

Diiron dithiolate complexes containing intra-ligand NH...S hydrogen bonds: [FeFe] hydrogenase active site models for the electrochemical proton reduction of HOAc with low overpotential

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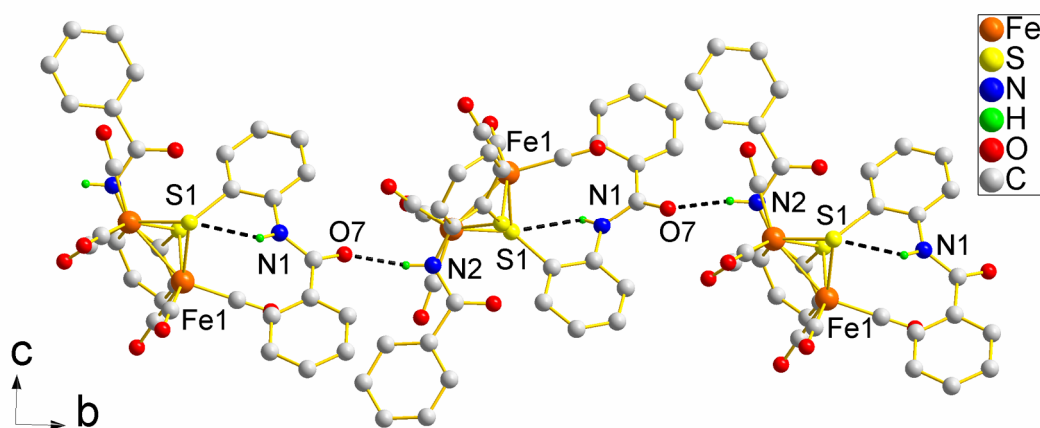


Fig. S1 The N(1)H...S(1) and N(2)H...O(7) hydrogen bonds in complex 3.

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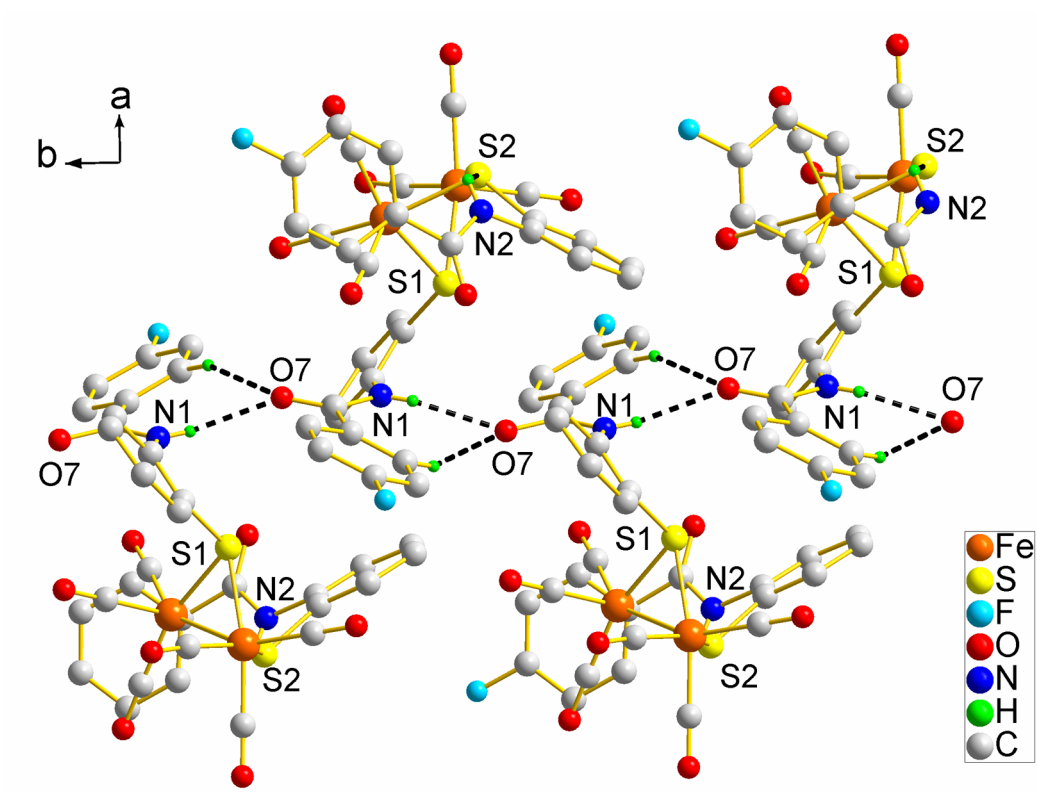


Fig. S2 The N(1)H...O(7) and *ortho*-H...O(7) hydrogen bonds in complex 4.

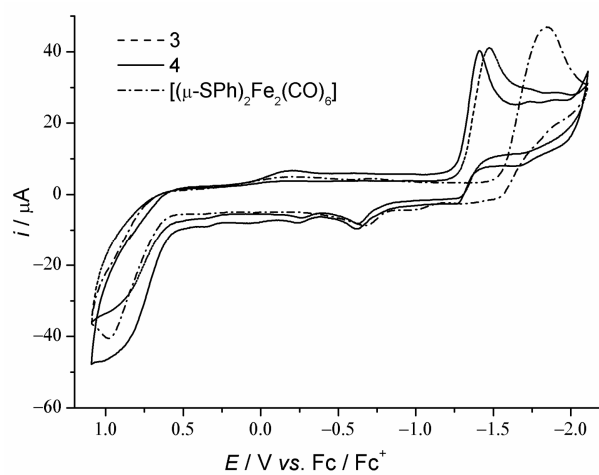


Fig. S3 Cyclic voltammograms of **3**, **4** and $[(\mu\text{-SPh})_2\text{Fe}_2(\text{CO})_6]$ (1.0 mM) in CH_2Cl_2 with 0.05 M $n\text{Bu}_4\text{NPF}_6$ at a scan rate of 100 mV s^{-1} .

Table S1 The NH...S data for complex 3.

Donor	--- H....	Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
N(1)	--H(1)	..S(1)	[]	0.86	2.63	2.9389	102
N(1)	--H(1)	..O(15)	[]	0.86	2.06	2.8580	155
N(2)	--H(2)	..O(7)	[2655.01]	0.85	2.04	2.8729	168
N(3)	--H(3)	..O(8)	[1455.01]	0.85	2.21	2.8807	135
N(4)	--H(4)	..S(4)	[]	0.91	2.63	2.9263	100
C(11)	--H(11A)	..O(7)	[]	0.93	2.43	2.8794	110
C(28)	--H(28A)	..O(7)	[2655.01]	0.93	2.59	3.2820	132
C(47)	--H(47A)	..O(15)	[]	0.93	2.49	2.8001	100
C(54)	--H(54A)	..O(3)	[2645.01]	0.93	2.59	3.2008	123
C(56)	--H(56A)	..O(16)	[]	0.93	2.55	2.9937	109

Table S2 The NH...S data for complex 4.

Donor	--- H....	Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
N(1)	--H(1)	..O(7)	[2655.01]	0.86	2.11	2.8849	150
N(2)	--H(2)	..S(2)	[]	0.86	2.62	2.9742	106
C(19)	--H(19A)	..O(7)	[2655.01]	0.93	2.59	3.4618	157