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Synthesis and Structural Characterization of a Novel Carboxy-Functionalized Diiron Dithiolate Complex

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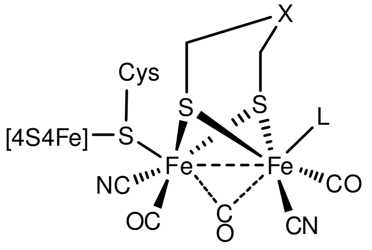
A novel carboxy-functionalized diiron dithiolate complex, $[(\mu\text{-}SCH_2)_2NCH_2CH_2CO_2CH_2CH_2Cl][Fe_2(CO)_6]$ (**I**) as active site model of [FeFe]-hydrogenase, has been successfully synthesized by condensation reaction of $[(\mu\text{-}SCH_2)_2NCH_2CH_2CO_2H][Fe_2(CO)_6]$ (**A**) with $HOCH_2CH_2Cl$ in the presence of 4-dimethylaminopyridine and dicyclohexylcarbodiimide. Its structure was characterized by combustion analysis, ESI-MS, IR and ^1H (^{13}C) NMR spectroscopic techniques.

Key Words: Carboxy-functionalized, Diiron dithiolate, Synthesis, Structural characterization.

INTRODUCTION

Over the last two decades, the diiron dithiolate complexes have received considerable attention, not only because of their interesting chemistry[1] but also due to their close relevance to the active site of [FeFe]-hydrogenase that can efficiently catalyze the production and the uptake of dihydrogen[2]. The crystallographic and theoretical investigations[3,4] have demonstrated that [FeFe]-hydrogenase features a butterfly $2Fe_2S$ subunit as its active site (**Scheme-I**). In the active site, the iron centers are coordinated by carbon monoxide, cyanide ligands and by a bridging dithiolate ligand between the two iron centers, one of which is coordinated by a cysteinyl-S-linked cubic $4Fe_4S$ cluster (**Scheme-I**). Further studies have revealed that the bridging dithiolate in the H-cluster could be supposed to be propanedithiolate ($SCH_2CH_2CH_2S$, namely, pdt)[5], azadithiolate (SCH_2NCH_2S, namely, adt)[6] and oxadithiolate (SCH_2OCH_2S, namely, odt)[7] (**Scheme-I**).



(L = H_2O, CO, or vacant; X = C, N, or O)

Scheme-I: Proposed active site of [FeFe]-hydrogenase

The above-mentioned information provoked chemists to design and prepare a range of diiron dithiolate complexes[8] in order to better mimic the active site of [FeFe]-hydrogenase. Åkermark and co-workers[9] prepared the carboxy-containing adt-diiron dithiolate complexes $[(\mu\text{-}SCH_2)_2NCH_2CH_2CO_2H][Fe_2(CO)_6]$ and $[(\mu\text{-}SCH_2)_2NCH_2CH_2CO_2H][Fe_2(CO)_4(PMe_3)_2]$, which are regarded as active site models of [FeFe]-hydrogenase.

In order to extend this study on such model complex, we herein report the synthesis and structural characterization of a new carboxy-functionalized diiron dithiolate complex $[(\mu\text{-}SCH_2)_2NCH_2CH_2CO_2CH_2CH_2Cl][Fe_2(CO)_6]$ (**I**) related to the active site of [FeFe]-hydrogenase.

EXPERIMENTAL

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 N_2. Dicyclohexylcarbodiimide (DCC), 4-dimethylamino pyridine (DMAP), $HOCH_2CH_2Cl$ and other materials were commercially available and used as received. $[(\mu\text{-}SCH_2)_2NCH_2CH_2CO_2H][Fe_2(CO)_6]$ (**A**) was prepared according to the literature procedures[9]. Preparative TLC was carried out on glass plates (25 cm × 20 cm × 0.25 cm) coated with silica gel H (10-40 mm). IR spectra were recorded on a Nicolet 670 FTIR spectrometer. ^1H (^{13}C) NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer. Mass spectrometric studies (ESI-MS) were carried out on Finnigan

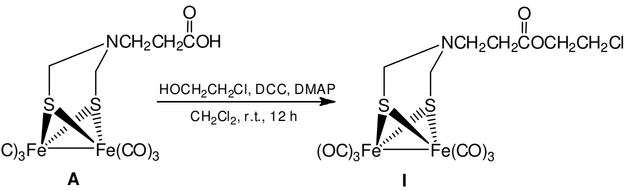
LCQ-Advantage spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer.

Synthetic procedure: The CH_2Cl_2 (20 mL) solution of $[(\mu\text{-}SCH_2)_2NCH_2CH_2CO_2H][Fe_2(CO)_6]$ (**A**) (0.458 g, 1.0 mmol), DCC (0.206 g, 1.0 mmol) and 4-dimethylamino pyridine (0.013 g, 0.1 mmol) was stirred at room temperature for 5 min. To this mixture $HOCH_2CH_2Cl$ (0.1 mL, 1.5 mmol) was added and the new mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was subjected to preparative TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:2) as eluent. From the main red band, the title complex (**I**) (0.209 g, 40 %) was obtained as a red oil. Anal. calcd (%) for $C_{13}H_{12}NO_8S_2ClFe_2$: C 29.94, H 2.32, N 2.69; found (%): C 29.68, H 2.52, N 2.71. ESI-MS (CH_2Cl_2, positive mode): m/z = 521.8 $[M + H]^+$ (calcd. (%) for 521.8); IR (KBr disk, cm^{-1}): $\nu_{C\equiv O}$ 2073 (vs), 2030 (vs), 1992 (vs); $\nu_{C(O)O}$ 1735 (s). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 4.30 (s, 2H, OCH_2), 3.66 (s, 2H, CH_2Cl), 3.58 (s, 4H, $2NCH_2S$), 3.04 (s, 2H, NCH_2), 2.36 (s, 2H, $CH_2C(O)$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, TMS): δ = 207.7 (FeCO), 171.2 (C(O)O), 64.3 (OCH_2), 52.7 (NCH_2S), 52.2 (NCH_2), 41.5 (CH_2Cl), 33.0 ($CH_2C(O)$) ppm.

RESULTS AND DISCUSSION

As shown in **Scheme-II**, the treatment of the starting material $[(\mu\text{-}SCH_2)_2NCH_2CH_2CO_2H][Fe_2(CO)_6]$ (**A**) with 0.1 equiv. 4-dimethylaminopyridine in the presence of dicyclohexylcarbodiimide as a dehydrating agent in CH_2CH_2 followed by addition of 1.5 equiv. $HOCH_2CH_2Cl$, afforded the title complex (**I**) in the yield of 40 %.

The title complex (**I**) was stable in air and soluble in most organic solvents such as dichloromethane, acetone and ethyl acetate, *etc*. Its molecular structure was fully characterized by satisfactory ESI-MS, IR, ^1H NMR, ^{13}C NMR spectroscopy and elemental analysis.



Scheme-II: Synthetic route of the title complex (**I**)

Mass spectrum: As displayed in Fig. 1, the positive mode ESI-MS spectrum of (**I**) gave the quasimolecular ion peak $[M + H]^+$ at m/z 521.8, which is in good agreement with its molecular formula of $C_{13}H_{12}ClFe_2NO_8S_2$.

Infrared spectrum: The IR spectrum of (**I**) in KBr displayed three strong absorption bands in the range of 2076-1992 cm^{-1} for the terminal carbonyls coordinated to iron atom. Especially, its IR data is very similar to that of the parent complex $[(\mu\text{-}SCH_2)_2NCH_2CH_2CO_2H][Fe_2(CO)_6]$ (**A**)[9] with exception of the disappearance of the 1709 cm^{-1} for (**A**) and the appearance of one new band 1735 cm^{-1} for (**I**), indicating that the carboxyl group was converted to the ester carbonyl functionality (Table-1).

TABLE-1
IR DATA OF THE TITLE COMPLEX (**I**) (IN KBr) AND THE PARENT COMPLEX (**A**) FOR COMPARISON

Complex	ν(CO)Fe (cm^{-1})	ν(C=O) (cm^{-1})
I	2073 (vs), 2030 (vs), 1992 (vs)	1735 (m)
A[a]	2073 (m), 2029 (s), 1991 (s)	1709 (m)

[a]Spectrum recorded in CH_2Cl_2

^1H (^{13}C) NMR spectrum: The ^1H NMR spectrum of (**I**) exhibited two singlets at δ 4.30 and 3.66 ppm assigned to the methylene protons, which was consistent with two carbon signals at δ 64.3 and 41.5 ppm for the respective oxygen- and chloride-bearing carbon atoms in the ^{13}C NMR spectrum,

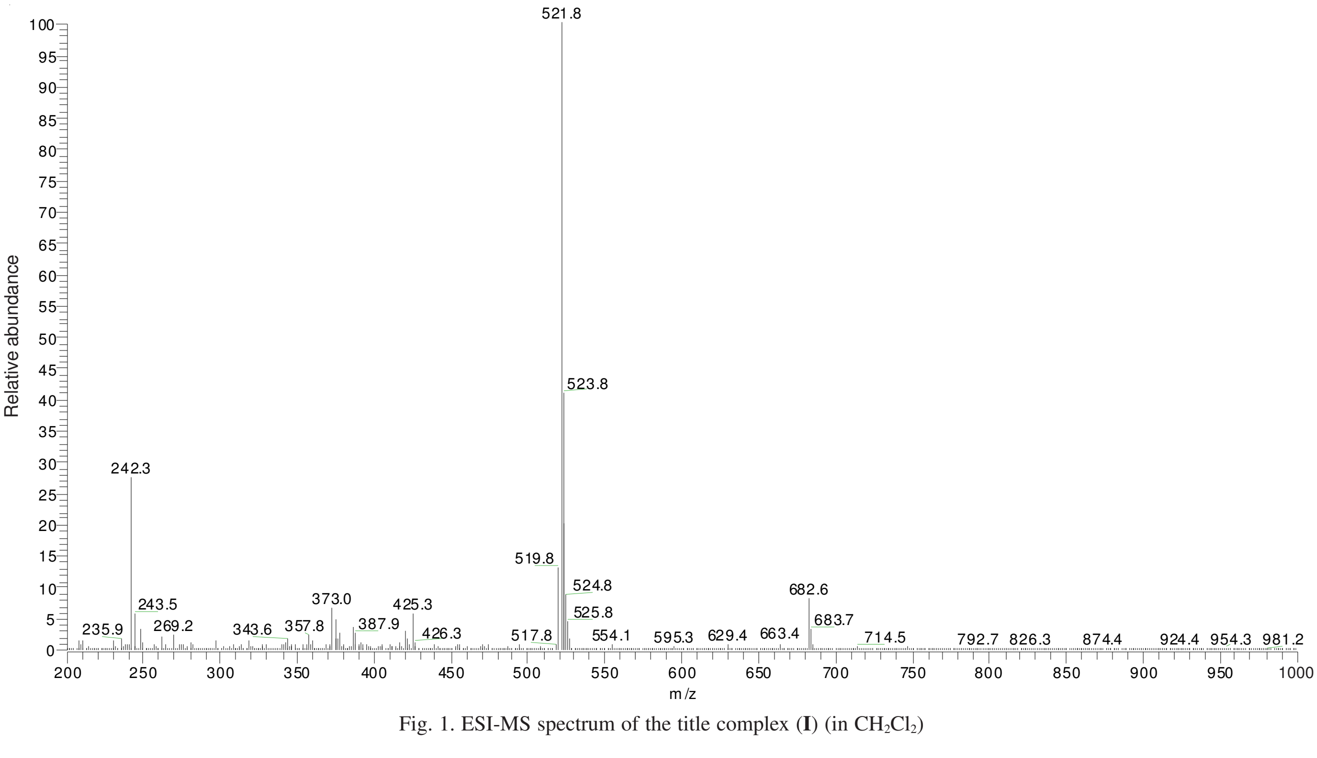


Fig. 1. ESI-MS spectrum of the title complex (**I**) (in CH_2Cl_2)

showing the appearance of the OCH_2CH_2Cl group. Meanwhile, because of the quick conversion of the iron dithiacyclohexane ring, its ^1H NMR spectrum displayed only one singlet at δ 3.58 ppm for four equivalently methylene protons, which was in accordance with one carbon signal at δ 52.7 ppm ascribed to nitrogen-containing carbon atoms in the ^{13}C NMR, demonstrating the existing of the azadithiolate unit (namely, the $-SCH_2NCH_2S-$ group). In addition, the ^{13}C NMR spectrum of (**I**) showed one downfield carbon signal at δ 207.7 ppm for the coordinated carbonyl carbon atoms linked to the iron atoms. Particularly, there was one typical ester carbonyl carbon signal at δ 171.2 cm^{-1} in ^{13}C NMR spectrum, further confirming that the carboxyl group of the parent complex (**A**) was transformed into the ester carbonyl group of the title complex (**I**) *via* the condensation reaction.

Conclusion

To better mimic the active site of [FeFe]-hydrogenase, we successfully synthesized a novel carboxy-functionalized diiron dithiolate complex $[(\mu\text{-}SCH_2)_2NCH_2CH_2CO_2CH_2CH_2Cl][Fe_2(CO)_6]$ (**I**) from (**A**) and $HOCH_2CH_2Cl$. The new model complex (**I**) was structurally characterized by various spectroscopic techniques including ESI-MS, FT-IR, ^1H NMR as well as ^{13}C NMR.

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REFERENCES

1. (a) H. Ogino, S. Inomata and H. Tobita, *Chem. Rev.*, **98**, 2093 (1998); (b) L.C. Song, *Trends Organomet. Chem.*, **3**, 1 (1999); (c) L.C. Song, *Acc. Chem. Res.*, **38**, 21 (2005); (d) L.C. Song, P.H. Zhao, Z.Q. Du, M.Y. Tang and Q.M. Hu, *Organometallics*, **29**, 5751 (2010).
2. (a) M. Stephenson and L.H. Stickland, *Biochem. J.*, **25**, 205 (1931); (b) R. Cammack, *Nature*, **397**, 214 (1999); (c) M.Y. Darensbourg, E.J. Lyon and J.J. Smee, *Coord. Chem. Rev.*, **206-207**, 533 (2000); (d) J.F. Capon, F. Gloaguen, P. Schollhammer and J. Talarmin, *Coord. Chem. Rev.*, **249**, 1664 (2005); (e) J.C. Fontecilla-Camps, A. Volbeda, C. Cavazza and Y. Nicolet, *Chem. Rev.*, **107**, 4273 (2007).
3. J.W. Peters, W.N. Lanzilotta, B.J. Lemon and L.C. Seefeldt, *Science*, **282**, 1853 (1998).
4. Y. Nicolet, C. Piras, P. Legrand, C.E. Hatchikian and J.C. Fontecilla-Camps, *Structure*, **7**, 13 (1999).
5. A. Le Cloirec, S.P. Best, S.C. Davies, D.J. Evans, D.L. Hughes and C.J. Pickett, *Chem. Commun.*, 2285 (1999).
6. H. Fan and M.B. Hall, *J. Am. Chem. Soc.*, **123**, 3828 (2001).
7. Y. Nicolet, B.J. Lemon, J.C. Fontecilla-Camps and J.W. Peters, *Trends Biochem. Sci.*, **25**, 138 (2000).
8. (a) C. Tard and C.J. Pickett, *Chem. Rev.*, **109**, 2245 (2009); (b) F. Gloaguen and T.B. Rauchfuss, *Chem. Soc. Rev.*, **38**, 100 (2009); (c) M.H. Harb, U.P. Apfel, T. Sakamoto, M. EI-khateeb and W. Weigand, *Eur. J. Inorg. Chem.*, 986 (2011); (d) M.Y. Darensbourg and W. Weigand, *Eur. J. Inorg. Chem.*, 994 (2011); (e) X.F. Liu and Y.B. Shao, *J. Coord. Chem.*, **63**, 4061 (2010); (f) X.F. Liu, X.W. Xiao and L.J. Shen, *J. Coord. Chem.*, **64**, 1023 (2011); (g) B.S. Yin, T.B. Li and M.S. Yang, *J. Coord. Chem.*, **64**, 2066 (2011).
9. W.M. Gao, J.L. Sun, T. Åkermark, M.R Li, L. Eriksson, L. Sun and B. Åkermark, *Chem. Eur. J.*, **16**, 2537 (2010).