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A combined experimental and computational study on the sulfoxidation by high-valent iron bispidine complexes

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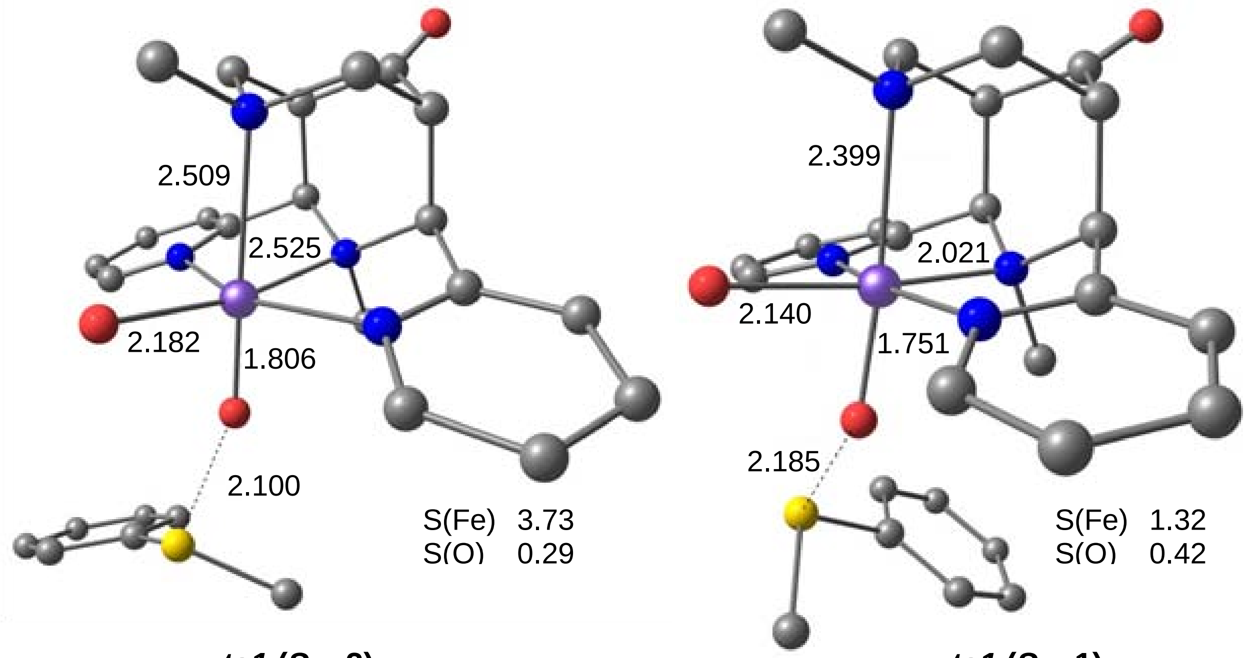
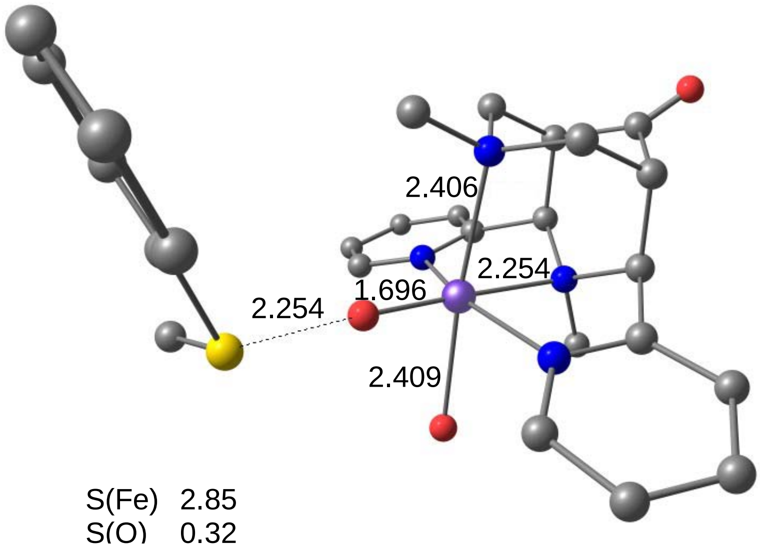
Supplementary Information

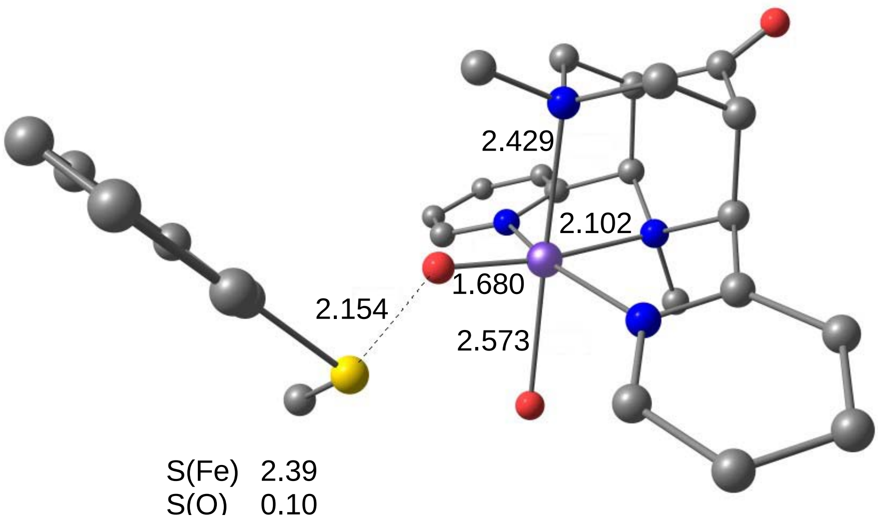


***ts1* (*S* = 2)** ***ts1* (*S* = 1)**

Figure S1. Transition states for the oxo-transfer step on the *S* = 2 and *S* = 1 surfaces of $[(L^1)Fe^{IV}{=}O(OH_2)]^{2+}$, *trans*-N7 isomer; distances in Å.



***ts1* (*S* = 2)**



***ts1* (*S* = 1)**

Figure S2. Transition states for the oxo-transfer step on the *S* = 2 and *S* = 1 surfaces of $[(L^1)Fe^{IV}{=}O(OH_2)]^{2+}$, *trans*N3 isomer, distances in Å.

Table S1. Selected geometric parameters (bond distances in Å, angles in deg) and spin densities for the *ts1*, *int*, *ts2*, and the products of $1_{transN7,}$ $1_{transN3}$ and 2 in the S = 2 and S = 1 spin states.

Species	Geometrical Parameters						Spin Denisty	
	Fe-N7	Fe-N3	Fe-O	Fe-OH_2	O-S	Fe-O-S	S(Fe)	S(O)
			$[(L^1)Fe^{IV}{=}O(H_2O)]^{2+}$ ($1_{transN3}$) + PhMeS					
ts1 (S=2)	2.41	2.13	1.70	2.41	2.25	168.3	2.85	0.32
ts1 (S=1)	2.43	2.10	1.68	2.54	2.15	133.2	2.39	0.10
int (S=2)	2.35	2.26	2.02	2.33	1.58	130.4	3.73	0.06
int (S=1)	2.45	2.06	2.02	2.45	1.57	130.8	2.00	0.01
			$[(L^1)Fe^{IV}{=}O(H_2O)]^{2+}$ ($1_{transN7}$) + PhMeS					
ts1 (S=2)	2.51	2.25	1.81	2.18	2.10	145.6	3.73	0.29
ts1 (S=1)	2.39	2.02	1.75	2.14	2.19	142.3	1.32	0.42
int (S=2)	2.36	2.26	2.21	2.19	1.57	135.1	3.74	0.03
int (S=1)	2.43	2.05	2.33	2.13	1.57	137.5	1.99	0.02
			$[(L^2)Fe^{IV}{=}O]^{2+}$ (2) + PhMeS					
ts1 (S=2)	2.45	2.26	1.88	-	2.04	132.5	3.72	0.19
ts1 (S=1)	2.38	2.05	1.76		2.11	142.7	1.37	0.04
int (S=2)	2.39	2.24	2.12	-	1.57	133.2	3.73	0.04
int (S=1)	2.46	2.07	2.20		1.56	133.8	1.98	0.03
ts2 (S=2)	2.30	2.22	3.29	3.51	1.56	154.7	3.73	0.001
pro (S=2)	2.36	2.25	3.88	2.15	-	-	3.74	0.0007