Supplementary Material (ESI) for Chemical Communications

Supporting Information for B503371C

Spectroscopic and crystallographic evidences for the N-protonated $Fe^{I}Fe^{I}$ azadithiolate complex related to the active site of Fe-only hydrogenases

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Experimental Section

Instrumentation. Infrared spectra were recorded on a JASCO FT/IR 430 spectrophotometer. ^{1}H NMR spectra were collected on a Varian INOVA 400NMR instrument. Mass spectra were recorded on an HP1100 MSD mass spectrometer. Elemental analyses were performed on a THERMOQUEST-FLASH EA 1112 elemental analyzer.

Synthesis of $[\{(\mu\text{-}SCH_2)_2N(CH_2C_6H_4\text{-}2\text{-}Br)\}Fe_2(CO)_6]$ (1).[1-3] The starting compound $[2\text{-}BrC_6H_4CH_2N(CH_2Cl)_2]$ was prepared in 72% yield according to the literature procedure.[4] Super hydride $LiBEt_3H$ (1.0 M solution in THF, 2.0 mL, 2.0 mmol) was dropped into the degassed solution of $[(\mu\text{-}S_2)Fe_2(CO)_6]$ (344 mg, 1 mmol) in THF (50 mL) at –78 °C over 10 minutes.[2] *N*,*N*-di(chloromethyl)-2-bromobenzylamine (1.132 g, 4.0 mmol) was added to the green solution at 5-10 °C, causing an immediate change in color to red. After the reaction mixture was allowed to warm up to room temperature, the solvent was removed *in vacuo* and the resulting red solid was purified by column chromatography (silica, hexane as eluent). Product **1**, $[\{(\mu\text{-}SCH_2)_2N(CH_2C_6H_4\text{-}2\text{-}Br)\}Fe_2(CO)_6]$, was obtained in 34% yield (189 mg). IR (CH_3CN, cm^{-1}): ν(CO) 2073(m), 2034(s), 1997(s). ^{1}H NMR (CD_3CN): δ 7.55 (d, 1H, C_6H_4Br), 7.31 (t, 1H, C_6H_4Br), 7.23 (d, 1H, C_6H_4Br), 7.16 (t, 1H, C_6H_4Br), 4.01 (s, 2H, CH_2Ph), 3.73 (s, 4H, CH_2S). Anal. Calc. for $C_{15}H_{10}BrFe_2NO_6S_2$: C, 32.40; H, 1.81; N, 2.52. Found: C, 32.39; H,

1.97; N, 2.54.

Protonation of 1 to [{(μ-SCH_2)$_2$NH($CH_2C_6H_4$-2-Br)}$Fe_2(CO)_6$]$^+ClO_4^-$ [1(NH)].[5,6] To a solution of complex **1** (50 mg) in $CHCl_3$ (3 mL) was added 40 μL $HClO_4$. The solution was stirred for 10 min, The red solution turned to pale orange and a yellow orange solid was precipitated. The solvent was decanted and the solid was washed three times with hexane and dried *in vacuo*. The N-protonated product **1**(NH), [{(μ-SCH_2)$_2$NH($CH_2C_6H_4$-2-Br)}$Fe_2(CO)_6$]$^+ClO_4^-$, was obtained in 71% yield (25 mg). IR (CH_3CN, cm^{-1}): ν(CO) 2089(m), 2052(vs), 2016(m). ^{1}H NMR (CD_3CN): δ 7.73 (d, 1H, C_6H_4Br), 7.52 (t, 1H, C_6H_4Br), 7.47 (d, 1H, C_6H_4Br), 7.43 (t, 1H, C_6H_4Br), 4.54 (s, 2H, CH_2Ph), 4.19 (br, 2H, CH_2S), 3.37 (br, 2H, CH_2S). MS (API-ES): *m/z* 555.7 (M^+). Anal. Calc. for $C_{15}H_{11}BrClFe_2NO_{10}S_2$: C, 27.45; H, 1.69; N, 2.13. Found: C, 27.27; H, 1.79; N, 2.41.

Crystallography. The single crystal X-ray diffraction data for **1** and **1**(NH) were collected on an AFE5R Rigaku diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 293 K using the ω–2θ scan mode. Data processing was accomplished with the SAINT processing program.[7] Intensity data were corrected for absorption by the SADABS program.[8] The structure was solved by direct methods and refined on F^2 against full-matrix least-squares methods by using the SHELXTL97 program package.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by geometrical calculation, but their positions and thermal parameters were fixed during the structure refinement. The N(H) hydrogen was located in the difference map and refined.

References:

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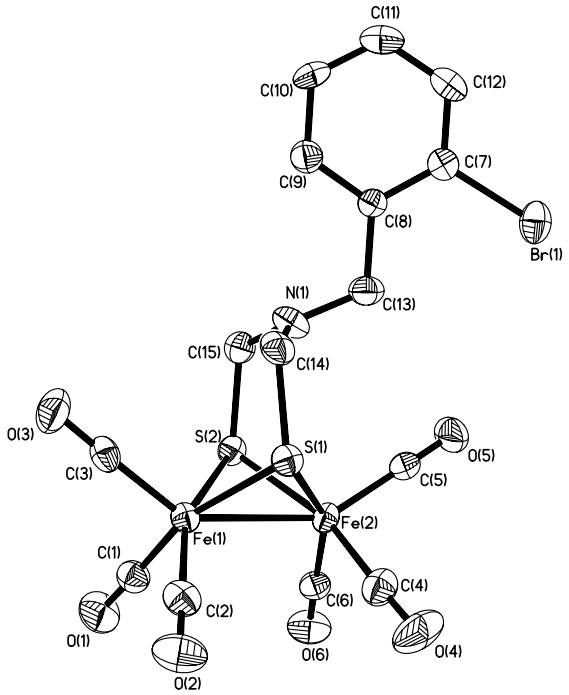
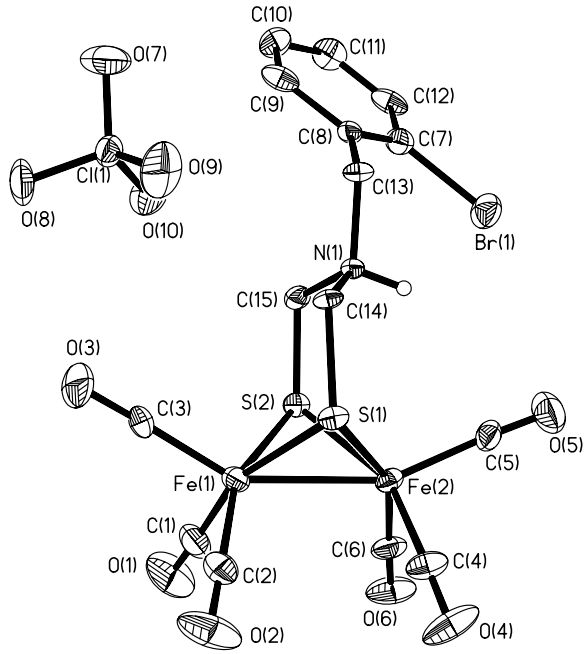


(a)



(b)

Molecular structures of (a) **1** and (b) **1**(NH) (ellipsoids at 30% probablility level).

Table 1. Crystallographic data and processing parameters for complexes **1** and **1**(NH)

Complex	**1**	**1**(NH)
Empirical formula	$C_{15}H_{10}BrFe_2NO_6S_2$	$C_{15}H_{11}BrClFe_2NO_{10}S_2$
M_w	555.97	656.43
T (K)	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*P*2 (1)/c
a (Å)	13.3549(9)	22.953(10)
b (Å)	14.8313(10)	6.611(3)
c (Å)	19.7845(11)	15.033(6)
α (°)	90.00	90.00
β (°)	90.00	104.63(3)
γ (°)	90.00	90.00
V (Å^3)	3918.7(4)	2207.2(16)
Z	8	4
ρ_{calc} (g cm^{-3})	1.885	1.975
F(000)	2192	1296
Crystal size (mm^3)	0.09 x 0.08 x 0.05	0.27 x 0.25 x 0.16
$\theta_{min/max}$ (°)	2.06/28.39	2.72/28.82
Reflns collected/unique	27109 / 4888	14151 / 5515

Parameters refined	244	290
Goodness-of-fit on F^2	0.786	0.961
Final $R1$ [$I > \sigma(I)$]	0.0403	0.0865
Final $wR2$	0.0607	0.1479
Residual electron density (e Å^{-3})	0.445 , -0.519	0.834 , -0.903

Table 2. Selected bond lengths (Å) and angles (°) for complexes **1** and **1**(NH)

Complex	**1**	**1**(NH)
Bond lengths		
Fe(1)-Fe(2)	2.5330(10)	2.498(2)
Fe(1)-S(1)	2.2539(13)	2.237(3)
Fe(1)-S(2)	2.2652(14)	2.244(3)
Fe(2)-S(1)	2.2622(14)	2.251(3)
Fe(2)-S(2)	2.2518(13)	2.257(3)
Fe(1)-C(1)	1.781(6)	1.831(13)
Fe(1)-C(2)	1.806(6)	1.767(11)
Fe(1)-C(3)	1.785(6)	1.781(10)
Fe(2)-C(4)	1.781(6)	1.782(11)
Fe(2)-C(5)	1.797(6)	1.810(11)
Fe(2)-C(6)	1.797(6)	1.787(11)
S(1)-C(14)	1.863(5)	1.819(7)
S(2)-C(15)	1.866(5)	1.813(8)
Br(1)-C(7)	1.905(5)	1.897(10)
N(1)-C(13)	1.462(6)	1.542(9)
N(1)-C(14)	1.416(6)	1.525(10)

N(1)-C(15)	1.420(5)	1.456(11)
Bond angles		
C(1)-Fe(1)-C(3)	99.0(2)	98.8(5)
C(1)-Fe(1)-C(2)	91.3(2)	90.3(5)
C(3)-Fe(1)-C(2)	101.3(2)	97.2(5)
C(1)-Fe(1)-S(1)	162.54(18)	159.8(4)
C(3)-Fe(1)-S(1)	98.40(15)	101.1(3)
C(2)-Fe(1)-S(1)	87.06(16)	90.3(3)
C(1)-Fe(1)-S(2)	89.48(16)	86.8(4)
C(3)-Fe(1)-S(2)	101.19(17)	105.3(3)
C(2)-Fe(1)-S(2)	157.12(18)	157.5(4)
S(1)-Fe(1)-S(2)	85.43(5)	84.95(9)
C(1)-Fe(1)-Fe(2)	107.63(18)	103.8(4)
C(3)-Fe(1)-Fe(2)	143.52(16)	149.4(3)
C(2)-Fe(1)-Fe(2)	102.60(18)	102.8(4)
S(1)-Fe(1)-Fe(2)	56.04(4)	56.44(7)
S(2)-Fe(1)-Fe(2)	55.64(4)	56.54(7)
C(4)-Fe(2)-C(5)	98.3(3)	97.8(5)
C(4)-Fe(2)-C(6)	91.9(2)	89.8(4)
C(5)-Fe(2)-C(6)	99.2(2)	95.2(5)
C(4)-Fe(2)-S(2)	162.2(2)	155.6(4)
C(5)-Fe(2)-S(2)	99.15(18)	106.6(3)
C(6)-Fe(2)-S(2)	88.84(15)	88.8(3)
C(4)-Fe(2)-S(1)	85.48(18)	86.5(3)
C(5)-Fe(2)-S(1)	108.89(18)	110.3(3)
C(6)-Fe(2)-S(1)	151.83(17)	154.5(4)
S(2)-Fe(2)-S(1)	85.54(5)	84.35(9)
C(4)-Fe(2)-Fe(1)	106.25(19)	100.4(4)
C(5)-Fe(2)-Fe(1)	148.95(18)	156.2(3)
C(6)-Fe(2)-Fe(1)	98.69(17)	100.2(4)
S(2)-Fe(2)-Fe(1)	56.14(4)	56.06(7)
S(1)-Fe(2)-Fe(1)	55.73(4)	55.93(7)
C(14)-S(1)-Fe(1)	108.34(16)	111.3(3)
C(14)-S(1)-Fe(2)	112.51(18)	113.9(3)
Fe(1)-S(1)-Fe(2)	68.23(4)	67.63(8)
C(15)-S(2)-Fe(2)	110.87(16)	113.7(3)
C(15)-S(2)-Fe(1)	110.29(17)	110.9(3)
Fe(2)-S(2)-Fe(1)	68.22(4)	67.63(8)
C(14)-N(1)-C(15)	117.8(4)	113.1(6)
C(14)-N(1)-C(13)	118.3(4)	105.8(6)
C(15)-N(1)-C(13)	121.7(4)	113.8(6)
C(12)-C(7)-Br(1)	118.5(4)	117.2(8)
C(8)-C(7)-Br(1)	119.7(4)	120.5(7)
C(13)-N(1)-H(1)		108.0

C(14)-N(1)-H(1)	108.0
C(15)-N(1)-H(1)	108.0

Table 3. Hydrogen bonds (Å) and angles (°) in **1**(NH)

D—H…A	d (D—H)	d (H…A)	d (D…A)	∠ (DHA)
N(1)—H(1)…O(8)*	0.91	2.20	2.826(9)	125.2
N(1)—H(1)…Br(1)	0.91	2.82	3.334(7)	117.2

* The O(8) is one of the oxygen in ClO_4^-.