

SUPPORTING INFORMATION

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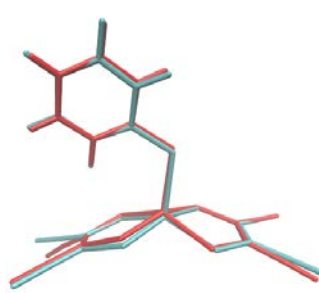
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Table S1. $\Delta E_{IS/HS}$ (kcal/mol) between the S=3/2 and S=5/2 state of complex **1** using different exchange-correlation functionals and the def2-TZVP basis set.

Exchange-correlation functional	$\Delta E_{IS/HS}$ [a]
B3LYP (c ₃ =0.00)	16.32
BP86	15.12
BLYP	12.82
B3LYP (c ₃ =0.05)	12.42
B3LYP** (c ₃ =0.10)	8.83
TPSSh (HF=10%)	8.41
B3LYP* (c ₃ =0.15)	5.57
B3LYP (c ₃ =0.20)	2.62
B3LYP (c ₃ =0.25)	-0.05
B3LYP (c ₃ =0.30)	-2.43

[a] A positive value of $\Delta E_{IS/HS}$ indicates that the intermediate-spin state (S=3/2) is lower than the high-spin state (S=5/2).

Table S2. Relevant spin state-dependent structural parameters of complex **1**.

Calculation	Structural parameters	X-ray structure [1]	Intermediate Spin S=3/2	Superposition of X-ray and optimized structure
B3LYP**, c ₃ =0.10/ def2-TZVP	Distances			
	Fe-S _{eq} [a]	2.27 Å	2.28 Å	
	Fe-S _{ax}	2.36 Å	2.42 Å	
	S ₁ ...H ₁₀	3.14 Å	3.00 Å	
	S ₂ ...H ₁₀	2.91 Å	3.19 Å	
	Angles			
	<(Fe-mnt1) [b]	88.8°	87.8°	
	<(Fe-mnt2) [c]	85.6°	87.7°	
	<(Fe-plane) [d]	152.4°	155.6°	
	<(S _{eq} -S _{ax}) [e]	103.7°	102.2°	
	<(Fe-S ₅ -C ₉)	113.7°	117.5°	
	Torsional Angles			
	<(S ₁ -Fe-S ₅ -C ₉)	66.8°	54.3°	
	<(S ₂ -Fe-S ₅ -C ₉)	0.0°	-9.7°	
<(Fe-S ₅ -C ₉ -C ₁₀)	336.2°	336.7°		
RMSD [f]	-	0.28 Å		

[a] Averaged over all equatorial Fe-S bonds. [b] Averaged over the bond angles S-Fe-S of each mnt ligand. [c] Averaged over the bond angles S-Fe-S of opposite mnt ligands. [d] Averaged over the bond angles S-Fe-S forming the plane. [e] Averaged over the bond angles each S_{eq}-Fe-S_{ax}. [f] The root mean square deviation (RMSD) was calculated from the superposition of X-ray and optimized structure.

Table S3. Expectation values of the $\langle \hat{S}^2 \rangle$ operator in dependency of the amount of exact Hartree-Fock exchange for B3LYP (c_3), the hybrid TPSSh functional and pure BP86 functional (def2-TZVP).

Spin state	BP86	B3LYP						TPSSh	exact
		$c_3=0.05$	$c_3=0.10$	$c_3=0.15$	$c_3=0.20$	$c_3=0.25$	$c_3=0.30$		
S=1/2	0.78	0.78	0.88	1.10	1.27	1.39	1.49	1.20	0.75
S=3/2	3.81	3.82	3.83	3.85	3.87	3.91	3.96	3.85	3.75
S=5/2	8.77	8.77	8.77	8.77	8.78	8.78	8.78	8.77	8.75

The deviation of $\langle \hat{S}^2 \rangle$ is a measure for the ability of the DFT to describe the electronic structure in a single determinant. For a pure S=1/2, S=3/2, and S=5/2 spin state, $\langle \hat{S}^2 \rangle$ values of 0.75, 3.75, and 8.75 were expected.^[2] For DFT calculations employing the BP86 functional $\langle \hat{S}^2 \rangle$ takes values which are almost identical to the exact expectation value (Table S3). For B3LYP with 20% of HF exchange, $\langle \hat{S}^2 \rangle$ is found to be 1.27, 3.87, and 8.78. Our findings show that spin contamination strongly depends on the exchange-correlation functional. For the pure functional and functionals with only small exact HF exchange ($c_3 \leq 0.05$), the spin contamination is only minor and justifies the choice of method to calculate the electronic structure of complex **1**. Studies for organic molecules revealed that less than 10 % deviation from the exact value renders spin contamination to be negligible.^[3] Using the B3LYP** functional the deviation of $\langle \hat{S}^2 \rangle$ from the exact value is 17.3 % for the S=1/2 state. This is slightly above the critical value of 10 % deviation but significantly smaller than the spin contamination for the TPSSh functional that reaches 60 % deviation for the low-spin state. However, original B3LYP calculations are also affected by spin contamination. The low-spin state is contaminated by higher spin states in an inadmissible extent. Similar observations were reported in studies examining the molecular geometry and spin state preference of penta-coordinate low-spin iron(III) complexes modelling the nitrile hydratase.^[4]

Table S4. Relative energies (in kcal/mol) and corresponding torsion angles θ for the S=1/2 and S=3/2 states using the BP86/B3LYP functional and COSMO where indicated.

θ	S=1/2			S=3/2		
	BP86/def2-TZVP	BP86/def2-TZVP + COSMO	B3LYP/def2-TZVP	BP86/def2-TZVP	BP86/def2-TZVP + COSMO	B3LYP/def2-TZVP
0 [a]	0.0	0.0	0.0	0.0	0.0	0.0
15	0.0	-0.5	-0.1	0.2	0.2	0.0
30	-0.5	-0.7	-0.1	1.0	0.8	0.6
45	-1.9	-1.9	-1.2	2.1	2.0	1.3
60	-3.0	-2.8	-2.0	2.9	3.0	1.5
75	-3.3	-3.0	-2.1	3.5	3.9	1.7
90	-2.8	-2.7	-1.8	3.6	4.0	1.8
105	-1.5	-1.6	-0.8	3.0	3.0	1.6
120	-0.2	-0.6	-0.1	2.4	2.3	1.4
135	0.0	-0.4	0.7	1.2	1.2	1.3
150	0.6	1.6	0.9	0.4	0.2	0.2
165	0.3	0.7	0.0	0.0	0.4	0.3
180	0.0	0.0	0.0	0.0	0.0	0.0

[a] $\theta = 0$ corresponds to the angle found in the X-ray structure and the calculated energies are relative to the energies calculated for the optimized structures.

Table S5. Atomic partial charges derived from a natural population analysis (B3LYP**, def2-TZVP).

Complex	Atom	Partial charge		
		S=1/2	S=3/2	S=5/2
1	Fe	+0.14	+0.43	+0.87
	S ₁	0.00	-0.07	-0.17
	S ₂	0.00	-0.02	-0.15
	S ₃	0.00	-0.03	-0.15
	S ₄	0.00	-0.06	-0.16
	S ₅	-0.03	-0.21	-0.22
3	Fe	+0.08	+0.55	+0.99
	S ₁	+0.04	-0.09	-0.14
	S ₂	+0.04	0.00	-0.14
	S ₃	+0.04	0.00	-0.15
	S ₄	+0.04	-0.09	-0.15
	C ^L	+0.11	-0.13	-0.21
	N ^L	-0.55	-0.53	-0.50
4	Fe	-0.11	+0.38	+0.82
	S ₁	+0.11	-0.01	-0.10
	S ₂	+0.11	-0.01	-0.11
	S ₃	+0.11	-0.01	-0.11
	S ₄	+0.11	0.00	-0.10
	C ^L	+0.25	+0.25	+0.25
	O ^L	-0.47	-0.43	-0.42

^L The carbon and nitrogen or oxygen atom, respectively, are part of the axial ligand

Table S6. Gibbs free energy differences ΔG (298 K) of **1** in kcal/mol as a function of HF exchange.

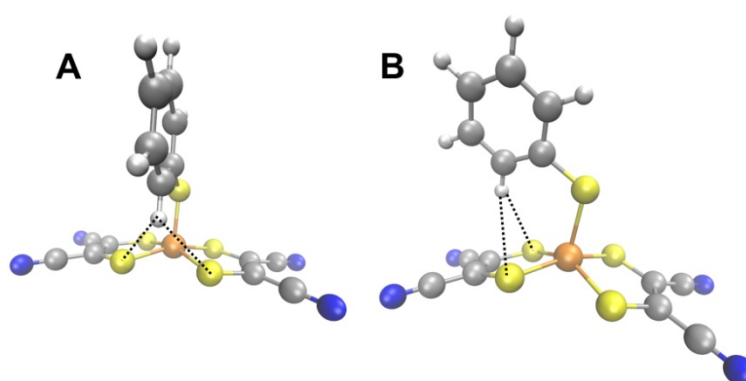
Spin state	$c_3=0.00$	$c_3=0.10$	$c_3=0.12$	$c_3=0.15$	$c_3=0.20$
S=1/2	+1.7	+7.7	+8.8	+10.4	+12.6
S=3/2	0	0	0	0	0
S=5/2	+13.9	+7.2	+5.9	+4.2	+1.6

Table S7. Relative energies $\Delta E(0\text{ K})$ and Gibbs free energy differences $\Delta G(298\text{ K})$ in kcal/mol between the global minima structures of the different spin states.

Spin state	BP86		BP86-D3		B3LYP**		B3LYP	
	$\Delta E(0\text{ K})$	$\Delta G(298\text{ K})$	$\Delta E(0\text{ K})$	$\Delta G(298\text{ K})$	$\Delta E(0\text{ K})$	$\Delta G(298\text{ K})$	$\Delta E(0\text{ K})$	$\Delta G(298\text{ K})$
S=1/2	0	0	0	0	3.9	5.4	+10.0	+13.2
S=3/2	+2.2	+0.3	+1.2	+0.2	0	0	0	0
S=5/2	+17.3	+13.7	+15.9	+12.7	8.8	7.3	+2.6	+1.6

Table S8. Influence of temperature on entropic and enthalpic differences between the low-spin (LS) and high-spin (HS) states (def2-TZVP/B3LYP**) of complex **1**.

	0 K	10 K	50 K	100 K	200 K	298 K
$\Delta G_{(LS/HS)}$ (kcal/mol)	+1.4	+1.4	+1.3	+1.0	+0.3	-0.5
$\Delta S_{(LS/HS)}$ (kcal/(mol·K))	-	$6 \cdot 10^{-4}$	$4 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	$8 \cdot 10^{-3}$	$8 \cdot 10^{-3}$
$\Delta H_{(LS/HS)}$ (kcal/mol)	+1.4	+1.4	+1.5	+1.7	+1.9	+2.0

Figure S1. Structures of the global energy minima in the **A**) S=1/2 and **B**) S=3/2 state (BP86/def2-TZVP). The CH...S distances are 2.74 Å and 2.77 Å for the low-spin state and 2.93 Å and 3.14 Å for the intermediate-spin state.

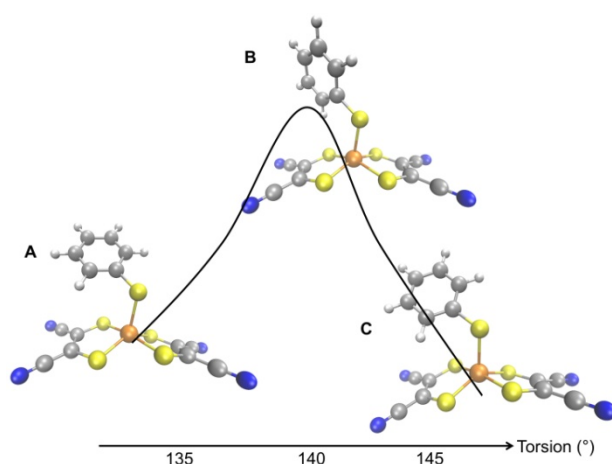


Figure S2. Detailed view on the displacement of the thiophenolate ligand at the end of the 180° torsion which is accompanied by a significant fluctuation of the complex potential energy in all calculations.

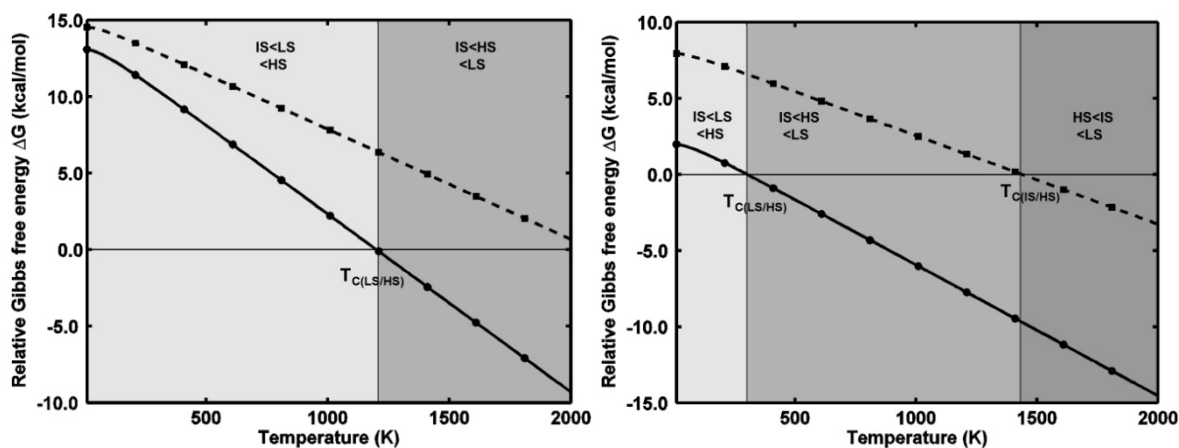


Figure S3. Spin transitions and critical temperatures T_C . The Gibbs free energy differences $\Delta G_{LS/HS}$ (solid line) and $\Delta G_{IS/HS}$ (dashed line) as a function of temperature are shown for the BP86 (left) and TPSSh functionals (right).

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- [2] G. D. Purvis, H. Sekino, R. J. Bartlett, *Collect. Czech. Chem. Commun.* **1988**, *53*, 2203-2213.
- [3] A. J. Boone, C. H. Chang, S. N. Greene, T. Herz, N. G. J. Richards, *Coord. Chem. Rev.* **2003**, *238*, 291-314.
- [4] C. H. Chang, A. J. Boone, R. J. Bartlett, N. G. J. Richards, *Inorganic Chemistry* **2004**, *43*, 458-472.