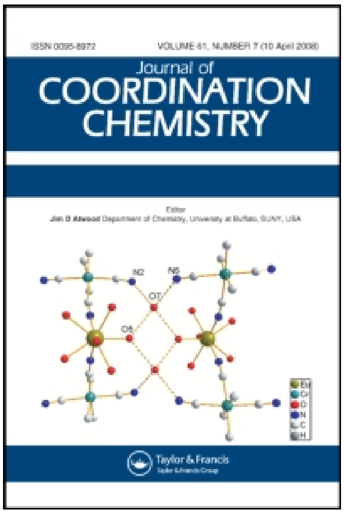


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation, characterization and electrochemistry of an iron-only hydrogenase active site model covalently linked to a ruthenium tris(bipyridine) photosensitizer

Hongguang Cui[a]; Mei Wang[a]; Lele Duan[a]; Licheng Sun[ab]
[a] State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology, Dalian 116012, P. R. China [b] Organic Chemistry, Royal KTH Chemical Science and Engineering, 10044, Stockholm, Sweden

To cite this Article Cui, Hongguang , Wang, Mei , Duan, Lele and Sun, Licheng(2008) 'Preparation, characterization and electrochemistry of an iron-only hydrogenase active site model covalently linked to a ruthenium tris(bipyridine) photosensitizer', Journal of Coordination Chemistry, 61: 12, 1856 — 1861

To link to this Article: DOI: 10.1080/00958970701767002

URL: http://dx.doi.org/10.1080/00958970701767002

Journal of Coordination Chemistry
Vol. 61, No. 12, 20 June 2008, 1856–1861

Preparation, characterization and electrochemistry of an iron-only hydrogenase active site model covalently linked to a ruthenium tris(bipyridine) photosensitizer

HONGGUANG CUI†, MEI WANG*†, LELE DUAN† and LICHENG SUN†‡

†State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research
Center on Molecular Devices, Dalian University of Technology,
Dalian 116012, P. R. China
‡Organic Chemistry, Royal KTH Chemical Science and Engineering,
10044, Stockholm, Sweden

(*Received 5 April 2007; in final form 13 June 2007*)

An NH_2-functionlized [Fe_2S_2] model complex of the iron-only hydrogenase active site was covalently linked to the tris(bipyridine)ruthenium photosensitizer. The [RuFeFe] trinuclear complex **1** was characterized by MS, IR, UV-vis, ^1H & ^{13}C NMR spectra. A quasi-reversible reduction peak at −1.41 V *versus* Ag/Ag^+ for the Fe^IFe^I/Fe^IFe^0 process is observed in the cyclic voltammogram of **1**.

Keywords: Diiron complex; Iron-only hydrogenase; Ruthenium photosensitizer; Trinuclear complex

1. Introduction

Structural and functional models of the iron-only hydrogenase active site have been a hot topic in bioinorganic chemistry. Numerous diiron dithiolate model complexes were prepared, either with a PDT- (propane-1,3-dithiolato) or an ADT-bridge (2-azapropane-1,3-dithiolato), and with different π ligands [1−5]. Diiron complexes as catalysts for electrochemical hydrogen generation have been reported [6, 7]. Bio-inspired photochemical catalysts based on diiron dithiolate complexes for proton reduction to molecular hydrogen is an attractive and challenging issue.

Only four complexes have been reported as photochemical catalyst candidates based on diiron complexes [8−12]. The first ruthenium-diiron dyad is comprised of a PDT-bridged diiron complex and a tris(2,2′-bipyridine)ruthenium(II) photosensitizer. The two units are covalently linked by a carboxamide bond in a top-on fashion [8]. In the other ruthenium-diiron assembly, the redox-active $[Ru(terpy)_2]^{2+}$ (terpy = 2,2′ : 6,2″-terpyridine) is tethered to the nitrogen of the ADT-bridged diiron complex by a phenyl acetylenic bridge [9, 10]. A side-on connected ruthenium-diiron dyad

---

*Corresponding author. Email: symbueno@dlut.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701767002

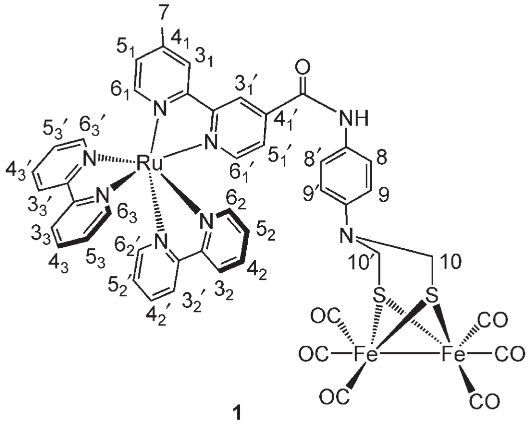
was reported, in which the photoactive trisbipyridine ruthenium unit is linked to a diiron site by a phosphine ligand [11]. Very recently, Song and co-workers described the preparation and spectroscopic characterization of a zinc-diiron complex, in which a tetraphenylporphyrin zinc group (TPP) unit is connected to an ADT-bridged diiron model by a vertically coordinated pyridine ligand [12].

We have recently engaged in preparation of photochemical catalysts based on diiron model complexes for light-driven hydrogen production. Complex **1** (Chart 1) was designed on the basis of the following considerations: (1) Since the lifetime ($\tau = 978$ ns) of the excited state of the *tris*(2,2′-bipyridine)ruthenium(II) is much longer than that ($\tau = 250$ ps) of the *bis*(2,2′:6,2″-terpyridine)ruthenium(II) complex [13], we chose this complex as the photosensitizer; (2) It was reported that the first reductive peak of ADT-bridged diiron complexes can be shifted to anodic direction generally by ca 300–400 mV upon protonation of the bridged-N atom [4, 6], indicating that the ADT-bridged diiron complex might be a reasonable choice as the lower overpotential catalyst for proton reduction in comparison to the PDT-bridged diiron complexes. Connection of the two units by a carboxamide bridge is synthetically approachable. Here, we report the preparation, characterization and electrochemical properties of covalently linked [RuFeFe] trinuclear complex **1**, where the catalyst unit is an ADT-bridged diiron complex and the photosensitizer is a *tris*(bipyridine)ruthenium(II) complex. The two units are connected by a carboxamide linkage between the primary amine of the [Fe_2S_2] moiety and the acyl chloride of the Ru(II) complex.

2. Experimental

2.1. *Reagents and instruments*

All reactions and operations of organometallic complexes were carried out under a dry, oxygen-free dinitrogen atmosphere with standard Schlenk techniques. All solvents were dried and distilled prior to use according to the standard methods.



1

Chart 1

Complexes *bis*(2,2′-bipyridine)(4-methyl-2,2′-bipyridine-4′-acylchloride)ruthenium *bis*(hexafluorophosphate) [14] and $[\{(\mu\text{-}SCH_2)_2N(4\text{-}NH_2C_6H_4)\}Fe_2(CO)_6]$ (**2**) [15] were prepared according to literature procedures.

Infrared spectra were recorded on a JASCO FT/IR 403 spectrophotometer. Proton and ^{13}C NMR spectra were collected on a Varian INOVA 400NMR spectrometer. Mass spectra were recorded on an HP1100 MSD instrument, and HR-MS was recorded on an HPLC-Q-Tof MS (Micro)system.

2.2. *Electrochemistry*

Acetonitrile (Aldrich, spectroscopy grade) used for electrochemistry was dried with 4 Å molecular sieve and then freshly distilled from CaH_2 under N_2. A solution of 0.05 M nBuNPF$_6$ (Fluka, electrochemistry grade) in CH_3CN was used as electrolyte. Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat. The electrolyte solution was degassed by bubbling with dry argon for 10 min before measurement. Cyclic voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 3 and 1 µm diamond pastes and sonicated in ion-free water for 10 min. The reference electrode was a non-aqueous Ag/Ag^+ electrode (0.01 M $AgNO_3$ in CH_3CN) and the auxiliary electrode was a platinum wire.

2.3. *Synthesis of photosensitizer-catalyst model (1)*

Complex $Ru(bpy)_2(Me,COCl\text{-}bpy)(PF_6)_2$, freshly prepared from the reaction of $Ru(bpy)_2(Me,COOH\text{-}bpy)(PF_6)_2$ (110 mg, 0.12 mmol) and $SOCl_2$, was dissolved in CH_3CN (10 mL), and then a solution of $[\{(\mu\text{-}SCH_2)_2N(4\text{-}NH_2C_6H_4)\}Fe_2(CO)_6]$ (**2**) (55 mg, 0.12 mmol) and triethylamine (0.21 mL) in CH_3CN (15 mL) was added at 0°C. The solution was stirred at room temperature in the dark for 20 h under nitrogen. The solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel using $CH_3CN/H_2O/KNO_3$(sat) 90 : 5 : 5 as eluent. The solvent was removed by evaporation and the product was redissolved in a small amount of CH_3CN. Red precipitate was obtained by addition of NH_4PF_6, which was washed by Et_2O and dried (52 mg, 33% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 2.56 (s, 3H), 4.43 (s, 4H), 6.85 (d, 2H), 7.28 (s, 1H), 7.40 (d, 4H), 7.56 (d, 1H), 7.69 (s, 2H), 7.72 (s, 4H), 7.79 (d, 1H), 7.89 (d, 1H), 8.05 (s, 4H), 8.49 (s, 4H), 8.57 (s, 1H), 8.92 (s, 1H), 9.24 (s, 1H). ^{13}C NMR (CD_3CN): δ 207.7, 171.1, 157.2, 152.3, 150.9, 146.1, 138.1, 127.8, 126.6, 125.8, 124.5, 122.6, 122.5, 116.4, 49.8, 20.5. IR(CH_3CN, cm^{-1}): ν(CO) 2075 (m), 2036 (s), 1999 (s), ν(C$=$O) 1604 (m). MS (API-ES): m/z 1232.8 $[M-PF_6^-]^+$ (Calcd 1232.7), 543.9 $[M-2PF_6^-]^{2+}$ (Calcd 534.8). HR$-$ESI$-$MS: $m/z =$ 543.9849$[M-2PF_6^-]^{2+}$(Calcd 543.9867).

3. Results and discussion

Complex **1** was characterized by HRMS, IR, UV-Vis, ^{1}H–^{1}H COSY and ^{1}H and ^{13}C NMR spectra. The doubly charged molecular ion, $[M-2PF_6]^{2+}$, was identified as the primary peak in the HR-MS spectrum. The peak of m/z 543.9849 is in good agreement with the calculated value ($m/z = 543.9867$).

Complex **1** displays three ν(CO) bands at 2075, 2036 and 1999 cm^{-1} in the IR spectrum, which are quite similar to the corresponding ν(CO) bands of **2** and comparable to those of the reported diiron dithiolate model complexes [16, 17], indicating that the [Fe_2S_2] unit does not change in **1**. The typical ν(C=O) of the carboxamide group in **1** is detected at 1604 cm^{-1}. In the UV-vis spectrum, **1** exhibits two absorption bands at 286 ($\pi \rightarrow \pi^*$) and 459 nm (MLCT). The absorptions are almost identical with those of the free *tris*(bipyridine)ruthenium(II) complex. The ^{1}H NMR spectrum of **1** is shown in figure 1, in which the signals are designated by ^{1}H–^{1}H COSY spectrum of **1**. Differences are observed in the ^{1}H NMR spectra of **1** and **2**. The phenyl group of **2** displays a broad singlet at δ 6.63 [15]. When the acyl chloride of the Ru(II) complex reacts with **2** and the carboxamide bond forms, the broad phenyl signal at δ 6.63 is shifted down-field and splits into two doublets at δ 6.85 and 7.72 for **1**. The methylene singlet at δ 4.20 for **2** is shifted to δ 4.43 for **1**. As the CH_2 group of the [Fe_2S_2] moiety is far from the Ru(II) chiral center, only one singlet is observed for the CH_2 group in **1**. The spectroscopic evidence strongly supports the formation of carboxamide linkage between the Ru(II) unit and the [Fe_2S_2] moiety.

The cyclic voltammogram of **1** in CH_3CN shows one quasi-reversible reduction peak for Fe^IFe^I/Fe^IFe^0 at −1.41 V *versus* Ag/$AgNO_3$, with an anodic shift of 70 mV in comparison to the first reduction peak of **2** because of the electron withdrawing effect of carboxamide group [15]. Further reduction of Fe^IFe^0 to Fe^0Fe^0 is detected at −1.96 V. Typical bpy-based reduction peaks are observed at −1.55, −1.86 and −2.14 V,

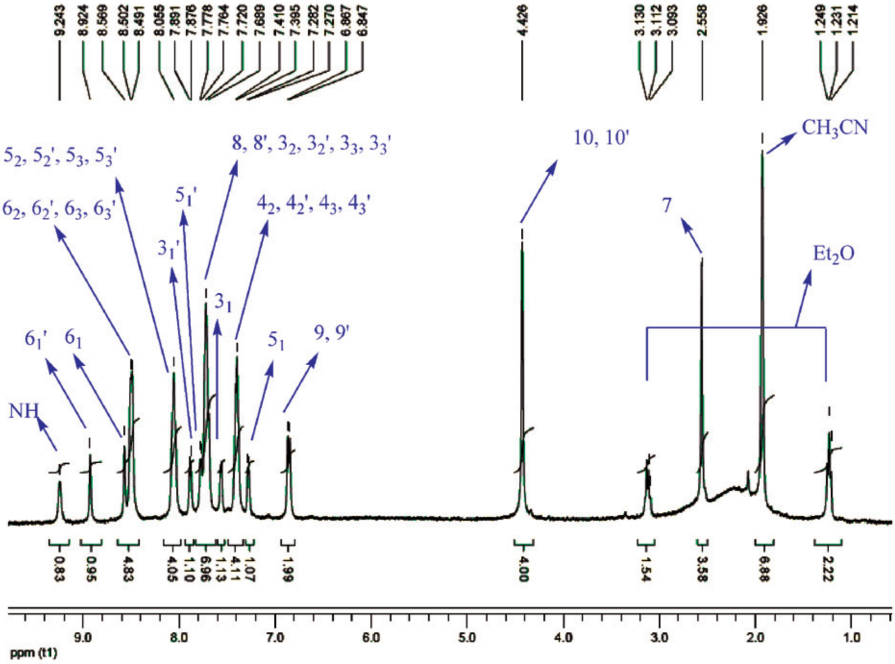


Figure 1. ^{1}H NMR spectrum of **1** in CD_3CN.

similar to the reduction potentials reported for the *tris*(bipyridine)ruthenium(II) complex [18]. The reduction current i_p^{red} at -1.55 V is apparently higher than those at -1.86 and -2.14 V for the second and the third reduction peaks of the bpy ligand, implying that the first reduction peak of the bpy ligand is overlapped with another reduction process, presumably the Fe^IFe^I/Fe^IFe^0 process relevant to the CH_3CN substituted species of **1**. This CO-displacement by CH_3CN for all-carbonyl 2Fe2S complexes is often observed in the CV measurements [19, 20]. A relatively negative reduction peak at -2.32 V is detected, which cannot be clearly assigned. Since the reduction potential of the excited state of the ruthenium(II) complex is ca -1.10 V [8], direct electron transfer from the excited state of the ruthenium(II) unit to the iron core in **1** is thermodynamically unfavorable. The desired intramolecular electron transfer from the photo-exited state of the $[Ru(bpy)_3]^{2+}$ unit to the dinuclear iron site in the presence of F_3CCOOH was not observed by laser flash photolysis of **1** with phenothiazine as electron donor in CH_3CN, because F_3CCOOH cannot protonate the bridged-N of **1** to shift the reduction potential for Fe^IFe^I/Fe^IFe^0. Compared with the lifetime ($\tau = 978$ ns) of the excited state of the *tris*(bipyridine)ruthenium complex, the lifetime ($\tau = 895$ ns) of the photo-excited ruthenium(II) unit linked to a diiron complex indicates that the diiron moiety covalently bonded to the *tris*(bipyridine)ruthenium(II) complex does not have a considerable effect on the lifetime of the excited state of the ruthenium(II) unit. If the redox potential (-1.5 V) of the diiron part can be adjusted to more positive values, direct electron transfer from the excited state of the ruthenium(II) complex to the diiron might be possible.

Acknowledgment

We are grateful to the Chinese National Natural Science Foundation (Grant Nos. 20471013 and 20633020), the Swedish Energy Agency, the Swedish Research Council and K & A Wallenberg Foundation for financial support of this work.

References

[1] I.P. Georgakaki, L.M. Thomson, E.J. Lyon, M.B. Hall, M.Y. Darensbourg. *Coord. Chem. Rev.*, **238–239**, 255 (2003).
[2] T.B. Rauchfuss. *Inorg. Chem.*, **43**, 14 (2004).
[3] X. Liu, S.K. Ibrahim, C. Tard, C.J. Pickett. *Coord. Chem. Rev.*, **249**, 1641 (2005).
[4] J.-F. Capon, F. Gloaguen, P. Schollhammer, J. Talarmin. *Coord. Chem. Rev.*, **249**, 1664 (2005).
[5] L. Sun, B. Åkermark, S. Ott. *Coord. Chem. Rev.*, **249**, 1653 (2005).
[6] F. Gloaguen, J.D. Lawrence, T.B. Rauchfuss. *J. Am. Chem. Soc.*, **123**, 9476 (2001).
[7] S. Ott, M. Kritikos, B. Åkermark, L. Sun, R. Lomoth. *Angew. Chem. Int. Ed.*, **43**, 1006 (2004).
[8] H. Wolpher, M. Borgström, L. Hammarström, J. Bergquist, V. Sundström, S. Styring, L. Sun, B. Åkermark. *Inorg. Chem. Comm.*, **6**, 989 (2003).
[9] S. Ott, M. Kritikos, B. Åkermark, L. Sun, Angew. *Chem. Int. Ed.*, **42**, 3285 (2003).
[10] S. Ott, M. Borgsrtröm, M. Kritikos, R. Lomoth, J. Bergquist, B. Åkermark, L. Hammarström, L. Sun. *Inorg. Chem.*, **43**, 4683 (2004).
[11] J. Ekström, M. Abrahamsson, C. Olson, J. Bergquist, F.B. Kaynak, L. Eriksson, L. Sun, H.-C. Becker, B. Åkermark, L. Hammarström, S. Ott. *Dalton Trans.*, 4599 (2006).
[12] L. Song, M. Tang, S. Mei, J. Huang, Q. Hu. *Organometallics*, **26**, 1575 (2007).
[13] J.R. Winkler, T.L. Netzel, C. Creutz, N. Sutin. *J. Am. Chem. Soc.*, **109**, 2381 (1987).

[14] B.M. Peek, G.T. Ross, S.W. Edwards, G.J. Meyer, T.J. Meyer, B.W. Erickson. *Int. J. Peptide Protein Res.*, **38**, 114 (1991).
[15] T. Liu, M. Wang, Z. Shi, H. Cui, W. Dong, J. Chen, B. Åkermark, L. Sun. *Chem. Eur. J.*, **10**, 4474 (2004).
[16] H. Li, T.B. Rauchfuss. *J. Am. Chem. Soc.*, **124**, 726 (2002).
[17] F. Gloaguen, J.D. Lawrence, T.B. Rauchfuss. *J. Am. Chem. Soc.*, **123**, 9476 (2001).
[18] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky. *Coord. Chem. Rev.*, **84**, 85 (1988).
[19] D. Chong, I.P. Georgakaki, R. Mejia-Rodriguez, J. Sanabria-Chinchilla, M.P. Soriaga, M.Y. Darensbourg. *Dalton Trans.*, 4158 (2003).
[20] P. Li, M. Wang, C. He, G. Li, X.Y. Liu, C. Chen, B. Åkermark, L. Sun. *Eur. J. Inorg. Chem.*, **12**, 2506 (2005).