

# On the Structure of a Proposed Mixed-Valent Analog of the Diiron Subsite of [FeFe]-Hydrogenase

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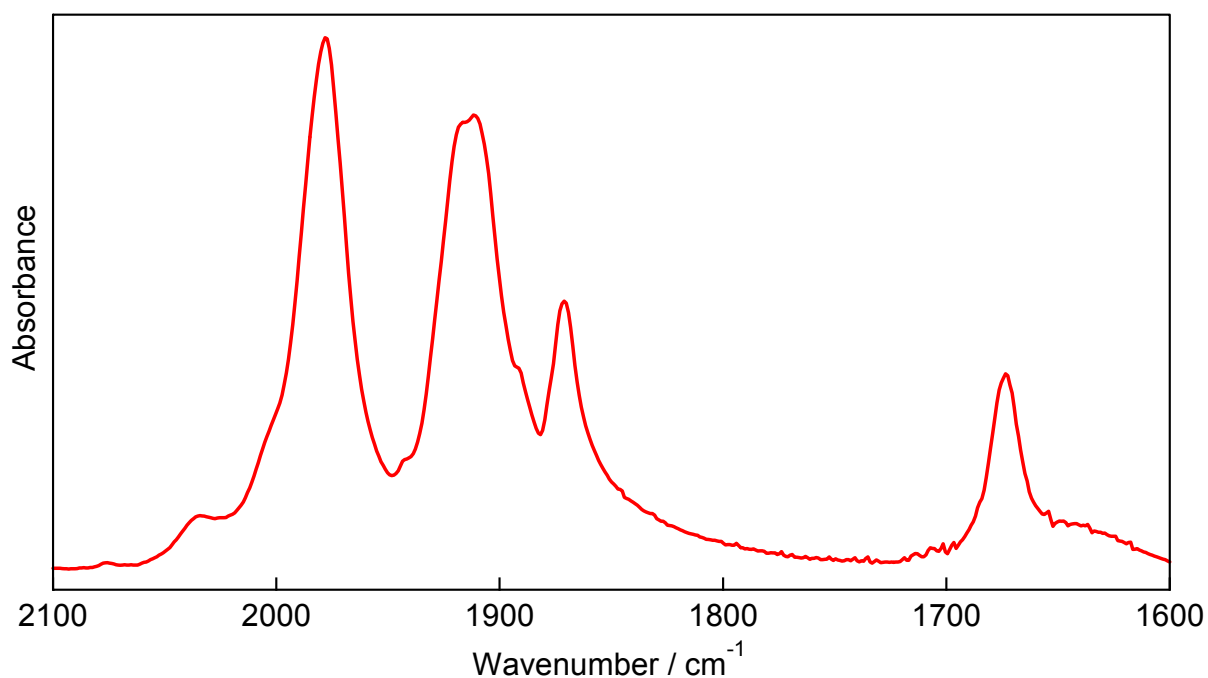
## Electronic Supplementary Information (ESI):

1. Synthesis of  $[\text{Fe}_4(\mu\text{-S}(\text{CH}_2)_2\text{S})_2(\mu\text{-}(\text{CO})_2(\text{CO})_8)]^{2-}$ , **2D**.
2. IR spectra of **2D**.
3. Spectral subtraction of the solution spectrum of **2D**.
4. Spectroelectrochemistry of  $[\text{Fe}_2(\mu\text{-S}(\text{CH}_2)_2\text{S})_2(\text{CO})_5(\text{NCCH}_3)]^{2-}$ , **2A**.
5. Spectral deconvolution of the spectroelectrochemical product.
6. Description of the structure of **2D**.
7. References

1. Synthesis of  $[\text{Fe}_4(\mu\text{-S}(\text{CH}_2)_2\text{S})_2(\mu\text{-(CO)}_2(\text{CO})_8)]^{2-}$ , **2D**.

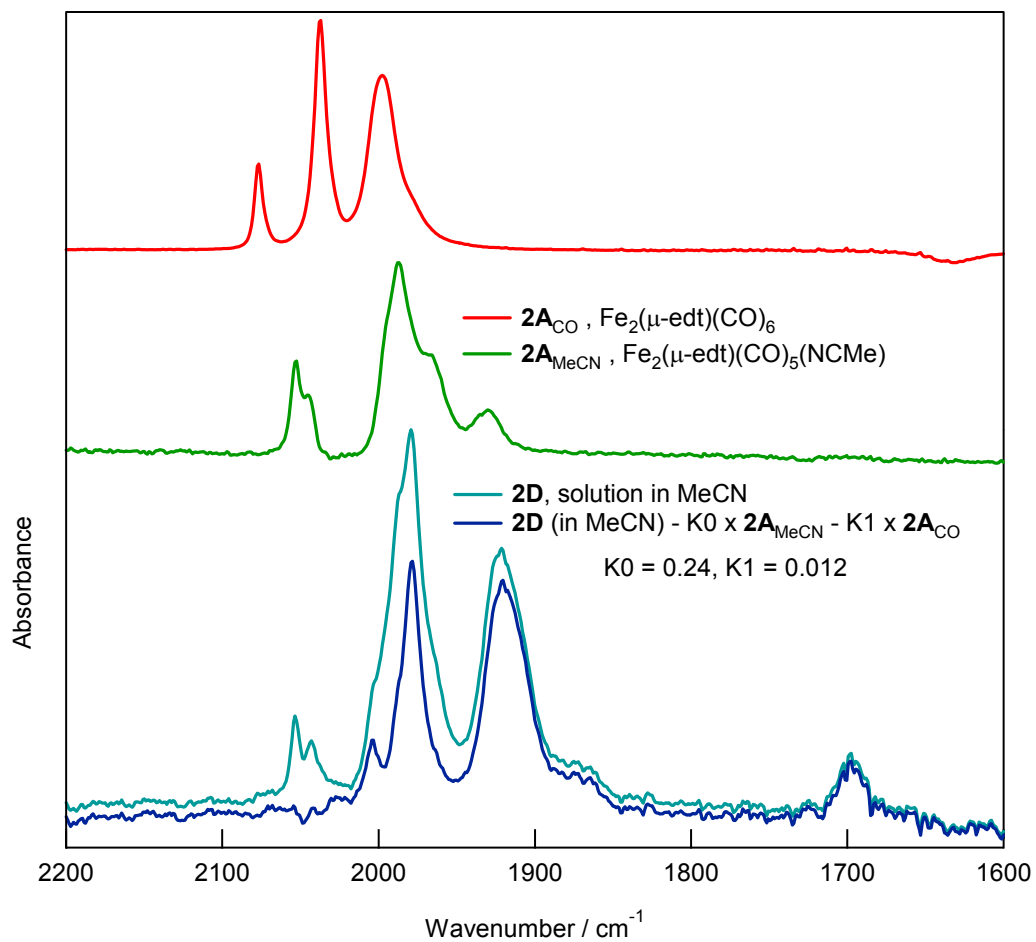
All operations were performed under strictly anaerobic conditions. A small excess of  $\text{Li}[\text{HBEt}_3]$  (100 mM in THF, 145  $\mu\text{L}$ ) was added dropwise to a solution of  $\text{Fe}_2(\mu\text{-S}(\text{CH}_2)_2\text{S})(\text{CO})_5(\text{NCMe})$ , **2A<sub>CO</sub>** (0.05 g, 0.134 mmol) in *ca.* 5 mL THF. This was accompanied by a change in the colour of the solution from orange/red to black. A solution of  $\text{NEt}_4\text{Cl}$  (0.025 g, 0.15 mmol) in  $\text{CH}_3\text{CN}$  was added and the mixture left to stand at room temperature whereupon large black prismatic crystals of  $[\text{NEt}_4]_2$  **2D** formed over the period of *ca.* 10 days. The yield of the air-sensitive compound was estimated to be *ca.* 40%. The homogeneity of the sample was confirmed by IR spectroscopy and the structure of **2D** determined by X-ray crystallography. IR (solid, KBr):  $\nu(\text{CO})$  1978 (s), 1917 (s), 1910 (sh), 1872 (m) and 1674 (m)  $\text{cm}^{-1}$ . IR ( $\text{CH}_3\text{CN}$ ):  $\nu(\text{CO})$  2053 (w), 2042 (w), 1978 (s), 1917 (s), 1872 (vw) and 1700 (w)  $\text{cm}^{-1}$ .

2. IR spectrum, in the  $\nu(\text{CO})$  region, of **2D** dispersed in KBr.

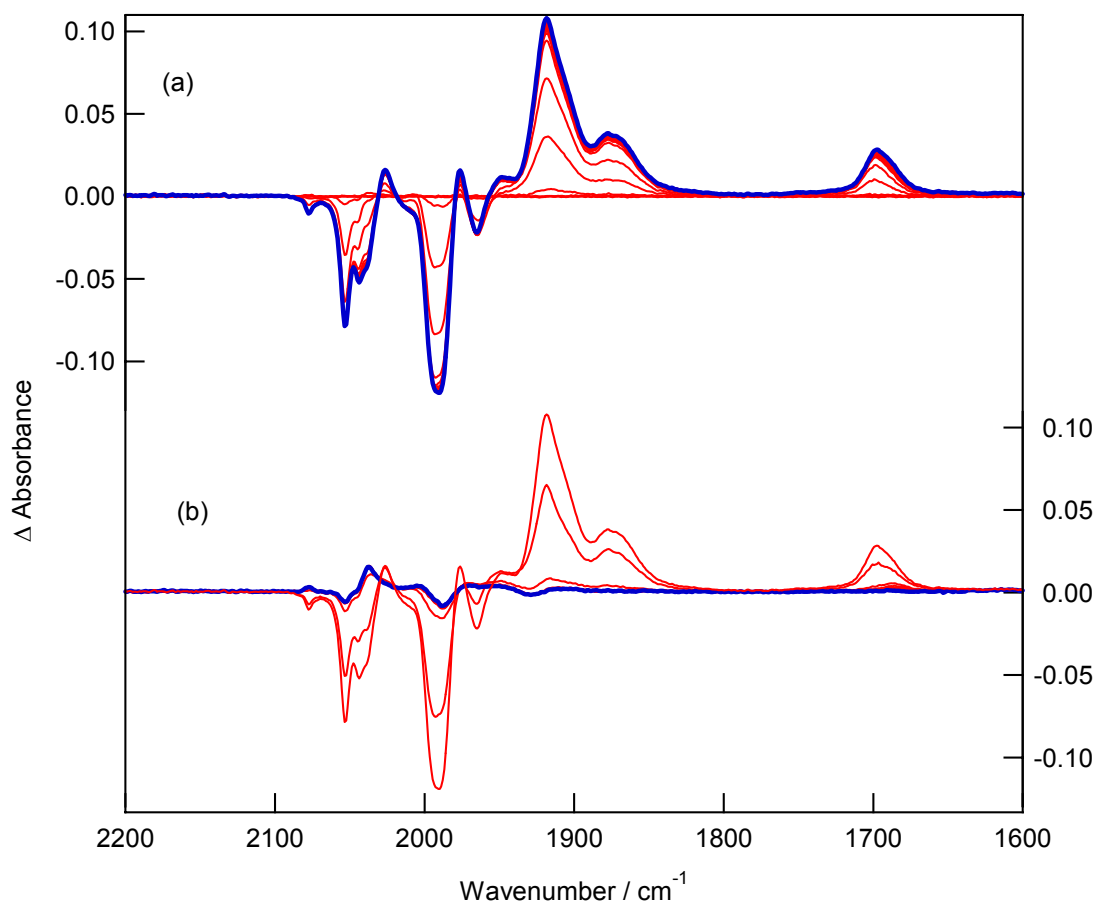


The solution IR spectrum of **2D** differs from that obtained from solid state samples in terms of the wavenumber and breadth of the bridging CO band, which may readily be explained in terms of differing ion pairing interactions, and the breadth of the 1872  $\text{cm}^{-1}$  band, which may reflect some conformational flexibility of the tetranuclear molecule in solution.

3. Spectral subtraction of the solution spectrum of **2D**.

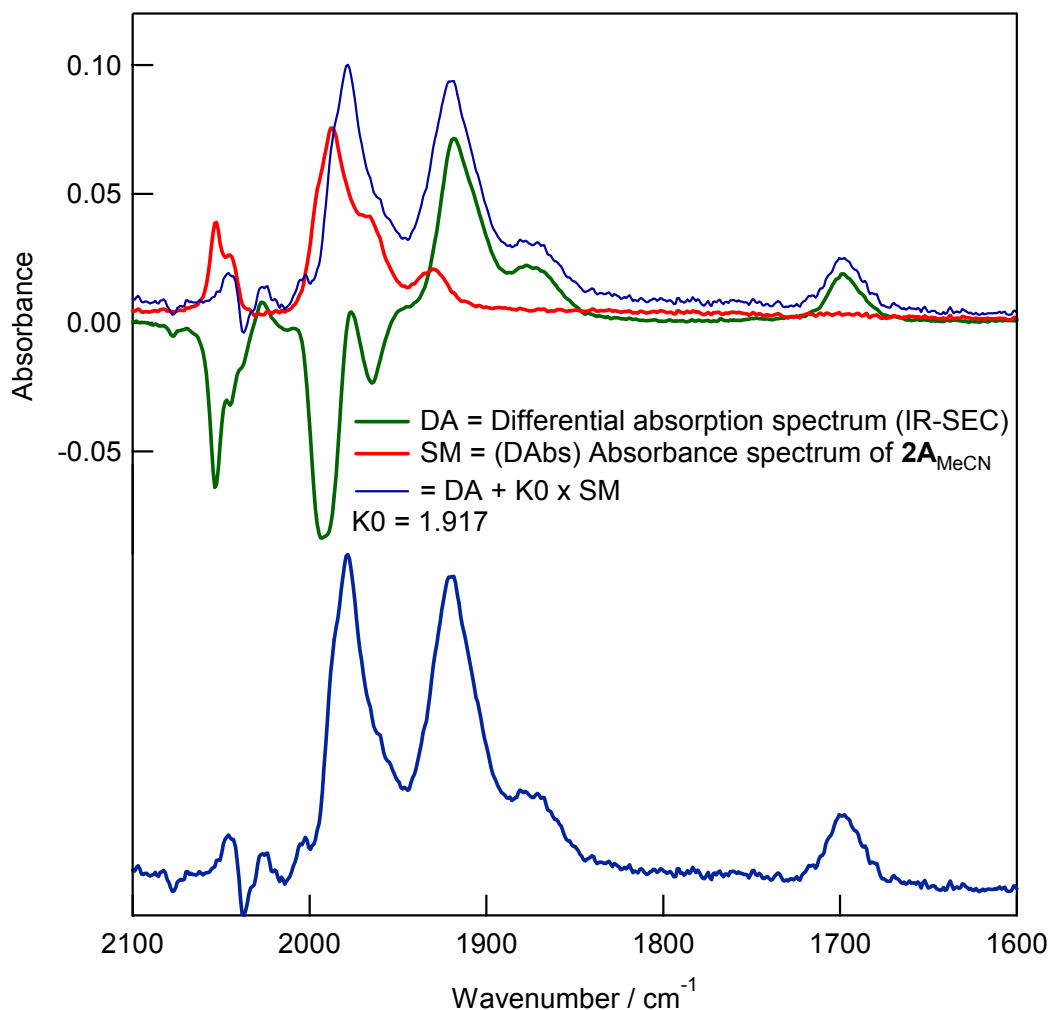


4. Spectroelectrochemistry of  $[\text{Fe}_2(\mu\text{-S}(\text{CH}_2)_2\text{S})_2(\text{CO})_5(\text{NCCH}_3)]^{2-}$ , **2A**.



Reflection absorption IR-SEC results obtained for dinitrogen-saturated solutions of **2D** (1 mM in  $\text{CH}_3\text{CN}$ , 0.2 M  $[\text{N}(\text{Et})_4][\text{ClO}_4]$ ). Spectra were recorded with an interval of 1.5 s following (a) reduction and (b) reduction. The bolded trace corresponds to the last recorded for the series. The IR-SEC cell has previously been described;<sup>1</sup> the electrodes comprised highly-polished 3 mm diameter vitreous carbon disc working electrode, silver pseudo-reference and platinum foil counter where a PAR model 362 scanning potentiostat was used to control the potential applied to the cell.

5. Spectral deconvolution of the spectroelectrochemical product.



Absorbance spectrum of the product obtained following reduction of **2A**<sub>MeCN</sub> in SEC experiments. The sample of **2A**<sub>MeCN</sub> is contaminated by a small amount of the parent hexacarbonyl, **2A**<sub>CO</sub>, and the depletion and growth bands associated with this compound and reduction products are evident in the spectra between 2000 and 2100 cm<sup>-1</sup>.

## 6. Description of the structure of **2D**.

The coordination environment about the four iron atoms of **2D** is square pyramidal (or  $\psi$ -octahedral, with the bent M-M bond the electron pair) and has a core geometry analogous to that reported for  $\text{Fe}_4[\text{MeC}(\text{SCH}_2)_3]_2(\text{CO})_8$ , **4Fe6S**.<sup>2</sup> For **4Fe6S** the diiron units are linked by bridging thiolato groups. The core geometry involving pairs of thiolate (or phosphido) bridged bimetallic units that are connected by a M-M bond supported by bridging ligands is otherwise unprecedented within iron-sulfur chemistry. The arrangement of terminally-bound CO groups of each diiron fragment of **2D** and **4Fe6S** matches that of the crystallographically-characterised apical-basal isomers of  $\text{Fe}_2(\mu\text{-S}(\text{CH}_2)_3\text{S})(\text{CO})_4(\text{PP})$ , PP =  $\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2$ <sup>3</sup> or  $\text{PPh}_2(\text{CH})_2\text{PPh}_2$ ,<sup>4</sup> and in each of these cases a similar pattern IR-active terminal- $\nu(\text{CO})$  bands is obtained. The three Fe-Fe contacts of **2D** are in the range 2.53 to 2.57 Å and this indicates Fe-Fe bonding interactions both within and between the CO-bridged diiron units as would be consistent with a formal  $\text{Fe}^{\text{I}}\text{Fe}^0\text{Fe}^0\text{Fe}^{\text{I}}$  oxidation state assignment. It is interesting to note that for **4Fe6S** the Fe-Fe distances are longer (2.54-2.63 Å) despite the  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$  formal oxidation state assignment. The terminal- $\nu(\text{CO})$  band band profile of **2D** is shifted by  $69 \pm 2 \text{ cm}^{-1}$  lower than that of **4Fe6S**, consistent with the higher oxidation state assignment for the latter although it is noted that this magnitude of shift of the CO frequencies is similar to that obtained by one-electron reduction of **4Fe6S**.<sup>5</sup>

## 7. References

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