10.0 mL). After being stirred for 0.5 h at $0\text{ }^\circ\text{C}$, the mixture changed into a green solution. The solvent was removed by vacuum pump to give a green solid, which was loaded onto a silica gel column and eluted with ethyl acetate. The first band was collected and concentrated with a vacuum pump to give a green liquid **2**. IR (THF, ν_{max} , cm^{-1}): 2036(s), 1989(s).

RESULTS AND DISCUSSION

HL_1 had been prepared according to literature procedures using L_2 reaction with propane sulfur heterocyclic¹⁰⁻¹³. HL_1 had been dehydrogenated by NaH to give rise to $\text{L}_1\text{-Na}^+$ due to $\text{L}_1\text{-Na}^+$ had better reactivity than HL_1 . Reactions of $\text{L}_1\text{-Na}^+$ and L_2 with $[\text{Fe}(\text{CO})_4\text{I}_2]$ in THF at $0\text{ }^\circ\text{C}$ separately formed complexes **1** and **2**. Complex **1** is a brown solid and soluble in

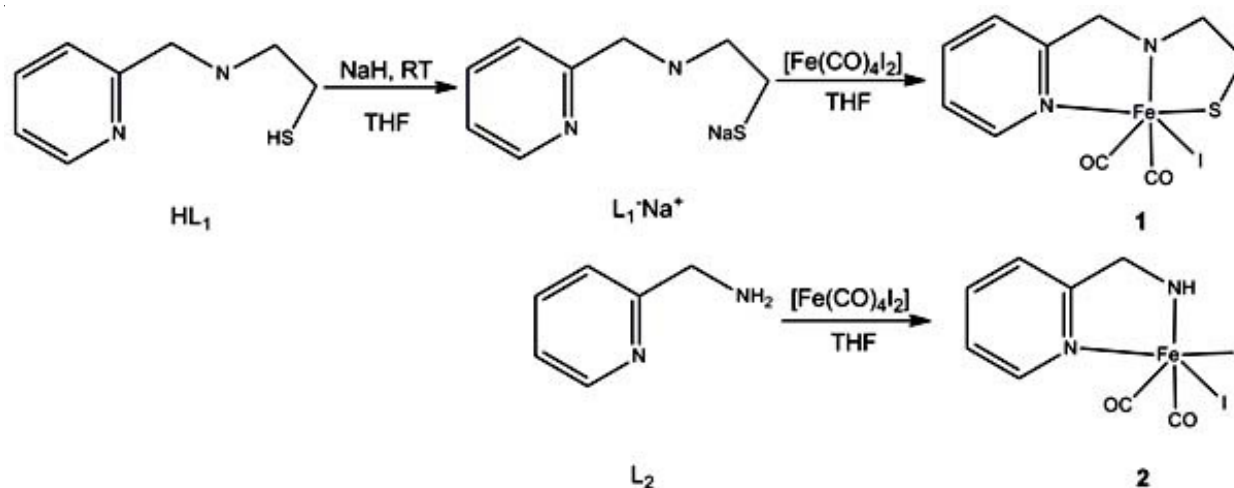
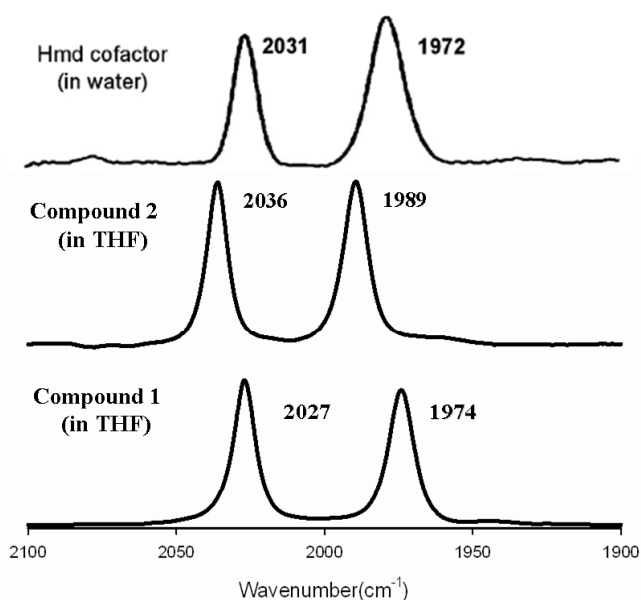
THF. The stability of complex **1** is very poor. If the THF solvent is removed by vacuum pump, or another solvent is added into THF solution, most of the complex **1** changed into an unknown product. IR spectrum of this unknown product shows two carbonyl absorptions at 2042 and 1990 cm^{-1} . However, it can not dissolve in most of the organic solvent, thus no other characterization was carried out on this complex. Similar to complex **1**, complex **2** is soluble in THF as well as it is unstable. At room temperature, complex **2** in THF solution changed into black oil and finally to a green product after being stand for few hours. IR spectrum of the black oil shows two carbonyl absorptions at 2072 and 2018 cm^{-1} . ^1H NMR spectrum of the black oil has no absorption bands, indicating that the black oil has no organic ligand except for I^- and CO to the Fe(II). The unstability of complexes **1** and **2** may caused by the coordinated I atoms are easily removed from the Fe atom in solution. After I atom was dispatched from the Fe atom, the free I^- ion may attack on the Fe atom of another molecule, leading to L_1 , L_2 or CO ligands be easily removed from complexes **1** and **2**.

Spectral analysis: In comparison to that of the starting material $[\text{Fe}(\text{CO})_4\text{I}_2]$, the $\nu(\text{CO})$ of complexes **1** and **2** are at lower wave numbers (Table-1). As shown in Fig. 1, the IR spectrum of complex **1** shows two strong CO stretching bands at 2027 and 1974 cm^{-1} , which are closed to 2031, 1972 cm^{-1} of the co-factor isolated from the enzyme¹⁴. The average wave number of the two absorption bands for the complex **1** is only 1 cm^{-1} lower than that for the isolated co-factor. Complex **2** is similarly to complex **1**, complex **2** shows two strong CO stretching bands at 2036 and 1989 cm^{-1} . The average wave number of the two absorption bands for the complex **2** is only 11 cm^{-1} higher than that for the isolated co-factor. The carbonyl absorption of complex **1** is lower than that of complex **2** due to L_1 can provide more electron than L_2 . IR spectra indicates that complexes **1** and **2** are similarly to $[\text{Fe}]$ -hydrogenase Hmd and the iron centre of **1** and **2** is diamagnetic, low-spin Fe(II), octahedral coordination. The two strong CO stretching bands support a *cis* orientation of two CO ligands.

TABLE-1
INFRARED SPECTROSCOPIC [$\nu(\text{CO})$] DATA FOR
 $[\text{Fe}(\text{CO})_4\text{I}_2]$, $[\text{Fe}(\text{CO})_2(\text{L}_1)\text{I}]$, $[\text{Fe}(\text{CO})_2(\text{L}_2)\text{I}_2]$ AND Hmd.
(REPORTED IN THF UNLESS Hmd)

| | $\nu(\text{CO})$ (cm^{-1}) |
|--|---------------------------------------|
| Hmd ¹⁴ | 2031, 1972 |
| $[\text{Fe}(\text{CO})_4\text{I}_2]$ | 2136, 2087, 2074 |
| $[\text{Fe}(\text{CO})_2(\text{L}_1)\text{I}]$ | 2027, 1974 |
| $[\text{Fe}(\text{CO})_2(\text{L}_2)\text{I}_2]$ | 2036, 1989 |

^1H NMR spectrum of complex **1** exhibits four absorption bands at 9.009, 7.774, 7.420 7.385 ppm that are assigned to the pyridine protons of L_1^- . A doublet observed at 4.213 ppm for a spectrum recorded is assigned to the methylene which is connected to the pyridine. A singlet observed at 2.249 ppm for a spectrum recorded is assigned to the two methylenes which is connected to the 2-aminomethylpyridine. Identified by IR and ^1H NMR, it is concluded that the structure of complex **1** was formed by binding the anionic L_1^- ligands to the Fe(II) atom in a tridentate manner, forming two five-membered chelate

Scheme-II: HL₁ and L₂ reaction with Fe(CO)₄I₂ in THFFig. 1. Infrared spectra of the co-factor, complexes **1** and **2**

rings. At the same time, the structure of **2** is inferred as constructed by coordination of L₂ ligands to the Fe(II) atom in a bidentate manner, forming a five-membered chelate ring (Scheme-II).

Conclusion

In this paper, we had synthesized and characterized two mononuclear carbonyl complexes **1** and **2** which have the similar character of the co-factor. Infrared and ¹H NMR of complexes **1** and **2** revealed their structures. These three compounds separately contain two *cis* carbonyls and a pyridone

derivative. Also, the structure of **1** and the active site of [Fe]-hydrogenase contain a S atom. However, complexes **1** and **2** are very unstable and no further characterization could carry on giving more information about these two products.

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