



NOTE

Synthesis and Structural Characterization of Diiron Ethanedithiolate Complex $(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_5(\text{Ph}_2\text{PNHPy})$ Relevant to the Active Site of [Fe-Fe]-Hydrogenases

WEI GAO¹ and XIAN LI^{2,*}

¹School of Pharmacy, Henan University of Traditional Chinese Medicine, Zhengzhou 450046, P.R. China

²Periodical Press, Henan University of Traditional Chinese Medicine, Zhengzhou 450046, P.R. China

*Corresponding author: E-mail: weigao415@aliyun.com

Received: 26 November 2013;

Accepted: 14 January 2014;

Published online: 16 September 2014;

AJC-15990

A diiron ethanedithiolate complex $(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_5(\text{Ph}_2\text{PNHPy})$ (**1**) has been prepared and characterized by spectroscopy. The title complex was prepared by reaction of $[(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_6]$ (**A**) with Ph_2PNHPy in the presence of the decarbonylating agent $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in acetonitrile at room temperature in 51 % yield. The new complex was characterized by IR, ¹H NMR, ³¹P NMR and ¹³C NMR spectroscopy.

Keywords: Diiron ethanedithiolate, Phosphine ligand, Synthesis, Characterization.

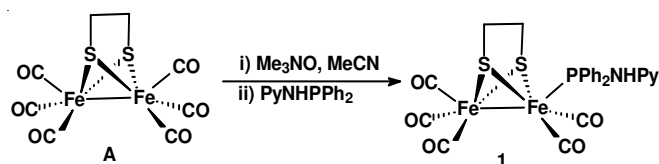
In recent years, [Fe-Fe]-hydrogenases have received considerable attention because it is helpful for the synthesis of new low-cost and highly efficient catalysts for hydrogen evolution¹. X-ray crystallography revealed that the active site of [Fe-Fe]-hydrogenases contains a butterfly [2Fe-2S] cluster linked to a cubane-like [4Fe-4S] cluster *via* the sulfur atom of a cysteinyl group². Recently, many researchers have reported a good number of diiron dithiolate complexes in order to mimic the active site of [Fe-Fe]-hydrogenases³. These derivatives were prepared by several methods⁴ and characterized by various techniques⁵. In this paper, we report the synthesis and structural characterization of diiron ethanedithiolate complex related to the active site of [Fe-Fe]-hydrogenases.

Reaction and operation was carried out under a dry, oxygen free nitrogen atmosphere with standard Schlenk and vacuum line techniques. Acetonitrile was distilled with CaH_2 under N_2 . $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$, PPh_3 and other materials were commercially available and used as received. Complex **A**⁶ and Ph_2PNHPy ⁷ were prepared according to the literature procedures. IR spectra were recorded on a Nicolet 670 FTIR spectrometer. ¹H (³¹P, ¹³C) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

Synthesis: A solution of $(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_6$ (0.186 g, 0.5 mmol) in CH_3CN (15 mL) was added a solution of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.056 g, 0.5 mmol) in CH_3CN (10 mL). The mixture was stirred at room temperature for 15 min and then was added Ph_2PNHPy (0.139 g, 0.5 mmol). The new mixture was stirred for 1 h to give a red solution. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using ethyl

acetate/petroleum ether (*v/v* = 1:1) as eluent. From the main red band afforded 0.160 g (51 %) of **1** as a red solid. IR (KBr, ν_{max} , cm^{-1}): C≡O 2046 (*vs*), 1982 (*vs*), 1934 (*vs*). ¹H NMR (500 MHz, CDCl_3): 8.17 (br, 2H, Py-H), 7.70, 7.46 (2s, 10H, $2\text{C}_6\text{H}_5$), 6.44 (s, 2H, Py-H), 5.60 (d, $J_{\text{P-H}} = 17.0$ Hz, 1H, NH), 1.96 (d, $J = 8.0$ Hz, 2H, SCH_2), 1.41 (m, 2H, SCH_2) ppm. ³¹P NMR (200 MHz, CDCl_3 , 85 % H_3PO_4): 98.37 (s) ppm. ¹³C NMR (125 MHz, CDCl_3): 213.74, 213.67 (C≡O), 150.18, 135.07, 134.71, 130.75, 130.56, 130.46, 129.02, 128.94, 113.09 (Ar-C), 34.96, 34.93 (CH_2) ppm.

As shown in **Scheme-I**, reaction of the starting material complex **A** with 1 equivalent of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ followed by addition of 1 equivalent of Ph_2PNHPy gave the title complex **1** in 51 % yield. The title complex **1** was air-stable red solids, which has been characterized by IR, ¹H NMR, ³¹P NMR and ¹³C NMR spectroscopy.



Scheme-1: Synthesis of the title complex **1**

Infrared spectrum: As shown in Fig. 1, the IR spectrum of **1** displayed three absorption bands in the range of 2046-1934 cm^{-1} for the terminal carbonyls and the $\nu(\text{C}\equiv\text{O})$ values are shifted toward lower frequencies relative to the parent complex **A** (2079, 2039, 2009, 1996 cm^{-1})⁶.

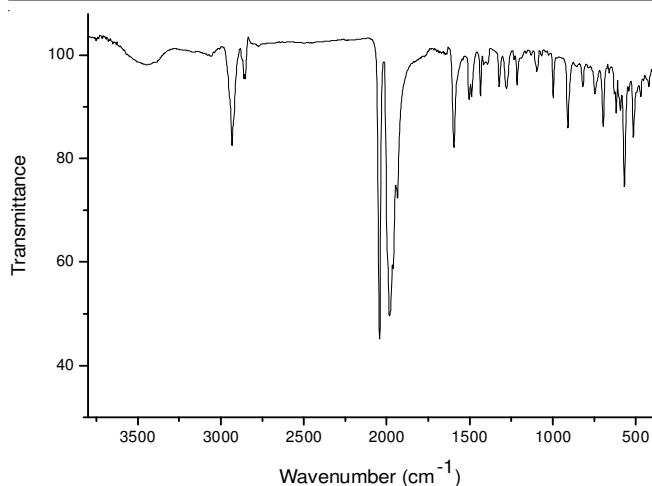
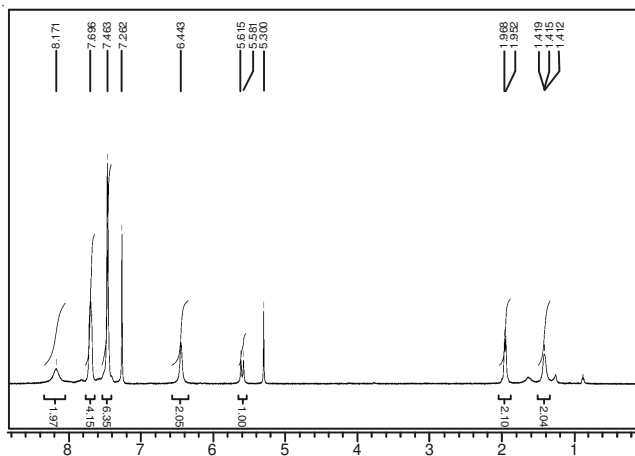
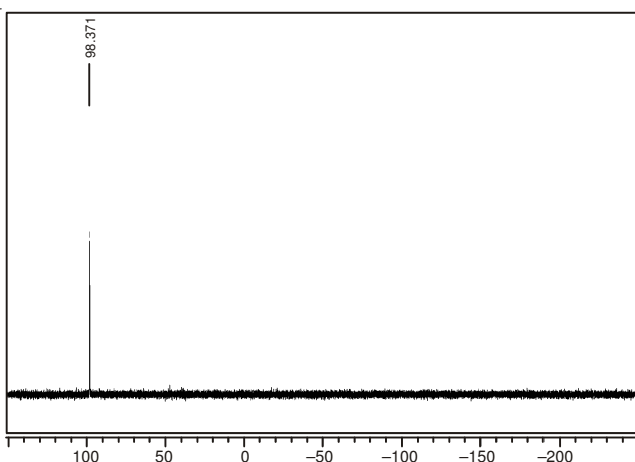


Fig. 1. IR spectrum of the title complex 1

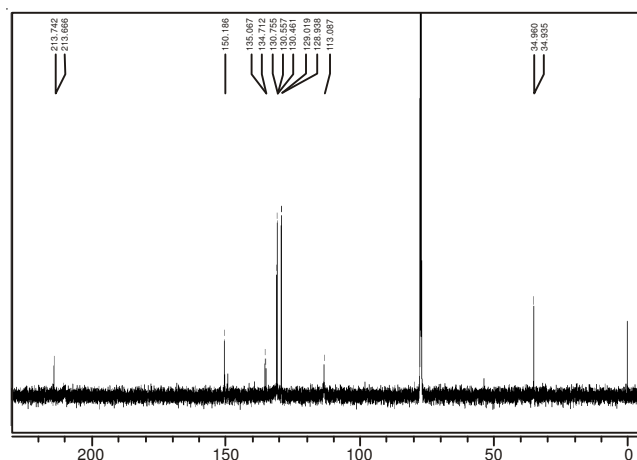
¹H NMR spectrum: As shown in Fig. 2, the ¹H NMR spectrum of **1** showed two singlets at δ 8.17 and 6.44 ppm for its pyridyl protons and a doublet at δ 5.60 ppm with coupling constant $J = 17.0$ Hz for NH group.

Fig. 2. ¹H NMR spectrum of the title complex 1

³¹P NMR spectrum: As shown in Fig. 3, the ³¹P NMR spectrum of **1** exhibited a singlet at δ 98.37 ppm for the phosphorus atom of Ph₂PNHPy coordinated to one Fe of the diiron subsite.

Fig. 3. ³¹P NMR spectrum of the title complex 1

¹³C NMR spectrum. As shown in Fig. 4, the ¹³C NMR spectrum of **1** demonstrated a doublet at δ 213.70 ppm for the terminal carbonyls and a doublet at δ 34.94 ppm for the methylene carbons.

Fig. 4. ¹³C NMR spectrum of the title complex 1

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support by the National Natural Science Foundation of China (81102808).

REFERENCES

- (a) P.-H. Zhao, Y.-Q. Liu and G.-Z. Zhao, *Polyhedron*, **53**, 144 (2013); (b) C.A. Mebi, D.S. Karr and B.C. Noll, *Polyhedron*, **50**, 164 (2013); (c) P.H. Zhao, Y.Q. Liu and X.A. Li, *Asian J. Chem.*, **25**, 5428 (2013); (d) B.S. Yin, T.B. Li and M.S. Yang, *J. Coord. Chem.*, **64**, 2066 (2011); (e) X.F. Liu, *Inorg. Chim. Acta*, **378**, 338 (2011); (f) X.F. Liu, X.W. Xiao and L.J. Shen, *Transition Met. Chem.*, **36**, 465 (2011).
- (a) J.W. Peters, W.N. Lanzilotta, B.J. Lemon and L.C. Seefeldt, *Science*, **282**, 1853 (1998); (b) Y. Nicolet, C. Piras, P. Legrand, C.E. Hatchikian and J.C. Fontecilla-Camps, *Structure*, **7**, 13 (1999).
- (a) X.F. Liu and B.S. Yin, *J. Coord. Chem.*, **63**, 4061 (2010); (b) X.F. Liu, Z.Q. Jiang and Z.J. Jia, *Polyhedron*, **33**, 166 (2012); (c) X.F. Liu, X.W. Xiao and L.J. Shen, *J. Coord. Chem.*, **64**, 1023 (2011); (d) X.F. Liu, *J. Organomet. Chem.*, **750**, 117 (2014).
- (a) X.F. Liu and B.S. Yin, *Z. Anorg. Allg. Chem.*, **637**, 377 (2011); (b) X.F. Liu and X.W. Xiao, *J. Organomet. Chem.*, **696**, 2767 (2011); (c) B.S. Yin, T.B. Li and M.S. Yang, *Acta Crystallogr.*, **E67**, m1502 (2011); (d) W.M. Gao and J.M. Li, *Acta Crystallogr. Sect. E Struct. Rep. Online*, **68**, m118 (2012); (e) X.F. Liu and H.Q. Gao, *J. Clust. Sci.*, **25**, 367 (2014); (f) X.F. Liu and H.Q. Gao, *J. Clust. Sci.*, **25**, 495 (2014).
- (a) X.H. Liu, J.Q. Weng, C.X. Tan, L. Pan, B.L. Wang and Z.M. Li, *Asian J. Chem.*, **23**, 4031 (2011); (b) P.Q. Chen, C.X. Tan, J.Q. Weng and X.H. Liu, *Asian J. Chem.*, **24**, 2808 (2012); (c) Y.L. Xue, Y.G. Zhang and X.H. Liu, *Asian J. Chem.*, **24**, 5087 (2012); (d) L.J. Luo, X.F. Liu and H.Q. Gao, *J. Coord. Chem.*, **66**, 1077 (2013); (e) X.F. Liu and H.Q. Gao, *Polyhedron*, **65**, 1 (2013).
- A. Winter, L. Zsolnai and G. Huttner, *Z. Naturforsch. C*, **37b**, 1430 (1982).
- W. Gao, J. Liu, W. Jiang, M. Wang, L. Weng, B. Åkermark and L. Sun, *C.R. Chim.*, **11**, 915 (2008).