

Synthesis, Structures and Electrochemistry studies of 2Fe₂S-Fe(II)(S-2N)₂ models for H-cluster of [FeFe]-hydrogenase

Ming-Qiang Hu,^a Hui-min Wen,^a Cheng-Bing Ma,^a La Li,^a Qing-Yun Yan,^a
Hui Chen^a and Chang-Neng Chen^{*a}

1. Experimental

1.1. Reagents and Measurements

All manipulations and reactions were carried out under dry oxygen-free N₂ using standard Schlenk techniques. All chemicals were analytical reagents and used without further purification. All solvents were dried and distilled prior to use according to the standard methods. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer using KBr pellets. Elemental analysis was carried out on a Vario EL III Elemental Analyser. The compound (μ -pdt)Fe₂(CO)₆ was prepared according to the literature.^{1,2}

1.2. X-ray crystallography

Diffraction measurements of single crystals of complexes **A** and **B2** were made on a Rigaku Mercury diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$), while single crystal of complex **B1** was performed on a Rigaku Saturn70 diffractometer. Crystal data collection, refinement and reduction were accomplished with the CrystalClear processing program. The structure was solved by direct methods with SHELXS-97³ and refined by using the SHELXL-97 crystallographic software package.⁴ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added in a riding model.

Crystallographic data of **A**, **B1** and **B2** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 776575 ~ 776577. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

1.3. Electrochemistry

Electrochemical measurements were made using a CH instrument Model 630A Electrochemical Workstation. Cyclic voltammetry and differential pulse voltammograms were obtained in a conventional and gastight three-electrode cell under Ar and at room temperature. The working electrode was a glassy carbon electrode (3 mm in diameter), the reference electrode a Ag|AgCl electrode (ca -0.43 V vs Fc/Fc⁺), and the counter electrode a platinum wire. The supporting electrolyte is 0.1 M Bu₄NPF₆ in CH₃CN.

2. Electrochemistry studies

In presence of HOAc (1 ~ 9 mM) as a source of protons, the first reductive peak does not shift and the current height shows a minor growing, indicating that H⁺ did not incorporate to the model complex at this step. Meanwhile, the third reduction peak increases in peak currents and shifts towards a more negative potential, which electrochemical behaviour features a proton relative process.⁵ The comparison of DVP before and after the addition of proton shows that the pulse peak area of reactive event at -1.33 V increases, which means another one-electron process involved, and suggests that some protonated intermediates acted stably in the H⁺/H₂ reduction activities. (Fig. S1.)

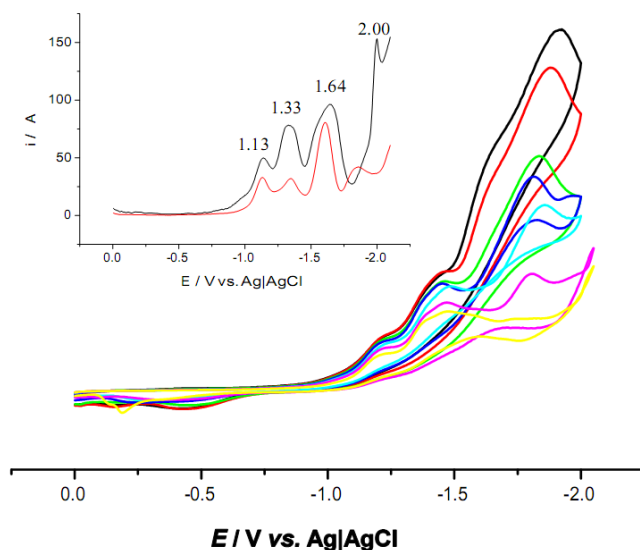


Fig.S1. CV of complex **A** (2.0 mM) with HOAc 1 ~ 9 mM and DVP of 4 mM HOAc inset. Supporting electrode is 0.1 M *n*-Bu₄NPF₆ in MeCN; working electrode: glassy carbon (0.071 cm²); reference electrode : Ag|AgCl; scan rate = 0.1 Vs⁻¹.

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