



NOTE

Synthesis and Structural Characterization of Diiron Azadithiolate Complex $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CO}_2\text{Me}]_2\text{Fe}_2(\text{CO})_4(\text{CN-}i\text{tert-Bu})_2$

HUI LI*, QIAOJUAN GONG, XIAOCHUAN CHAI, CHENZHONG YAO and QIUPING HAN

Department of Applied Chemistry, Yuncheng University, Yuncheng 044000, Shanxi Province, P.R. China

*Corresponding author: E-mail: lihuiwangf@163.com

Received: 5 February 2014;

Accepted: 4 May 2014;

Published online: 4 February 2015;

AJC-16838

A diiron azadithiolate complex $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CO}_2\text{Me}]_2\text{Fe}_2(\text{CO})_4(\text{CN-}i\text{tert-Bu})_2$ (**1**), as the active site of [FeFe]-hydrogenases, has been prepared by carbonyl substitution and structurally characterized. The title complex was prepared by reaction of $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CO}_2\text{Me}]_2\text{Fe}_2(\text{CO})_6$ (**A**) with *tert*-BuNC in CH_2Cl_2 in 46 % yield. The new complex was characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy.

Keywords: Diiron azadithiolate, Isocyanide.

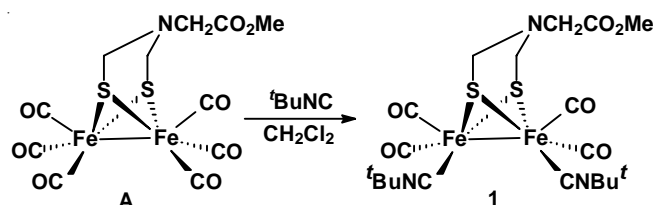
Over the past decades, research on iron-sulfur has attracted great attention due to their close relationship with the active site of [FeFe]-hydrogenases¹⁻⁵. [FeFe]-hydrogenases are metallo-enzymes which can catalyze hydrogen metabolism in several microorganism⁶⁻⁸. The well-established structure of the active site of [FeFe]-hydrogenases has provoked chemists to design and prepared a great number of [FeFe]-hydrogenases model complexes⁹⁻¹². In this paper, we report the synthesis and structural characterization of diiron azadithiolate complex $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CO}_2\text{Me}]_2\text{Fe}_2(\text{CO})_4(\text{CN-}i\text{tert-Bu})_2$ containing an isocyanide ligand relevant to the active site of [FeFe]-hydrogenases.

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

Synthesis: A solution of $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CO}_2\text{Me}]_2\text{Fe}_2(\text{CO})_6$ (0.100 g, 0.22 mmol) in MeCN (10 mL) was added a solution of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.024 g, 0.22 mmol) in MeCN (5 mL). The mixture was stirred at room temperature for 15 min and then was added *tert*-BuNC (0.048 mL, 0.44 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. From the main

red band afforded 0.056 g (46 %) of **1** as a red solid. IR (KBr disk, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2143 (s); $\nu(\text{C}=\text{O})$ 2002 (*v_s*), 1968 (*v_s*), 1951 (*v_s*), 1928 (*v_s*); $\nu(\text{C}=\text{O})$ 1736 (s). ^1H NMR (500 MHz, CDCl_3): 3.64, 3.61 (2s, 9 H, 3SCH₂ and CH₃), 1.45 (s, 18 H, 2C(CH₃)₃) ppm. ^{13}C NMR (125 MHz, CDCl_3): 213.53 (C=O), 171.23 (C=O), 158.14 (NC), 57.44 (C(CH₃)₃), 57.16 (OCH₃), 52.19 (NCH₂S), 51.78 (NCH₂), 30.83 (CH₃) ppm.

As shown in **Scheme-I**, treatment of complex **A** with 2 equivalents of *tert*-BuNC in CH_2Cl_2 afforded the title complex in 46 % yield. The title complex **1** was air-stable red solids, which has been characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy.



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

Infrared spectrum: The IR spectrum of **1** showed one absorption band at 2143 cm^{-1} for isocyanide group, one absorption band at 1736 cm^{-1} for ester carbonyls and four absorption bands in the range of 2002-1828 cm^{-1} for the terminal carbonyls and the $\nu(\text{C}=\text{O})$ values are shifted toward lower frequencies relative to the parent complex **A** (2073, 2025, 1994, 1965 cm^{-1})¹³.

¹H NMR spectrum: The ¹H NMR spectrum of **1** displayed two singlets at δ 3.64 and 3.61 ppm for its methylene and methyl protons and a singlet at δ 1.45 ppm for methyl protons of *tert*-Bu.

¹³C NMR spectrum: The ¹³C NMR spectrum of **1** demonstrated a singlet at δ 213.53 ppm for the terminal carbonyls, a singlet at δ 171.23 ppm for ester carbonyl and a singlet at δ 158.14 ppm for isocyanide.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge to the Natural Science Foundations of China (51101138).

REFERENCES

- (a) R. Cammack, *Nature*, **397**, 214 (1999); (b) J.W. Peters, W.N. Lanzilotta, B.J. Lemon and L.C. Seefeldt, *Science*, **282**, 1853 (1998); (c) Y. Nicolet, C. Piras, P. Legrand, C.E. Hatchikian and J.C. Fontecilla-Camps, *Structure*, **7**, 13 (1999).
- A.L. De Lacey, C. Stadler, C. Cavazza, E.C. Hatchikian and V.M. Fernandez, *J. Am. Chem. Soc.*, **122**, 11232 (2000).
- (a) X. Wang, Z. Wei, X. Jiang, J. Zhao and X. Liu, *Inorg. Chim. Acta*, **392**, 112 (2012); (b) Y.N. Feng, F.F. Xu, R.P. Chen, N. Wen, Z.H. Li and S.W. Du, *J. Organomet. Chem.*, **717**, 211 (2012); (c) G. Durgaprasad and S.K. Das, *J. Organomet. Chem.*, **717**, 29 (2012).
- (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) X.F. Liu and H.Q. Gao, *Polyhedron*, **65**, 1 (2013); (d) G. Durgaprasad, R. Bolligarla and S.K. Das, *J. Organomet. Chem.*, **706-707**, 37 (2012); (e) X.F. Liu, *Polyhedron*, **72**, 66 (2014).
- (a) P.H. Zhao, Y.F. Liu, K.K. Xiong and Y.Q. Liu, *J. Clust. Sci.*, **25**, 1061 (2014); (b) X.F. Liu, Z.Q. Jiang and Z.J. Jia, *Polyhedron*, **33**, 166 (2012); (c) W.M. Gao and J.M. Li, *Acta Crystallogr.*, **E68**, m118 (2012).
- (a) L.J. Luo, X.F. Liu and H.Q. Gao, *J. Coord. Chem.*, **66**, 1077 (2013); (b) X.F. Liu, M.Y. Chen and H.Q. Gao, *J. Coord. Chem.*, **67**, 57 (2014).
- (a) Y.L. Li, B. Xie, L.K. Zou, X. Lin and L. Wang, *Chinese J. Struct. Chem.*, **32**, 1105 (2013); (b) Y.L. Li, B. Xie, L.K. Zou, X. Lin and S.S. Zhu, *Z. Anorg. Allg. Chem.*, **639**, 1011 (2013); (c) Y.L. Li, B. Xie, L.K. Zou, X. Lin and S.S. Zhu, *Asian J. Chem.*, **26**, 183 (2014).
- (a) C.G. Li, Y. Zhu, X.X. Jiao and X.Q. Fu, *Polyhedron*, **67**, 416 (2014); (b) B.S. Yin, T.B. Li and M.S. Yang, *J. Coord. Chem.*, **64**, 2066 (2011); (c) X.F. Liu, X.W. Xiao and L.J. Shen, *Transition Met. Chem.*, **36**, 465 (2011).
- (a) X.F. Liu and H.Q. Gao, *J. Clust. Sci.*, **25**, 367 (2014); (b) X.F. Liu and H.Q. Gao, *J. Clust. Sci.*, **25**, 495 (2014).
- (a) X.F. Liu, *J. Organomet. Chem.*, **750**, 117 (2014); (b) X.F. Liu and X.W. Xiao, *J. Organomet. Chem.*, **696**, 2767 (2011); (c) Y.L. Li, B. Xie, L.K. Zou, X. Lin, Y. Yang, S.S. Zhu and T. Wang, *Polyhedron*, **67**, 490 (2014).
- (a) P.H. Zhao, Y.Q. Liu and X.A. Li, *Asian J. Chem.*, **25**, 5428 (2013); (b) M. El-Khateeb, M. Harb, Q. Abu-Salem, H. Görlls and W. Weigand, *Polyhedron*, **61**, 1 (2013); (c) X.F. Liu and B.S. Yin, *J. Coord. Chem.*, **63**, 4061 (2010); (d) X.F. Liu, *Inorg. Chim. Acta*, **378**, 338 (2011).
- Y.L. Li, B. Xie, L.K. Zou, X.L. Zhang and X. Lin, *J. Organomet. Chem.*, **718**, 74 (2012).
- X.F. Liu, X.W. Xiao and L.J. Shen, *J. Coord. Chem.*, **64**, 1023 (2011).