

Supporting Information

Versatile Reactivity of a Solvent-Coordinated Diiron(II) Compound: Synthesis and Dioxygen Reactivity of a Mixed Valent Fe^{II}Fe^{III} Species

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Table S1. Selected distances (Å).[†]

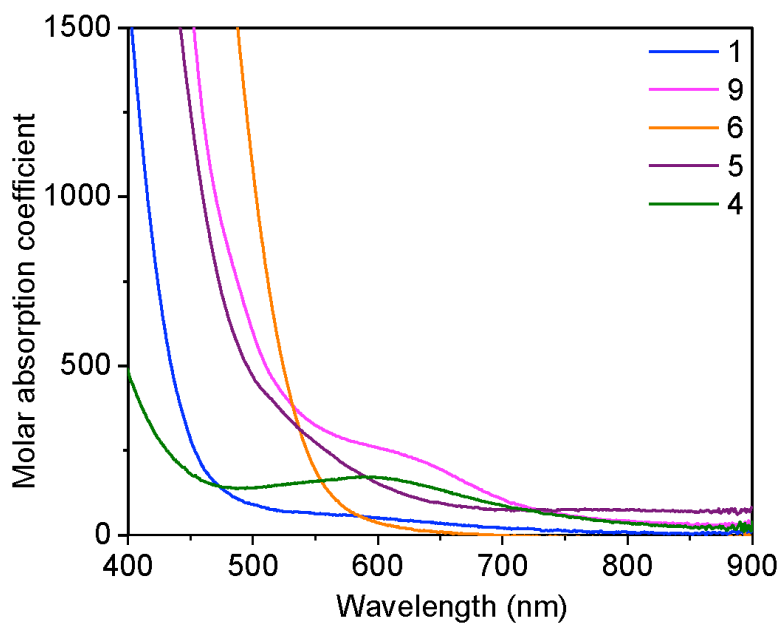
	Fe—Fe	Fe—O _{μ-COO⁻}	Fe—O _{μ-aqua}	Fe—O _{μ-OH}	Fe—O _{μ-O}	Fe—O _{DMF}	Fe—O _{Ligand}	Fe—N _{Ligand}
1	3.716	-----	-----	-----	-----	2.115(2) 2.373(2) 2.128(2) 2.21(3)	2.0121(19) 2.0626(19)	2.329(2) 2.163(3) 2.169(2) 2.300(2) 2.109(2) 2.187(2)
2	3.635	-----	-----	-----	-----	-----	1.997(2) 2.005(2)	2.287(2) 2.189(3) 2.136(3) 2.280(2) 2.138(3) 2.123(3)
3	3.500	2.029(4) 2.059(3)	-----	-----	-----	-----	1.954(4) 1.991(3)	2.293(4) 2.069(4) 2.066(4) 2.321(4) 2.070(5) 2.068(4)
4	3.453	2.0424(16) 2.0435(16)	-----	-----	-----	-----	1.9655(16) 1.9770(16)	2.0785(19) 2.3069(19) 2.065(2) 2.0765(19) 2.2930(19) 2.0468(19)
5[‡]	3.575 3.582	1.947(2) 2.069(2)	-----	-----	-----	2.037(2) 2.070(2)	1.929(2) 2.047(2)	2.269(2) 2.097(3) 2.104(2) 2.262(3) 2.160(3) 2.125(3) 2.267(3) 2.245(3)
6	3.774	-----	-----	-----	-----	2.051(2)	1.989(2) 2.104(2)	2.069(3) 2.138(3) 2.102(3) 2.100(3)
7	3.530 3.522 3.597 ^a 3.636 ^a 3.098 ^b 3.342 ^c	-----	-----	1.973(4) 2.004(4) 1.953(4) 1.994(4) 1.956(4) 2.171(4) 1.958(4) 2.068(4)	1.770(4) 1.829(4)	2.234(4) 2.113(4)	1.979(4) 1.989(4) 1.971(4) 2.024(4)	2.318(5) 2.111(6) 2.087(5) 2.327(5) 2.098(5) 2.084(6) 2.375(5) 2.117(5) 2.142(5) 2.358(5) 2.094(5) 2.138(5)
8	3.715 3.709 3.531 ^c 3.324 ^c 3.527 ^c	-----	1.972(3) 1.968(3)	-----	1.831(3) 1.955(3) 1.828(3) 1.832(3) 1.829(3) 1.955(3) 1.805(3) 1.812(3)	-----	1.999(3) 2.096(3) 2.002(3) 2.086(3)	2.300(4) 2.100(4) 2.179(4) 2.297(4) 2.162(4) 2.170(4) 2.300(4) 2.171(4) 2.103(4) 2.296(4) 2.161(4) 2.147(4)
9	3.571 3.573 3.359 ^c 3.553 ^c 3.418 ^c	-----	-----	-----	2.035(3) 1.903(3) 1.910(3) 1.895(3) 2.014(3)	-----	2.005(3) 2.016(3) 2.008(3) 2.024(3)	2.266(4) 2.157(4) 2.111(4) 2.304(4) 2.134(4) 2.134(4) 2.301(4) 2.149(4) 2.122(4) 2.271(4) 2.117(4) 2.157(4)
10^f	-----	-----	-----	-----	-----	-----	-----	2.144(2) 2.141(2) 2.297(3) 2.141(2) 2.144(2) 2.297(3)
11	3.575	2.065(12) ^d 2.058(5) ^e	-----	-----	-----	-----	1.993(4) 2.004(4)	2.348(5) 2.086(4) 2.096(5) 2.327(5) 2.061(6) 2.068(4)
12	3.595	-----	-----	1.823(3) 1.817(3)	-----	2.028(3) 2.081(7)	1.979(3) 2.002(3)	2.262(3) 2.113(4) 2.074(3) 2.273(4) 2.090(4) 2.096(4)

a, mono hydroxo bridged; b, di hydroxo bridged; c, oxo bridged; d, acetamide O; e, acetamide N; f, Fe—N_{Ligand} distances made equal by symmetry. † Fe—N(MeCN) distances (Å) in **2** = 2.227(3), 2.117(3), 2.241(3), 2.114(3); Fe—Cl distances (Å) in **6** = 2.2459(9), 2.2205(9), 2.3603(10). ‡ **5** contains two independent molecules with slightly different bond distances in its asymmetric unit. Distances for one of them are shown here.

Table S2. Selected Angles (Deg).

	Fe—O—Fe	Fe—O _{μ-OH} —Fe	Fe—O _{μ-O} —Fe
1	131.56(10)	-----	-----
2	130.54(9)	-----	-----
3	125.09(18)	-----	-----
4	122.31(8)	-----	-----
5	128.06(10)	-----	-----
	128.15(10) [†]	-----	-----
6	134.46(11)	-----	-----
		132.2(2)	
7	125.7(2)	131.4(2)	136.5(2)
	123.7(2)	97.17(17)	
		100.60(18)	
8	130.23(15)	-----	137.65(16)
	130.27(15)		130.53(18)
			137.55(17)
			136.46(18)
9	125.25(15)	-----	131.09(14)
	124.77(14)		127.42(15)
			130.63(14)
11	126.87(18)	-----	
12	129.12(15)	-----	-----

[†]5 contains two independent molecules with slightly different bond distances in its asymmetric unit.

**Figure S1.** Electronic absorption spectroscopic signatures for selected compounds.

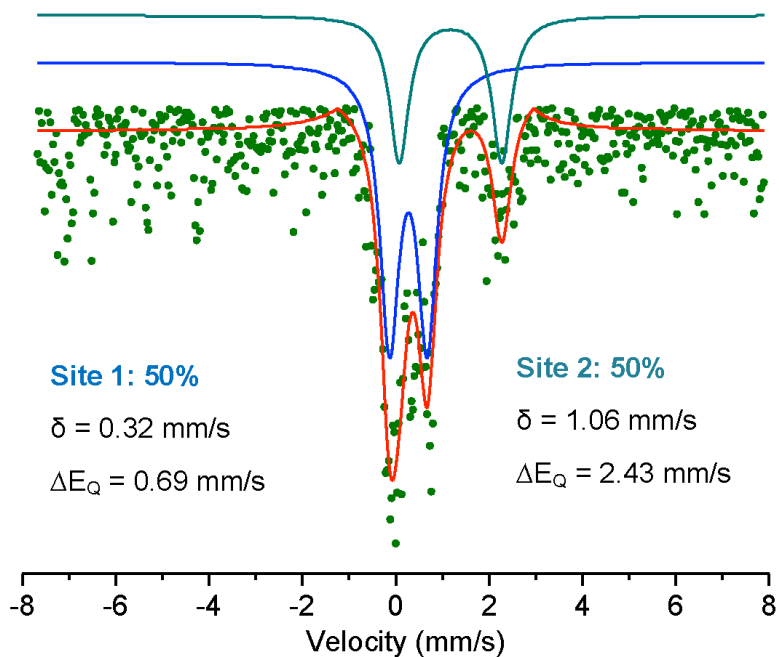


Figure S2. ^{57}Fe Mössbauer spectra of **5** at r.t.

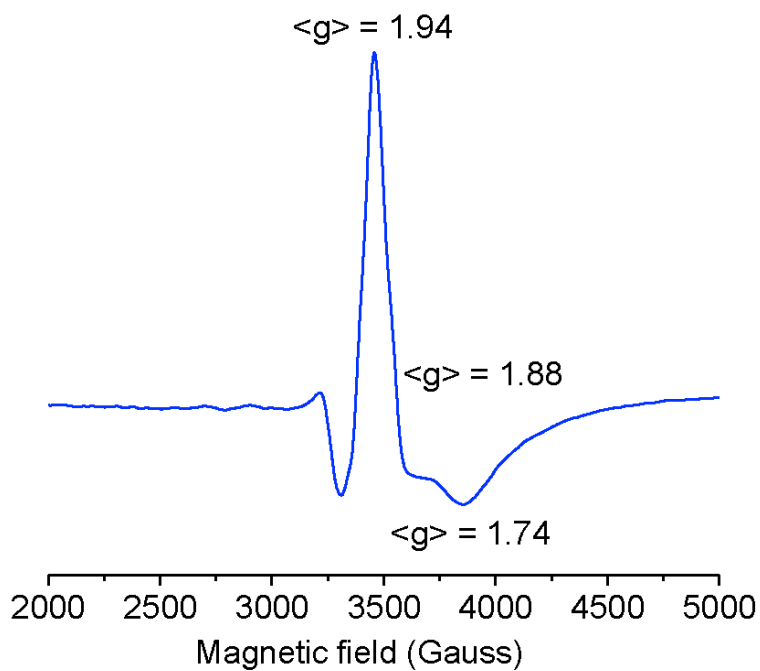


Figure S3. EPR spectra of **5** in DMF/MeCN (1:1) at 4K. Conditions: [**5**] = 0.2 mM, 9.39 GHz MW frequency, 20 mW micro-wave power, 10 G modulation amplitude, and 0.2 s time constant.