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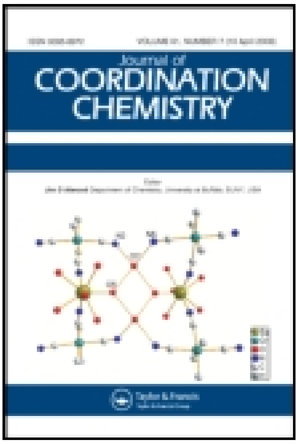

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, characterization, and crystal structures of N-functionalized diiron azadithiolate complexes related to the active site of [FeFe]-hydrogenases

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Published online: 07 Mar 2011.

To cite this article: Xu-Feng Liu , Xun-Wen Xiao & Liang-Jun Shen (2011) Synthesis, characterization, and crystal structures of N-functionalized diiron azadithiolate complexes related to the active site of [FeFe]-hydrogenases, Journal of Coordination Chemistry, 64:6, 1023-1031, DOI: 10.1080/00958972.2011.561838

To link to this article: http://dx.doi.org/10.1080/00958972.2011.561838

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Journal of Coordination Chemistry
Vol. 64, No. 6, 20 March 2011, 1023–1031

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Synthesis, characterization, and crystal structures of N-functionalized diiron azadithiolate complexes related to the active site of [FeFe]-hydrogenases

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(*Received 17 November 2010; in final form 23 December 2010*)

A series of N-functionalized diiron azadithiolate complexes, $[(\mu\text{-}SCH_2)_2NCH_2CO_2Me]Fe_2(CO)_5L$ [L = CO (**1**); PPh_3 (**2**); $Ph_2PCH_2PPh_2$ (**3**)], as active site models of [FeFe]-hydrogenases has been prepared and characterized. While **1** was prepared by a sequential reaction of $(\mu\text{-}HS)_2Fe_2(CO)_6$ with two equiv. of aqueous HCHO, followed by treatment of $(\mu\text{-}HOCH_2S)_2Fe_2(CO)_6$ with one equiv. of $H_2NCH_2CO_2Me$ in 46% yield; **2** and **3** were prepared by a carbonyl substitution reaction of **1** with PPh_3 or $Ph_2PCH_2PPh_2$ in the presence of $Me_3NO \cdot 2H_2O$ in 90% and 85% yields, respectively. The crystal structures of **1** and **2** revealed that the substituent attached to the bridgehead nitrogen occupies an equatorial position and the PPh_3 ligand resides in an axial position of the square pyramid of Fe2.

Keywords: Diiron azadithiolate; [FeFe]-hydrogenases; Synthesis; Crystal structure

1. Introduction

[FeFe]-hydrogenases are a class of natural enzymes that catalyze the production and consumption of hydrogen gas in several microorganisms [1–3]. X-ray crystallography [4, 5] revealed that the active site of [FeFe]-hydrogenases (so called H-cluster) contains a butterfly [2Fe2S] cluster with one of its irons connected to a cubane-like [4Fe4S] cluster *via* the sulfur of a cysteinyl ligand (scheme 1). The bridging dithiolate was supposed to be propanedithiolate ($SCH_2CH_2CH_2S$) [6], azadithiolate (SCH_2NCH_2S) [7], or oxadithiolate (SCH_2OCH_2S) [8]. Based on structural information, a great number of [FeFe]-hydrogenase model complexes were prepared and characterized [9–14]. We report herein synthesis, characterization, and crystal structures of N-functionalized diiron azadithiolate complexes $[(\mu\text{-}SCH_2)_2NCH_2CO_2Me]Fe_2(CO)_5L$ [L = CO (**1**); PPh_3 (**2**); $Ph_2PCH_2PPh_2$ (**3**)] related to the active site of [FeFe]-hydrogenases.

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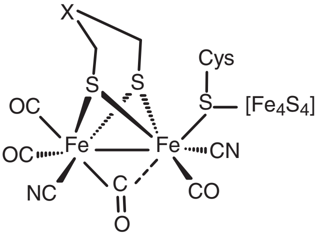
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.561838



Scheme 1. H-cluster structure of [FeFe]-hydrogenases, X = CH_2, NH, or O.

2. Experimental

2.1. *Materials and methods*

All reactions were performed using standard Schlenk and vacuum-line techniques under N_2. Acetonitrile was distilled over CaH_2 under N_2. Tetrahydrofuran was distilled from Na/benzophenone ketyl under N_2. $H_2NCH_2CO_2Me \cdot HCl$, $Me_3NO \cdot 2H_2O$, $Ph_2PCH_2PPh_2$, Et_3BHLi (1 mol L^{-1} in THF), and other materials were available commercially and used as received. (μ-S_2)$Fe_2(CO)_6$ [15] was prepared according to literature procedures. IR spectra were recorded on a Nicolet MAGNA 560 FTIR spectrometer. ^1H (^{31}P, ^{13}C) NMR spectra were obtained on a Bruker Avance 300 or 500 MHz spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer.

2.2. *Synthesis of [(μ-SCH$_2$)$_2$NCH$_2$CO$_2$Me]Fe$_2$(CO)$_6$ (1)*

A solution of (μ-S_2)$Fe_2(CO)_6$ (0.344 g, 1 mmol) in THF (15 mL) was cooled to −78°C and then Et_3BHLi (2 mL, 2 mmol) was slowly added to give a green solution. After stirring for 15 min, CF_3CO_2H (0.16 mL, 2 mmol) was added to give a red solution. The mixture was stirred at −78°C for 10 min and then 37% aqueous HCHO (0.17 mL, 2 mmol) was added. The new mixture was allowed to warm to room temperature and stirred for 1 h. A solution of $H_2NCH_2CO_2Me \cdot HCl$ (0.126 g, 1 mmol) and Et_3N (0.14 mL, 1 mmol) in THF (10 mL) was added and the new mixture was stirred for an additional 5 h. The solvent was removed *in vacuo* and the residue was subjected to TLC using CH_2Cl_2/petroleum ether (v/v = 1 : 1) as eluent. Collecting the main red band afforded **1** (0.212 g, 46%) as a red solid. Anal. Calcd for $C_{11}H_9Fe_2NO_8S_2$ (%): C, 28.78; H, 1.98; N, 3.05. Found (%): C, 28.61; H, 2.05; N, 3.03. IR (KBr disk, cm^{-1}): $\nu_{C\equiv O}$ 2073 (vs), 2025 (vs), 1994 (vs), 1965 (vs); $\nu_{C=O}$ 1732. ^1H NMR (300 MHz, $CDCl_3$): 3.67 (s, 3H, CH_3), 3.54 (s, 4H, $2NCH_2S$), 3.45 (s, 2H, NCH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): 207.69 ($C\equiv O$), 162.33 (C=O), 58.88 (CH_3), 52.82 (NCH_2S), 51.91 (NCH_2) ppm.

2.3. *Synthesis of [(μ-SCH$_2$)$_2$NCH$_2$CO$_2$Me]Fe$_2$(CO)$_5$(PPh$_3$) (2)*

To a solution of [(μ-SCH_2)$_2$$NCH_2CO_2Me$]$Fe_2(CO)_6$ (0.100 g, 0.22 mmol) in CH_3CN (10 mL) was added a solution of $Me_3NO \cdot 2H_2O$ (0.024 g, 0.22 mmol) in CH_3CN (5 mL). The mixture was stirred at room temperature for 15 min and then PPh_3 (0.058 g, 0.22 mmol) was added. 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 0.137 g (90%) of **2** as a red solid. Anal. Calcd for $C_{28}H_{24}Fe_2NO_7PS_2$ (%): C, 48.51; H, 3.49; N, 2.02. Found (%): C, 48.68; H, 3.65; N, 1.88. IR (KBr disk, cm^{-1}): $\nu_{C\equiv O}$ 2043 (vs), 1978 (vs), 1930 (vs); $\nu_{C=O}$ 1737 (m). ^1H NMR (300 MHz, $CDCl_3$): 7.54–7.26 (m, 15H, $3C_6H_5$), 3.37–3.35 (m, $2H_e$), 2.90 (d, $J_{HeHa} = 8.7$ Hz, $2H_a$), 2.58 (s, 3H, CH_3), 2.34 (s, 2H, CH_2) ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): 59.86 (s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 213.46, 213.38, 209.61 (C≡O), 170.23 (C=O), 136.18, 135.86, 133.46, 133.37, 130.06, 128.49, 128.42 (Ph), 59.58 (CH_3), 51.45, 50.77 (CH_2) ppm.

2.4. *Synthesis of [(μ-SCH2)2NCH2CO2Me]Fe2(CO)5(Ph2PCH2PPh2) (3)*

The procedure was similar to that of **2** except $Ph_2PCH_2PPh_2$ (0.084 g, 0.22 mmol) was used instead of PPh_3; 0.151 g (85%) of **3** was obtained as a red solid. Anal. Calcd for $C_{35}H_{31}Fe_2NO_7P_2S_2$ (%): C, 51.56; H, 3.83; N, 1.72. Found (%): C, 51.30; H, 4.09; N, 1.84. IR (KBr disk, cm^{-1}): $\nu_{C\equiv O}$ 2043 (vs), 1979 (vs), 1927 (vs); $\nu_{C=O}$ 1739 (m). ^1H NMR (500 MHz, $CDCl_3$): 7.65–7.17 (m, 20H, $4C_6H_5$), 3.59 (s, 3H, CH_3), 3.30 (d, $J_{HeHa} = 8.0$ Hz, $2H_e$), 3.09–3.05 (m, 4H, $2CH_2$), 2.85 (d, $J_{HeHa} = 10.0$ Hz, $2H_a$) ppm. ^{31}P NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): 56.41 (d, $J_{p\text{–}p} = 90.2$ Hz), −26.18 (d, $J_{p\text{–}p} = 90.6$Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 214.56, 214.46, 209.68 (C≡O), 170.25 (C=O), 138.54, 138.48, 138.42, 138.36, 132.92, 132.76, 132.66, 132.57, 130.01, 128.62, 128.42, 128.36, 128.22, 128.15 (Ph), 59.41 (CH_3), 51.60, 51.29 ($4CH_2$) ppm.

2.5. *X-ray structure determination*

Single crystals of **1** and **2** suitable for X-ray diffraction analysis were grown by slow evaporation of CH_2Cl_2/hexane solution at 4°C. A single crystal of **1** was mounted on a Rigaku SCX-mini CCD diffractometer. Data were collected at room temperature by using a graphite monochromator with Mo-Kα radiation ($\lambda = 0.71073$ Å) in the ω–ϕ scanning mode. Absorption correction was performed by SADABS program [16]. A single crystal of **2** was mounted on a Rigaku MM-007 CCD diffractometer equipped with a Saturn 70CCD. Data were collected at 113(2) K by using a graphite monochromator with Mo-Kα radiation ($\lambda = 0.71073$ Å) in the ω–ϕ scanning mode. Data collection, reduction, and absorption correction were performed by CRYSTALCLEAR program [17]. The structures were solved by direct methods using SHELXS-97 [18] and refined by full-matrix least-squares techniques (SHELXL-97) [19] on F^2. Hydrogens were located using the geometric method. Details of crystal data, data collections, and structure refinement are summarized in table 1.

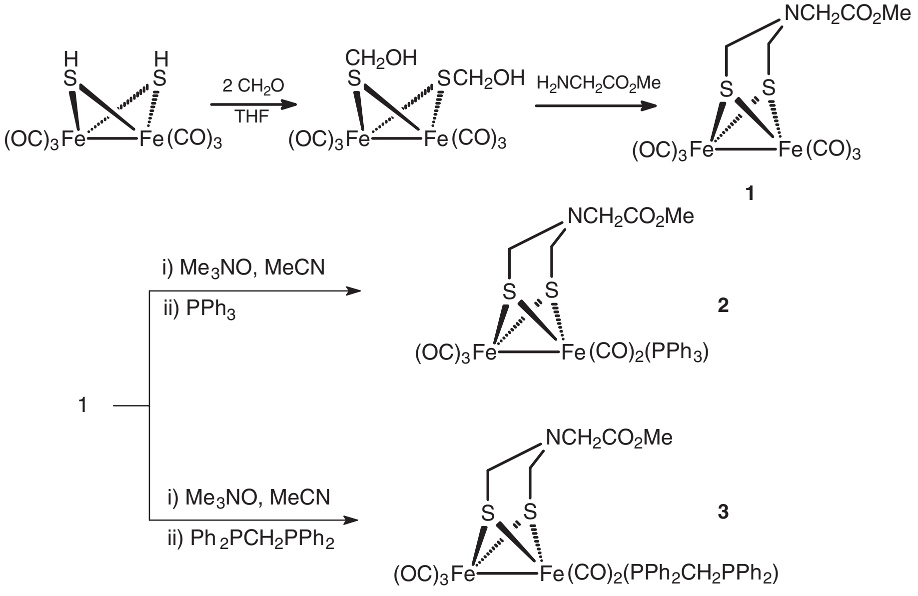
3. Results and discussion

3.1. *Synthesis and characterization*

Synthetic methods for **1–3** are shown in scheme 2. We prepared **1** by a condensation reaction of $(\mu\text{-HS})_2Fe_2(CO)_6$ [20] (generated *in situ* from $(\mu\text{-S}_2)Fe_2(CO)_6$ and S–S bond

Table 1. Crystal data and structure refinements details for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{11}H_9Fe_2NO_8S_2$	$C_{28}H_{24}Fe_2NO_7PS_2$
Formula weight	459.03	693.27
Temperature (K)	293(2)	113(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	14.043(3)	10.881(2)
b	9.0810(18)	11.247(2)
c	13.253(3)	13.720(3)
α	90	99.26(3)
β	97.14(3)	109.69(3)
γ	90	104.80(3)
Volume (Å^3), Z	1677.0(6), 4	1471.0(5), 2
Calculated density (g cm^{-3})	1.818	1.565
Absorption coefficient, μ (mm^{-1})	2.017	1.229
F(000)	920	708
Crystal size (mm^3)	$0.29 \times 0.26 \times 0.21$	$0.20 \times 0.18 \times 0.12$
θ range for data collection (°)	3.00–25.00	1.64–25.02
Limiting indices	$-16 \le h \le 16$; $-10 \le k \le 10$; $-15 \le l \le 15$	$-12 \le h \le 12$; $-13 \le k \le 13$; $-16 \le l \le 16$
Reflections collected	13,248	15,264
Independent reflection	2947 [R(int) = 0.0904]	5186 [R(int) = 0.0505]
Completeness to θ_{max} (%)	99.8	99.9
Data/restraints/parameters	2947/0/218	5186/0/372
Goodness-of-fit on F^2	1.220	1.024
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0742$; $wR_2 = 0.0946$	$R_1 = 0.0422$; $wR_2 = 0.0872$
R indices (all data)	$R_1 = 0.1080$; $wR_2 = 0.1023$	$R_1 = 0.0586$; $wR_2 = 0.0949$
Largest difference peak and hole (e Å^{-3})	0.419 and −0.354	0.379 and −0.360



Scheme 2. Preparation of **1**–**3**.

cleavaging agent Et_3BHLi, followed by treatment of the resulting dianion $(\mu\text{-LiS})_2Fe_2(CO)_6$ with CF_3COOH) with two equiv. of 37% aqueous HCHO, followed by treatment of the intermediate $(\mu\text{-HOCH}_2S)_2Fe_2(CO)_6$ with one equiv. of $H_2NCH_2CO_2Me$ in 46% yield [21]. Complexes **2** and **3** could be prepared by carbonyl substitution of **1** with PPh_3 or $Ph_2PCH_2PPh_2$ in the presence of the decarbonylating agent $Me_3NO \cdot 2H_2O$ in 90% and 85% yields, respectively.

Complexes **1**–**3** have been characterized by elemental analysis, IR, and NMR spectroscopic techniques. For example, IR spectra of **1**–**3** showed three to four absorption bands around $2000\,cm^{-1}$ for their terminal carbonyls and one absorption band in the range $1739-1732\,cm^{-1}$ for their ester carbonyls; the $\nu_{C\equiv O}$ values of **2** and **3** are markedly shifted to lower frequencies relative to **1**. The ^1H NMR spectra of **1** displayed a singlet at δ 3.54 ppm for NCH_2S, whereas **2** and **3** exhibited a multiplet and a doublet or two doublets for their NCH_2S groups at a relatively high field [22]. The ^{31}P NMR spectra of **2** showed a singlet at δ 59.86 ppm for PPh_3 coordinated to one Fe of the diiron subsite and **3** displayed two doublets at δ 56.41 and −26.18 ppm with coupling constants $J_{p-p} = 90.2$ and 90.6 Hz for only one phosphorus of $Ph_2PCH_2PPh_2$ coordinated to one Fe of the [2Fe2S] cluster [23]. ^{13}C NMR spectra of **1** have a singlet at δ 207.69 ppm for its terminal carbonyls, whereas **2** and **3** exhibited a doublet at about δ 214 ppm and a singlet at about δ 209 ppm for their terminal carbonyls.

3.2. *X-ray crystal structures*

The molecular structures of **1** and **2** have been determined by X-ray crystal diffraction analysis. ORTEP and crystal packing diagrams of **1** and **2** are shown in figures 1–4 and selected bond lengths and angles are given in tables 2 and 3, respectively. Both **1** and **2** contain two fused six-membered rings, in which one six-membered ring (N1C7S2Fe2S1C8 for **1** and N1C6S1Fe1S2C7 for **2**) has a chair conformation and the other six-membered ring (N1C7S2Fe1S1C8 for **1** and N1C6S1Fe2S2C7 for **2**) has a boat conformation. The substituent attached to the bridgehead N1 of **1** and **2** lies in an equatorial position and the unpaired electrons of nitrogen lie in an axial position which is consistent with corresponding diiron azadithiolate complexes such as $[(\mu\text{-SCH}_2)_2NCH_2CO_2Et]Fe_2(CO)_6$ [24]. The sum of the C–N–C angles around nitrogen is 349.8° for **1** and 341.2° for **2**, which means there is no p–π conjugation between the substituent group and the p-orbital of nitrogen [24].

Complex **1** contains a butterfly [2Fe2S] with six carbonyls and one azapropanedithiolate, whereas **2** has five carbonyls and one PPh_3. The PPh_3 attached to Fe2 in **2** occupies an axial position of the square-pyramidal geometry, in accord with previously reported [FeFe]-hydrogenase models substituted by monophosphine ligands such as $[Fe_2(CO)_5(PPh_3)(\mu\text{-adt})C_6H_4I\text{-}4]$ [25], $[Fe_2(CO)_5(PPh_3)(\mu\text{-adt})C_6H_4C{\equiv}CNO_2\text{-}4]$ [25], and $[Fe_2(CO)_5(Me_2NCH_2PPh_2)(\mu\text{-adt})]$ [26].

The Fe1–Fe2 bond length of **2** [2.5176(13) Å] is longer than that of **1** [2.4986(12) Å] and all carbonyl diiron azadithiolate complexes such as $[(\mu\text{-SCH}_2)_2NCH_2CO_2Et]Fe_2(CO)_6$ [2.5089(10) Å] [24], $[(\mu\text{-SCH}_2)_2NC_6H_4C(O)Me\text{-}p]Fe_2(CO)_6$ [2.4950(9) Å] [24], and $[(\mu\text{-SCH}_2)_2NC_6H_4CO_2Me\text{-}p]Fe_2(CO)_6$ [2.5065(9) Å] [24] but shorter than those in crystal structures of natural enzymes from *Clostridium pasteurianum* and *Desulfovibrio desulfuricans* (2.55−2.62 Å) [4, 5]. The average Fe–S bond length of **2** (2.2548 Å) is slightly longer than that of **1** (2.2435 Å). Furthermore, the Fe–S–Fe angles of **2**

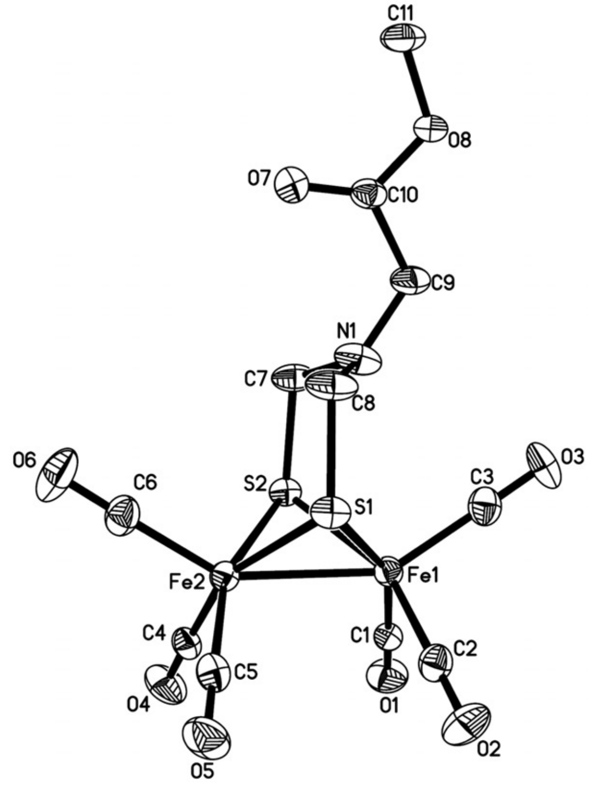


Figure 1. ORTEP view of **1** with 30% probability level ellipsoids (hydrogens are omitted for clarity).

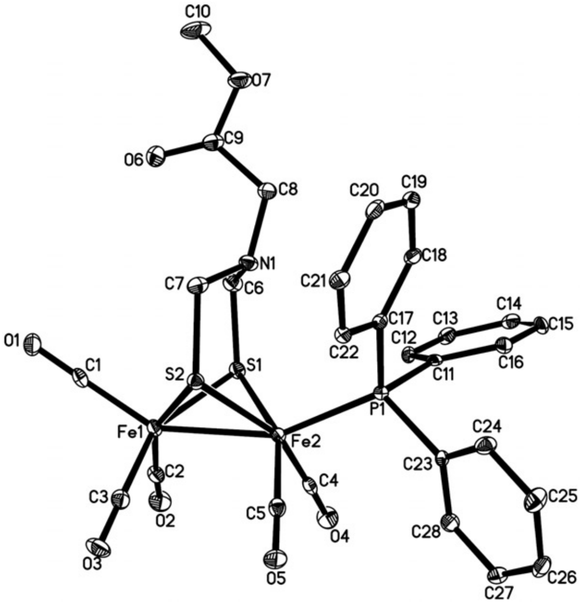


Figure 2. ORTEP view of **2** with 30% probability level ellipsoids (hydrogens are omitted for clarity).

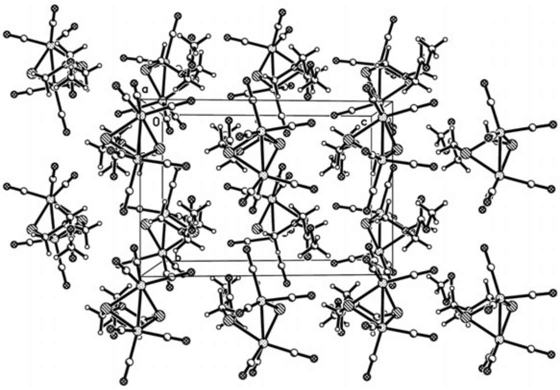


Figure 3. Crystal packing diagram of **1** along the *a*-axis.

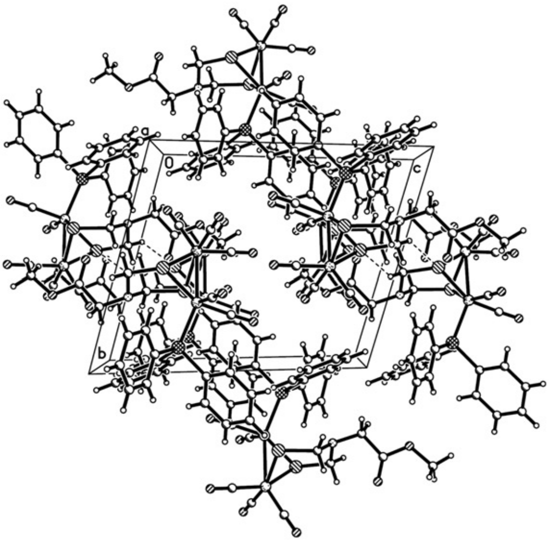


Figure 4. Crystal packing diagram of **2** along the *a*-axis.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Fe(1)–S(1)	2.2445(17)	Fe(2)–S(1)	2.2457(18)
Fe(1)–S(2)	2.2492(16)	C(7)–N(1)	1.431(7)
Fe(1)–Fe(2)	2.4986(12)	C(8)–N(1)	1.422(7)
Fe(2)–S(2)	2.2347(17)	C(9)–N(1)	1.426(7)
C(7)–S(2)	1.829(6)	C(11)–O(8)	1.430(6)
C(8)–S(1)	1.824(6)	C(9)–C(10)	1.515(8)
C(10)–O(7)	1.177(7)	C(10)–O(8)	1.320(7)
Fe(1)–S(1)–Fe(2)	67.62(5)	S(2)–Fe(2)–Fe(1)	56.41(4)
Fe(2)–S(2)–Fe(1)	67.73(5)	C(8)–N(1)–C(9)	117.2(5)
S(2)–Fe(1)–Fe(2)	55.86(5)	C(8)–N(1)–C(7)	113.9(5)
S(2)–Fe(2)–S(1)	85.22(6)	C(9)–N(1)–C(7)	118.7(5)
N(1)–C(7)–S(2)	113.0(4)	N(1)–C(8)–S(1)	113.5(4)
N(1)–C(9)–C(10)	115.1(5)	O(7)–C(10)–O(8)	125.9(6)
O(7)–C(10)–C(9)	125.2(6)	O(8)–C(10)–C(9)	108.9(5)

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Fe(1)–S(1)	2.2480(11)	Fe(2)–S(2)	2.2589(12)
Fe(1)–S(2)	2.2542(10)	N(1)–C(6)	1.440(4)
Fe(1)–Fe(2)	2.5176(13)	N(1)–C(7)	1.446(4)
Fe(2)–S(1)	2.2581(13)	N(1)–C(8)	1.455(4)
S(1)–C(6)	1.821(3)	S(2)–C(7)	1.833(3)
P(1)–C(17)	1.828(3)	P(1)–C(11)	1.830(3)
P(1)–C(23)	1.840(3)	O(6)–C(9)	1.205(4)
O(7)–C(9)	1.342(4)	O(7)–C(10)	1.449(4)
Fe(1)–S(1)–Fe(2)	67.93(4)	S(2)–Fe(2)–Fe(1)	56.01(4)
Fe(1)–S(2)–Fe(2)	67.81(4)	C(6)–N(1)–C(7)	114.2(3)
S(2)–Fe(1)–Fe(2)	56.18(3)	C(6)–N(1)–C(8)	112.7(3)
S(1)–Fe(2)–Fe(1)	55.84(4)	C(7)–N(1)–C(8)	114.3(3)
C(17)–P(1)–C(11)	104.92(14)	C(17)–P(1)–C(23)	101.42(14)
C(11)–P(1)–C(23)	100.76(14)	C(9)–O(7)–C(10)	115.9(3)
N(1)–C(6)–S(1)	114.6(2)	N(1)–C(7)–S(2)	114.6(2)
N(1)–C(8)–C(9)	115.7(3)	O(6)–C(9)–O(7)	124.1(3)
O(6)–C(9)–C(8)	126.5(3)	O(7)–C(9)–C(8)	109.4(3)

[Fe1–S1–Fe2 = 67.93(4)° and Fe1–S2–Fe2 = 67.81(4)°] are very close to those in **1** [Fe1–S1–Fe2 = 67.62(5)° and Fe2–S2–Fe1 = 67.73(5)°].

Crystal packing diagrams of **1** and **2** are shown in figures 3 and 4; van der Waals' interactions stabilize the solid-state structure.

4. Conclusions

A series of [FeFe]-hydrogenase model complexes has been prepared by condensation and substitution reactions and fully characterized. Furthermore, the structures of **1** and **2** were determined by X-ray crystallography.

Supplementary material

CCDC 800424 (**1**) and 800425 (**2**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the start-up foundation of Ningbo University of Technology, the National Natural Science Foundation of China (20902051), Foundation of the Education Committee of Zhejiang Province (Z200906833), and Ningbo Natural Science Foundation (2010A610186).

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