

NOTE

Synthesis and Structural Characterization of Diiron Ethanedithiolate Complex $[(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_4](\text{PPh}_3)_2$ Related to the Active Site of [Fe-Fe]-Hydrogenases

WEI GAO, TING-TING ZHANG and YAN-JUN SUN*

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

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

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A diiron ethanedithiolate complex $[(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_4](\text{PPh}_3)_2$ (**1**), as the active site of [Fe-Fe]-hydrogenases, has been prepared and characterized. The title complex was prepared by reaction of $[(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_6]$ (**A**) with PPh_3 at reflux in xylene in 50 % yield. The new complex was characterized by IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy.

Keywords: Diiron ethanedithiolate, Triphenylphosphine, Synthesis, Characterization.

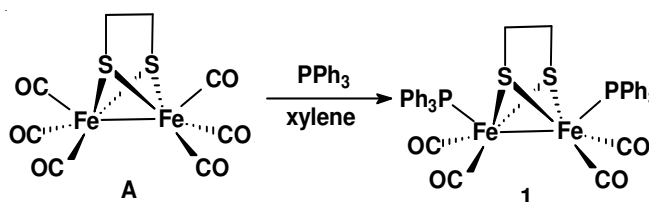
In recent years, butterfly $[\text{2Fe-2S}]$ have received special attention due to their unique structure and close relationship with the natural enzymes of [Fe-Fe]-hydrogenases¹. Protein crystallographic studies revealed that the active site of [Fe-Fe]-hydrogenases consists of a butterfly $[\text{2Fe-2S}]$ cluster linked to a cubane-like $[\text{4Fe-4S}]$ cluster *via* the sulfur atom of a cysteinyl group². Based on structural information, a good number of diiron dithiolate complexes³⁻⁵ were prepared and structurally characterized by various techniques⁶ in order to mimic the natural properties of [Fe-Fe]-hydrogenases. 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** was prepared according to the literature procedures⁷. IR spectra were recorded on a Nicolet 670 FTIR spectrometer. ^1H (^{31}P , ^{13}C) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

Synthesis: A mixture of $(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_6$ (0.186 g, 0.5 mmol), PPh_3 (0.262 g, 1 mmol) and xylene (20 mL) was refluxed for 4 h to give a brown-red solution. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2 /petroleum ether (*v/v* = 1:1) as eluent. Collecting the main red band afforded 0.201 g (48 %) of **1** as a red solid. Anal. Calcd. for $\text{C}_{42}\text{H}_{34}\text{O}_4\text{P}_2\text{S}_2\text{Fe}_2$: C, 60.02; H, 4.08. Found: C, 60.31; H, 4.24. IR (KBr, ν_{max} , cm^{-1}): $\text{C}\equiv\text{O}$ 1994 (vs), 1932 (vs). ^1H NMR (500 MHz, CDCl_3): 7.58, 7.39

(2s, 30 H, Ar-H), 1.57, 1.28 (2s, 4H, 2SCH_2) ppm. ^{31}P NMR (200 MHz, CDCl_3 , 85 % H_3PO_4): 60.03 (s) ppm. ^{13}C NMR (125 MHz, CDCl_3): 216.78, 216.74 ($\text{C}\equiv\text{O}$), 136.93, 136.64, 133.21, 133.16, 133.12, 129.59, 128.34, 128.31 (Ar-C), 32.83 (CH_2) ppm.

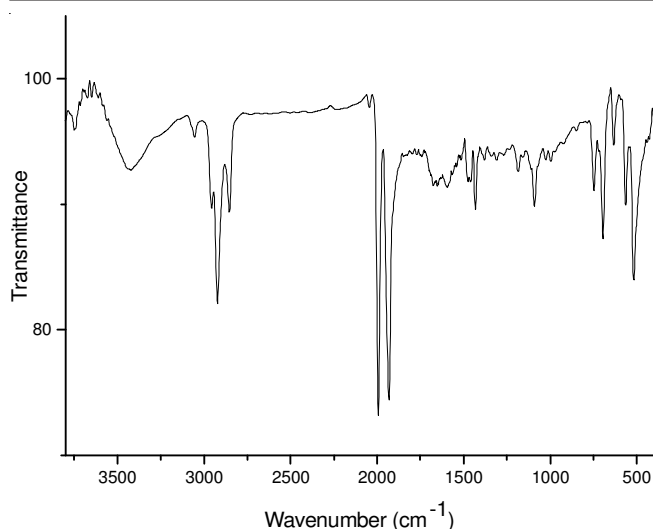
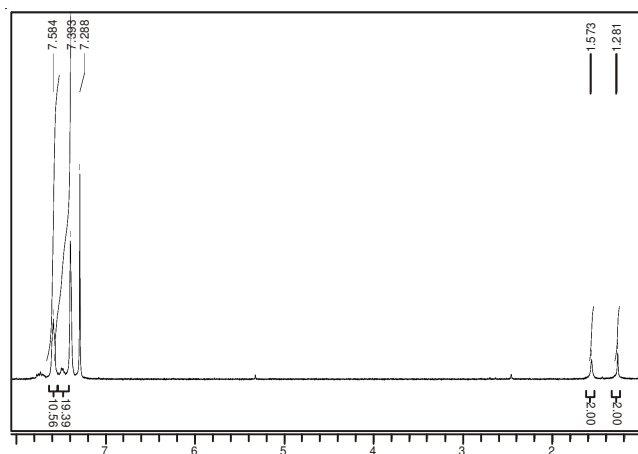
As shown in **Scheme-I**, treatment of complex **A** with 2 equivalent of PPh_3 at reflux in xylene afforded the title complex **1** in 50 % yield. The title complex **1** was air-stable red solids, which has been characterized by IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy.



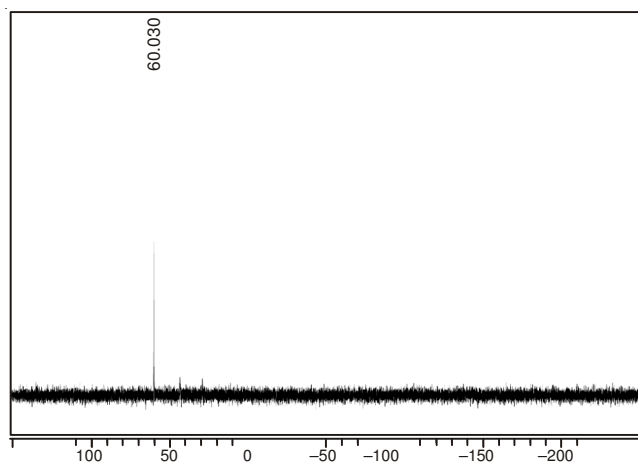
Scheme-I: Synthesis of the title complex **1**

Infrared spectrum: As shown in Fig. 1, the IR spectrum of **1** displayed two strong absorption bands at 1993 and 1933 cm^{-1} for the terminal carbonyls and the $\nu(\text{C}\equiv\text{O})$ values of complex **1** are shifted toward lower frequencies relative to the parent complex **A** (2079, 2039, 2009, 1996 cm^{-1})⁷ because PPh_3 is stronger electron donating than CO.

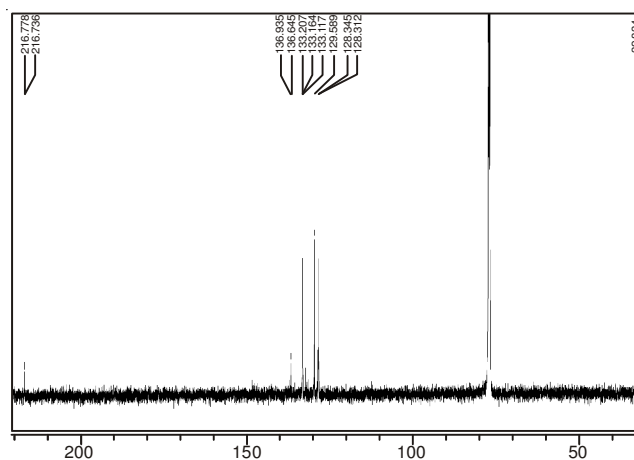
^1H NMR spectrum: As shown in Fig. 2, the ^1H NMR spectrum of **1** showed two singlets at δ 7.58 and 7.39 ppm for its phenyl protons and two singlets at δ 1.57 and 1.28 ppm for the methylene protons.

Fig. 1. IR spectrum of the title complex **1**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 60.03 ppm for the phosphorus atom of PPh₃ 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 216.76 ppm for the terminal carbonyls and a singlet at δ 32.83 ppm for the methylene carbons.

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

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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 and H.Q. Gao, *J. Clust. Sci.*, **25**, 367 (2014); (d) X.F. Liu and H.Q. Gao, *J. Clust. Sci.*, **25**, 495 (2014).
- (a) X.F. Liu, X.W. Xiao and L.J. Shen, *J. Coord. Chem.*, **64**, 1023 (2011); (b) 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) W.M. Gao and J.M. Li, *Acta Crystallogr. Sect. E Struct. Rep. Online*, **68**, m118 (2012).
- (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).