On the structure of a proposed mixed-valent analogue of the diiron subsite of [FeFe]-hydrogenase†

Stephen P. Best,*[a] Stacey J. Borg,[a] Jonathan M. White,[a] Mathieu Razavet[b] and Christopher J. Pickett*[b]

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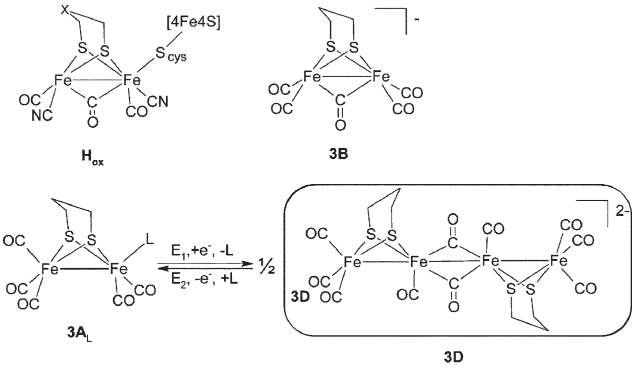
We show that a dinuclear assembly apparently providing the first example of a synthetic molecule exhibiting key features of the diiron subsite of [FeFe] hydrogenase, *viz*. CO-bridging of a coordinatively unsaturated, dithiolate-bridged mixed-valence diiron centre, is in fact a diamagnetic tetranuclear complex.

The resting state diiron unit of the active site iron-only hydrogenase is a low-valent, coordinatively unsaturated, mixed valence diiron species possessing a bridging carbonyl,[1] Scheme 1. Much attention has been given to the synthesis or generation of analogues with structural, spectroscopic and electronic features of the subsite in order to understand its chemistry.[2,3] We were therefore intrigued to see the report in this journal of a synthetic species **3B**‡ (Scheme 1) which was claimed to possess several of these key attributes.[4] It was reported that **3B** is formed by one-electron reduction of either of two precursors $\mathbf{3A}_L$ (L = MeCN or NH_2Pr) and that this process is chemically reversible. However, given (i) the known instability of single-electron reduction products of related systems;[5] (ii) the commensurate complexity of their following chemistry;[5–7] (iii) related Fe^IFe^0 complexes give an EPR spectrum[5,8] and no such spectra were obtained to support the formulation; and (iv) the biological and technological relevance of this chemistry, it is important to clarify the reductive chemistry of **3A** and of closely related systems, **2A** (bridge = $S(CH_2)_2S$). The following experiments suggest that the structure proposed for the **B**-type species is incorrect and that one-electron reduction of $\mathbf{3A}_L$, where L is a hemilabile ligand, results in an unusual CO-bridged tetranuclear structure, **3D**.



Scheme 1 Oxidised form of the [FeFe]-hydrogenase H-cluster, $\mathbf{H}_{ox}$, reduction product of $\mathbf{3A}_L$ (**3B**) proposed in ref. 4 and the structure of the long-lived product (**3D**) proposed herein.

Spectroelectrochemical (SEC) experiments conducted during reduction and reoxidation of $\mathbf{2A}_{MeCN}$ give a stable reduction product. Spectral subtraction reveals an IR spectrum† essentially identical to that reported for the putative product **3B** (Fig. 1a). As reported earlier,[4] there is good reversibility of the spectral changes in SEC experiments.† The product of chemical reduction of $\mathbf{3A}_{MeCN}$, or $\mathbf{2A}_{MeCN}$, gives a spectrum similar to that obtained in SEC experiments (Fig. 1b). Despite the stability of the reduction products, we were unable to obtain an EPR spectrum from solutions of $\mathbf{2A}_{MeCN}$ or $\mathbf{3A}_{MeCN}$ reduced using an *in situ* electrosynthesis cell or from solutions generated by continuous-flow electrosynthesis. Similar approaches allow collection of the EPR spectra of the transiently stable $\mathbf{A}_{CO}^-$-type species.[5]

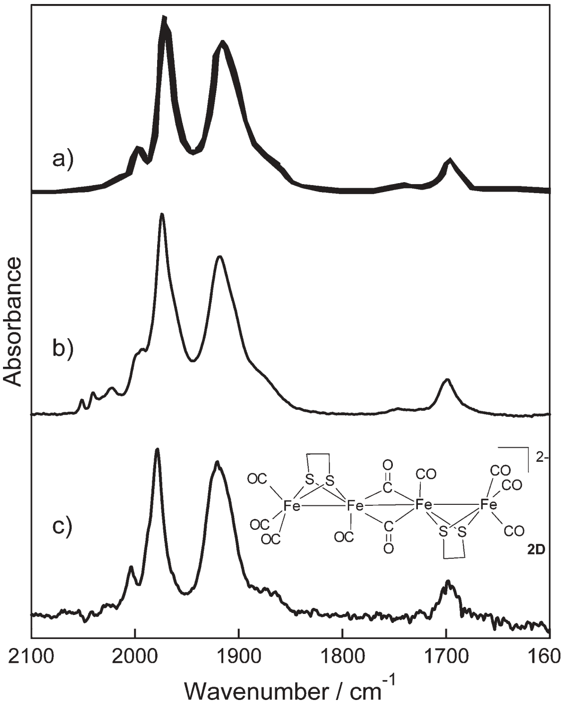


Fig. 1 IR spectra of (a) the electrochemical reduction product of $\mathbf{3A}_{MeCN}$ (reproduced from ref. 4), (b) the product obtained from $Li[HB(Et)_3]$ reduction of $\mathbf{2A}_{MeCN}$ and (c) **2D** in MeCN solution. Note that solutions of **2D** are very air sensitive, giving small amounts of the parent and $\mathbf{2A}_{CO}$. The spectrum shown is corrected by spectral subtraction of these species.†

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[a] *School of Chemistry, University of Melbourne, Melbourne, Australia. E-mail: spbest@unimelb.edu.au; Fax: +61 (3) 9347 5180*
[b] *School of Chemistry and Pharmacy, University of East Anglia, Norwich, UK NR4 7TJ. E-mail: c.pickett@uea.ac.uk; Fax: +44 1603 458 553*

† Electronic supplementary information (ESI) available: Preparation and IR spectra of $\mathbf{3A}_L$ and $[NEt_4]_2\mathbf{2D}$. See DOI: 10.1039/b712758h

Chemical reduction of $\mathbf{2A_{CO}}$ or $\mathbf{2A_{MeCN}}$ using $Li[HB(Et)_3]$ followed by addition of $[N(Et)_4]Cl$ allows isolation of a microcrystalline solid, $[NEt_4]_2$**2D**.† The solution IR spectrum of **2D** is shown in Fig. 1c. The similarity of the solution spectra of **2D** and the reduction product of $\mathbf{2A_{MeCN}}$ strongly suggests that both species are identical. Since an EPR spectrum is not obtained from reduced solutions of $\mathbf{2A_{MeCN}}$ the product cannot be a simple diiron compound.

The molecular structure of **2D** was determined by X-ray analyses of single crystals of $[NEt_4]_2$**2D** and this reveals an unusual tetranuclear formulation with two diiron units bridged by CO ligands (Fig. 2).§ The two inner iron atoms and bridging CO groups form a near-planar arrangement where, for both diiron fragments, the bridging CO groups occupy a pair of apical and basal coordination positions. Alternative formulations of **2D** as a (di)hydride are excluded based on the observation that the IR spectra of solutions of **2D** are identical with those generated electrochemically by reduction of $\mathbf{2A_{MeCN}}$ in the absence of a proton source. It is important to note that the spectra of reduced solutions of $\mathbf{2A_{MeCN}}$ are very similar in profile and wavenumber to those reported for electrochemical reduction of $\mathbf{3A_{MeCN}}$ (Fig. 1).

In addition to the structural evidence, the IR spectra suggest a structure of **3B** (and **2B**) based on **3A** with four CO groups and apical/basal substituents at a single iron atom. This structural motif is also present for $Fe_4[MeC(SCH_2)_3]_2(CO)_8$, **4Fe6S**,[9] and the apical/basal isomers of $Fe_2(\mu\text{-}S(CH_2)_3S)(CO)_4(PPh_2(CH_2)_2PPh_2)$[10] and $Fe_2(\mu\text{-}S(CH_2)_2S)(CO)_4(PPh_2(CH)_2PPh_2)$.[3] In each of the four structurally-characterised cases, and the reduction products of $\mathbf{3A_{MeCN}}$ and $\mathbf{2A_{MeCN}}$, a similar pattern of IR-active terminal-ν(CO) bands is obtained. The IR spectra, together with the EPR silence of solutions of **2D**, rule out equilibria with significant concentrations of mixed-valence diiron species.

While the electrochemistry of the dithiolato-bridged diiron carbonyl compounds appears deceptively simple, SEC investigations[5,6] and rapid-scan voltammetry[11] make it clear that several dominant reaction paths may complicate the chemistry. In the present case, dissociation of a ligand from each diiron unit following one-electron reduction leaves a 35 electron diiron complex, where an electron precise configuration may be achieved by formation of an Fe–Fe bond between two such units to give the tetrairon core. The system becomes coordinatively saturated by switching the coordination mode of two CO groups from terminal to bridging. The interconversion is surprisingly fast and chemically reversible and a current response due to reoxidation of **2D** is evident in the electrochemistry of $\mathbf{2A_{CO}}$ under N_2 in MeCN. The reaction product is, however, sensitive to the bridging dithiolate, where the tetrairon compound obtained from $\mathbf{3A_{CO}}^-$ has a structure completely different from **2D** in which there is no additional Fe–Fe bond but one of the dithiolates links the two diiron centres.[5,12] The difference in chemistry of the respective one-electron reduced products is important from a functional perspective and is responsible for the differing CO inhibition of electrocatalytic proton reduction by $\mathbf{3A_{CO}}$ and $\mathbf{2A_{CO}}$.[6]

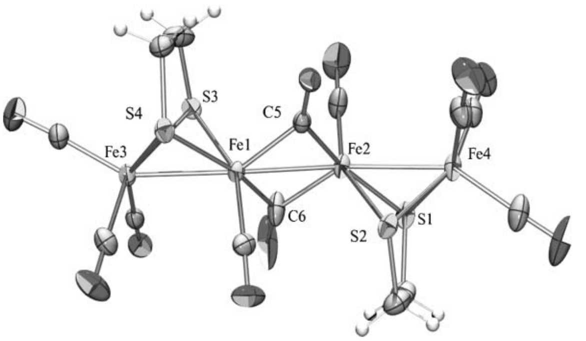

Fig. 2 Ortep view (ellipsoids at 50% probability level) of $[Fe_4(\mu\text{-}S(CH_2)_2S)_2(\mu\text{-}(CO))_2(CO)_8]^{2-}$, **2D**. Selected bond lengths (Å) and angles (°); where an averaged value is reported the standard deviation is given in parentheses: Fe1–Fe2 2.5327(5), Fe1–Fe3 2.5417(5), Fe2–Fe4 2.5671(5), Fe–S (av) 2.271 (13), Fe–C_{term} (av) 1.775 (18), C_{term}–O (av) 1.150 (6), Fe–C_{br} (av) 1.915 (10), Fe3–Fe1–Fe2 153.19(2), Fe1–Fe2–Fe4 151.65(2), Fe1–C5–Fe2 82.7(1), Fe1–C6–Fe2 82.8(1).

Well-defined odd-electron dithiolate-bridged diiron compounds have been obtained by reduction of $\mathbf{3A_{CO}}$[5] or by oxidation to yield $Fe^{II}Fe^{I}$ species.[13,14] In each of these cases the products have been identified by EPR spectroscopy[5,13,14] and/or X-ray crystallography.[13] For the enzyme, the one-electron redox chemistry of the matrix isolated diiron fragment of $\mathbf{H_{ox}}$ gives well-defined products. In order to reproduce this chemistry for isolated diiron compounds it is necessary to prevent formation of higher nuclearity species, *e.g.* tethering diiron complexes to an electrode[15] or polymer support.[16] Higher nuclearity compounds can, however, have intrinsic interest in the context of the H-cluster; notably two electron reduction of **4Fe6S**[17] provides mixed-valence diiron centres with bridging carbonyl groups and open coordination sites.

Finally, rapid and reversible reorganisation of these biologically-relevant systems, particularly in mixed-valence states, is well primed to confound structural assignment based on limited voltammetric and spectroscopic data.

Notes and references

‡ The number prefix used for the compound labels indicates the number of C atoms of the bridging dithiolate.

§ Crystal data for **2D**. $[C_{14}H_8O_{10}S_4Fe_4]\cdot[C_8H_{20}N]_2$, M = 948.36, T = 130.0(2) K, λ = 0.71069, monoclinic, space group $P2(1)/c$, a = 17.051(1), b = 13.4111(8), c = 17.963(1) Å, β = 104.289(1)°, V = 3980.5(4) Å^3, Z = 4, D_c = 1.586 Mg m^{-3}, μ(Mo-Kα) 1.691 mm^{-1}, $F(000)$ = 1966, crystal size 0.50 × 0.45 × 0.40 mm. 28405 reflections measured, 7015 independent reflections (R_{int} = 0.023) the final R was 0.0331 [$I > 2\sigma(I)$] and w$R(F^2)$ was 0.1029 (all data). CCDC 658323. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712758h

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