Asian Journal of Chemistry; Vol. 26, No. 19 (2014), 6691-6692

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16765

NOTE

Synthesis and Structural Characterization of Diiron Ethanedithiolate Complex $[(\mu\text{-}SCH_2)_2Fe_2(CO)_5]_2(Ph_2PCH_2CH_2CH_2CH_2PPh_2)$ Containing Bridging Diphosphine Ligand

WEI GAO*, DE-MEI SUN and PENG GAO

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

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

Received: 27 November 2013; *Accepted*: 14 January 2014; *Published online*: 16 September 2014; AJC-15991

A diiron ethanedithiolate complex $[(\mu\text{-}SCH_2)_2Fe_2(CO)_5]_2(Ph_2PCH_2CH_2CH_2CH_2PPh_2)$ (**1**) has been prepared and characterized by spectroscopy. The title complex was synthesized by reaction of $[(\mu\text{-}SCH_2)_2]Fe_2(CO)_6$ (**A**) with dppb ($Ph_2PCH_2CH_2CH_2CH_2PPh_2$) in the presence of the decarbonylating agent $Me3NO\cdot 2H_2O$ in MeCN at room temperature in 66 % yield. The new complex was characterized by IR, ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy.

Keywords: Diiron ethanedithiolate, Dppb, Synthesis, Characterization.

[Fe-Fe]-hydrogenases are metalloenzymes that catalyze hydrogen metabolism in several microorganisms[1]. X-ray crystallographic[2] and IR[3] studies have revealed that the active site of [Fe-Fe]-hydrogenases consists of a butterfly [2Fe-2S] cluster linked to a cubic [4Fe-4S] cluster *via* the sulfur atom of a cysteinyl group. The bridging dithiolate could most likely be propanedithiolate (PDT)[4]. Recently, many PDT model complexes[5] for the active site of [Fe-Fe]-hydrogenases have been reported and characterized by various techniques[6]. In this paper, we report the synthesis and structural characterization of diiron ethanedithiolate complex containing a bridging diphosphine ligand dppb 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 vacuumline techniques. MeCN was distilled with CaH_2 under N_2. $Me_3NO\cdot 2H_2O$, dppb and other materials were commercially available and used as received. Complex **A**[7] was prepared according to the literature procedures. IR spectra were recorded on a Nicolet 670 FTIR spectrometer. ^{1}H (^{31}P, ^{13}C) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

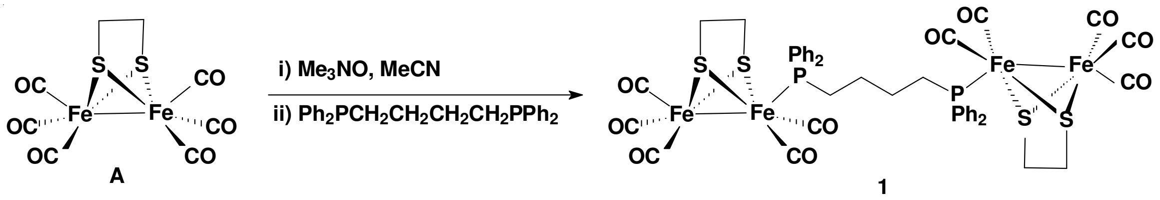
Synthesis: To a solution of $(\mu\text{-}SCH_2)_2Fe_2(CO)_6$ (0.186 g, 0.5 mmol) in CH_3CN (20 mL) was added a solution of $Me_3NO\cdot 2H_2O$ (0.056 g, 0.5 mmol) in CH_3CN (10 mL). The mixture was stirred at room temperature for 15 min and then was added dppb (0.107 g, 0.25 mmol). The new mixture was stirred for 1 h to give a red solution. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:2) as eluent. Collecting the main red band afforded 0.183 g (66 %) of **1** as a red solid. IR (KBr ν_{max}, cm^{-1}): C≡O 2043 (vs), 1975 (*vs*), 1923 (vs) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54, 7.40 (2s, 10 H, $2C_6H_5$), 3.41 (s, 2H, PCH_2), 2.39 (s, 2H, PCH_2CH_2), 1.88 (s, 4H, $2SCH_2$) ppm. ^{31}P NMR (200 MHz, $CDCl_3$, 85 % H_3PO_4): δ 53.74 (s) ppm. ^{13}C NMR (125 MHz): δ 215.55, 215.47, 210.16 (C≡O), 136.43, 136.14, 132.07, 131.99, 130.26, 128.71, 128.64 (PhC), 34.92 (SCH_2), 33.68 (d, $J_{P\text{-}C}$ = 26.0 Hz, PCH_2), 25.64 (d, $J_{P\text{-}C}$ = 14.1 Hz, PCH_2CH_2) ppm.

As shown in **Scheme-I**, the title complex could be prepared by reaction of complex **A** with 0.5 equivalent of dppb in the presence of the decarbonylating agent $Me_3NO\cdot 2H_2O$ in MeCN at room temperature in 66 % yield. The title complex **1** was air-stable red solids, which has been characterized by IR, ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy.

Infrared spectrum: As shown in Fig. 1, the IR spectrum of **1** showed three absorption bands in the range of 2043-1923 cm^{-1} for the terminal carbonyls and the ν(C≡O) values are shifted toward lower frequencies relative to the parent complex **A** (2079, 2039, 2009, 1996 cm^{-1})[7].

^{1}H NMR spectrum: As shown in Fig. 2, the ^{1}H NMR spectrum of **1** displayed two singlets at δ 7.54 and 7.40 ppm for its phenyl protons and two singlets at δ 3.41 and 2.39 ppm for the methylene protons of dppb.

^{31}P NMR spectrum: As shown in Fig. 3, the ^{31}P NMR spectrum of **1** exhibited a singlet at δ 53.74 ppm for the two phosphorus atoms of dppb, each one coordinated to one Fe of the diiron subsite.



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

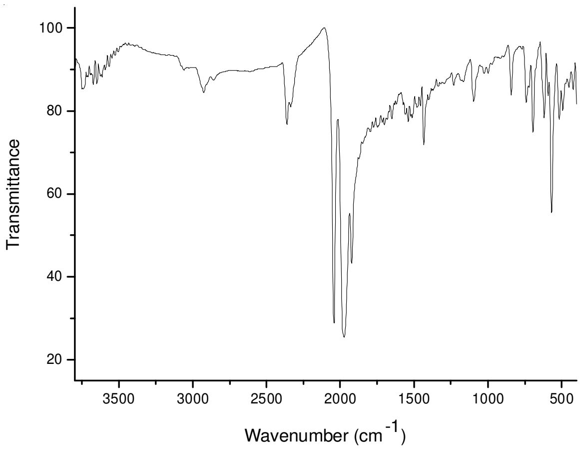


Fig. 1. IR spectrum of the title complex **1**

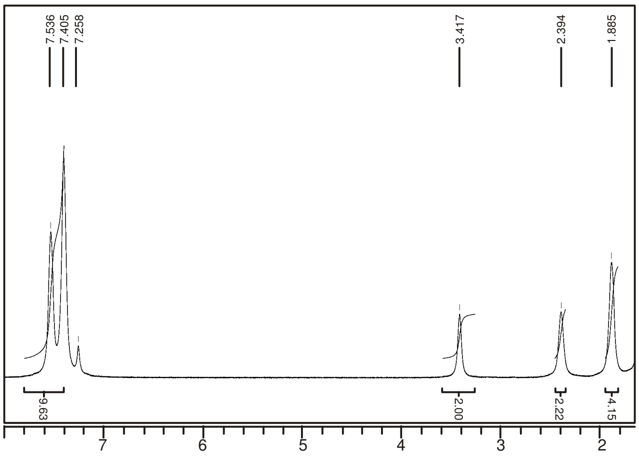


Fig. 2. ^{1}H NMR spectrum of the title complex **1**

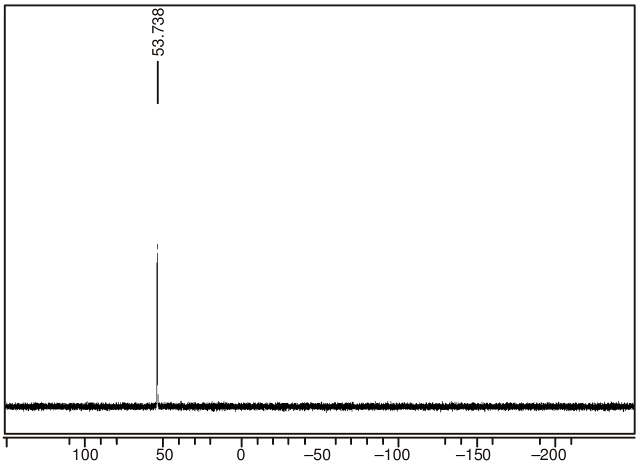


Fig. 3. ^{31}P NMR spectrum of the title complex **1**

^{13}C NMR spectrum: As shown in Fig. 4, the ^{13}C NMR spectrum of **1** demonstrated a doublet at δ 215.51 ppm and a singlet at δ 210.16 ppm for the terminal carbonyls and two doublets at δ 33.68 and 25.64 ppm with coupling constants of $J_{P\text{-}C}$ = 26, 14.1 Hz for the methylene carbons of dppb.

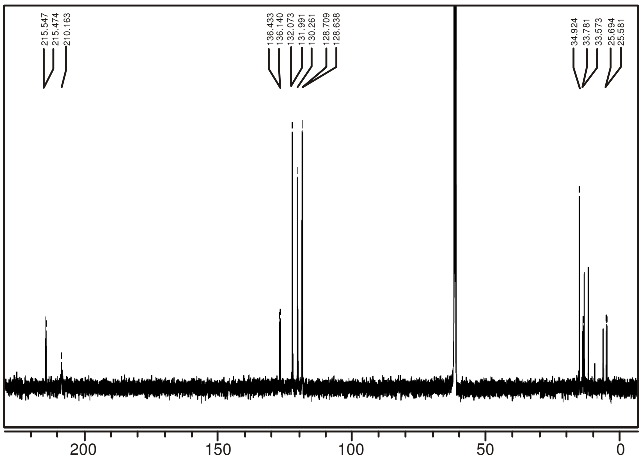


Fig. 4. ^{13}C NMR spectrum of the title complex **1**

ACKNOWLEDGEMENTS

The authros gratefully acknowledge the financial support by the Doctoral Research Fund of Henan University of Traditional Chinese Medicine.

REFERENCES

1. R. Cammack, *Nature*, **397**, 214 (1999).
2. Y. Nicolet, C. Piras, P. Legrand, C.E. Hatchikian and J.C. Fontecilla-Camps, *Structure*, **7**, 13 (1999).
3. A.L. De Lacey, C. Stadler, C. Cavazza, E.C. Hatchikian and V.M. Fernandez, *J. Am. Chem. Soc.*, **122**, 11232 (2000).
4. P.H. Zhao, Y.Q. Liu and X.A. Li, *Asian J. Chem.*, **25**, 5428 (2013).
5. X.F. Liu and H.Q. Gao, *J. Clust. Sci.*, **25**, 495 (2014).
6. (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).
7. A. Winter, L. Zsolnai and G. Huttner, *Z. Naturforsch. C*, **37b**, 1430 (1982).