Supplementary Material

Accurate calculations of geometries and singlet–triplet energy differences for active-site models of [NiFe] hydrogenase

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Table S1. Ni–S and S–H bond lengths in the optimised structures of $[Ni(SH)_4]^{2-}$ in the singlet (top) and triplet (bottom) states in pm. For CASPT2 the actual values are given, whereas for the DFT methods, errors compared to the CASPT2 results are listed (a negative sign indicates that the DFT distances are too short). MUE is the mean unsigned error.

	Ni-S		S-H		MUE
Singlet					
CASPT2[a]	221.0	221.0	134.0	134.0	
SVWN	-2.1	-2.1	2.4	2.4	2.2
BP86[a]	4.0	4.0	2.0	2.0	3.0
BP86	5.7	5.7	2.0	2.0	3.8
BP86-D	6.0	6.0	1.9	1.9	3.9
BLYP	10.5	10.5	1.9	1.9	6.2
PBE	5.3	5.3	2.0	2.0	3.7
TPSS	5.8	5.8	1.3	1.3	3.5
B97-D	10.1	10.1	1.0	1.0	5.5
M06-L[a]	6.4	6.4	0.3	0.3	3.3
M06[a]	5.6	5.6	0.6	0.7	3.1
TPSSH	6.0	6.0	0.8	0.8	3.4
B3LYP[a]	8.2	8.2	0.5	0.5	4.4
B3LYP	9.7	9.7	0.6	0.7	5.2
B3LYP-D	10.0	10.0	0.5	0.5	5.2
PBE0	5.8	5.8	0.5	0.5	3.2
BHLYP	11.4	11.4	-0.7	-0.7	6.1
Triplet					
CASPT2[a]	233.5	233.5	133.9	133.9	
SVWN	-10.4	-4.4	2.3	1.9	4.7
BP86[a]	-0.8	-0.8	1.8	1.8	1.3
BP86	-0.5	5.0	1.7	1.7	2.2
BP86-D	-1.6	4.7	1.7	1.6	2.4
BLYP	4.1	10.1	1.7	1.7	4.4
PBE	-0.9	4.8	1.8	1.7	2.3
TPSS	0.5	5.6	1.1	1.1	2.0
B97-D	1.8	9.4	0.9	0.9	3.3
M06-L[a]	1.5	1.5	0.3	0.3	0.9
M06[a]	-0.6	-0.6	0.9	0.9	0.7
TPSSH	1.8	6.5	0.6	0.6	2.4
B3LYP[a]	4.4	4.4	0.7	0.7	2.6
B3LYP	5.1	10.1	0.6	0.7	4.1
B3LYP-D	4.1	9.1	0.5	0.6	3.6
PBE0	2.7	6.7	0.4	0.5	2.6
BHLYP	8.2	11.6	-0.6	-0.5	5.2

[a] Calculated with the MOLCAS software.

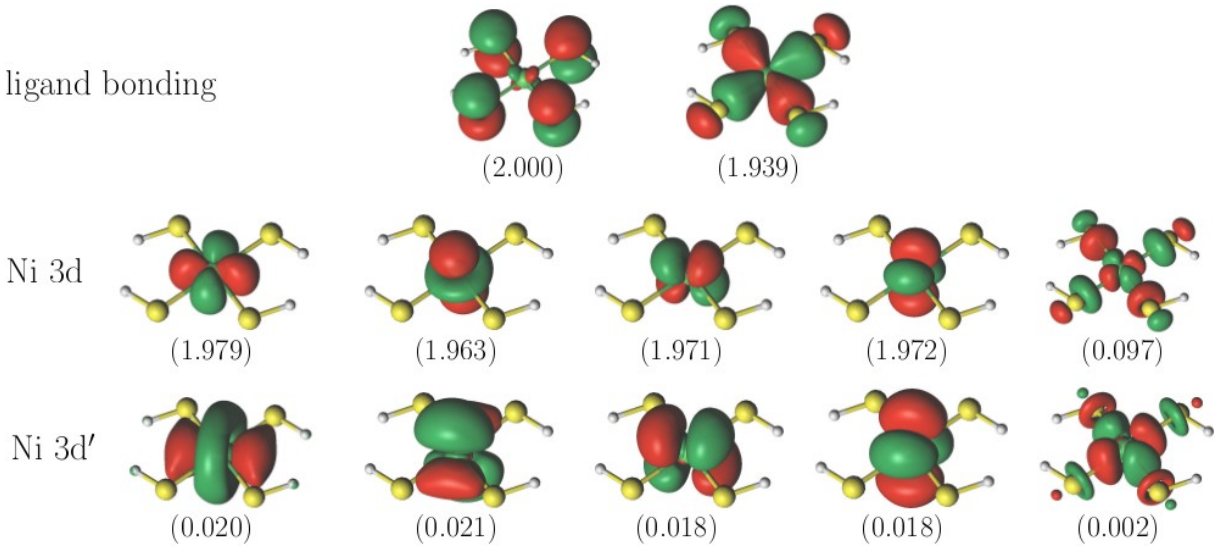
Table S2. Symmetry-distinct bond lengths in the optimised structures of the NiFe $[(SH)_2Ni(SH)_2Fe(CO)(CN)_2]^{2-}$ model in the singlet (top) and triplet (bottom) states in pm (C_s symmetry).

Method	Fe–CN	Fe–CO	Fe–Ni	Fe–S1	Ni–S1	Ni–S2	Ni–S4	C–N	C–O	S1–H1	S2–H2	S4–H4	φ
Singlet													
SVWN	185.0	165.8	272.1	220.8	215.6	216.7		117.2	117.0	136.9	136.0		4.9
BP86[a]	189.2	168.3	288.3	227.0	220.8	222.0		117.2	116.8	136.4	135.9		5.0
BP86	189.8	168.9	289.2	228.1	222.1	223.3		117.8	117.7	136.1	135.7		4.4
BP86-D	189.7	169.1	287.4	228.3	222.2	223.1		117.8	117.7	135.9	135.6		3.4
BLYP	192.7	170.7	299.2	233.1	226.5	227.2		117.7	117.8	135.9	135.6		4.0
PBE	189.5	168.7	286.9	227.6	221.7	222.9		117.9	117.7	136.2	135.7		4.3
TPSS	191.1	169.8	287.2	228.3	222.0	223.0		117.5	117.3	135.2	135.0		4.2
B97-D	191.1	169.0	302.8	232.2	225.2	226.3		117.5	117.4	134.9	134.8		2.8
M06-L[a]	191.0	169.4	284.8	230.0	222.8	223.1		116.5	115.6	134.6	134.2		4.0
M06[a]	192.5	171.7	303.0	229.2	224.3	222.3		115.6	114.2	135.1	134.8		2.2
TPSSH	191.8	170.0	300.4	229.1	222.7	222.9		116.9	116.2	134.6	134.6		3.3
B3LYP[a]	192.7	170.4	309.4	232.1	226.4	224.2		115.8	114.8	135.1	134.9		2.0
B3LYP	193.8	171.8	318.6	233.3	227.6	225.6		116.3	115.3	134.5	134.6		2.5
B3LYP-D	193.8	172.1	315.2	233.3	227.6	225.6		116.3	115.3	134.3	134.5		1.7
PBE0	191.3	170.1	310.1	229.1	223.7	222.3		116.3	115.0	134.4	134.4		2.3
BHLYP	199.0	183.6	331.2	237.7	231.8	226.3		114.9	112.1	133.0	133.2		0.9
Triplet													
SVWN	184.9	166.2	268.8	221.8	223.1	221.8	218.8	117.2	117.0	136.5	135.9	136.3	90
BP86[a]	188.6	167.6	308.4	229.5	232.4	228.9	224.3	117.2	116.7	136.1	135.7	135.8	90
BP86	189.3	168.3	307.5	230.3	234.1	230.0	225.4	117.8	117.6	135.9	135.6	135.7	90
BP86-D	189.3	168.5	305.6	230.8	233.5	229.2	224.7	117.8	117.6	135.7	135.5	135.7	90
BLYP	192.2	170.0	321.5	235.5	239.7	234.5	229.0	117.7	117.6	135.7	135.6	135.8	90
PBE	189.0	168.1	304.3	229.8	233.6	229.6	225.1	117.9	117.6	136.0	135.6	135.8	90
TPSS	190.7	169.2	309.2	230.8	235.0	230.6	226.2	117.5	117.2	135.1	134.9	135.1	90
B97-D	190.6	168.4	315.7	234.8	237.5	232.4	227.8	117.5	117.3	134.8	134.8	135.0	90
M06-L[a]	190.6	168.9	313.9	233.7	237.8	231.3	225.9	116.5	115.4	134.3	134.1	134.3	90
M06[a]	192.2	171.6	312.5	231.5	236.1	230.1	224.7	115.6	114.1	134.6	134.7	134.8	90
TPSSH	191.3	169.8	318.2	231.5	237.5	231.2	227.9	116.9	116.1	134.5	134.5	134.7	90
B3LYP[a]	192.8	171.2	331.1	234.9	240.2	232.4	230.3	115.8	114.5	134.7	134.7	134.9	90
B3LYP	193.5	171.9	329.5	236.1	242.5	233.7	231.2	116.3	115.2	134.4	134.5	134.7	90
B3LYP-D	193.5	172.2	324.0	236.2	241.1	232.9	230.5	116.3	115.2	134.3	134.4	134.7	90
PBE0	190.9	170.3	321.3	231.7	239.3	231.0	229.2	116.3	114.9	134.4	134.3	134.5	90
BHLYP	200.8	198.2	338.1	242.7	245.9	235.4	235.7	114.9	111.7	133.1	133.3	133.5	90

[a] Calculated with the MOLCAS software.

Figure S1. Active natural orbitals and their occupation number resulting from the CAS(12,12) calculation on the (a) singlet and (b) triplet states of $[Ni(SH)_4]^{2-}$.

(a) singlet



(b) triplet

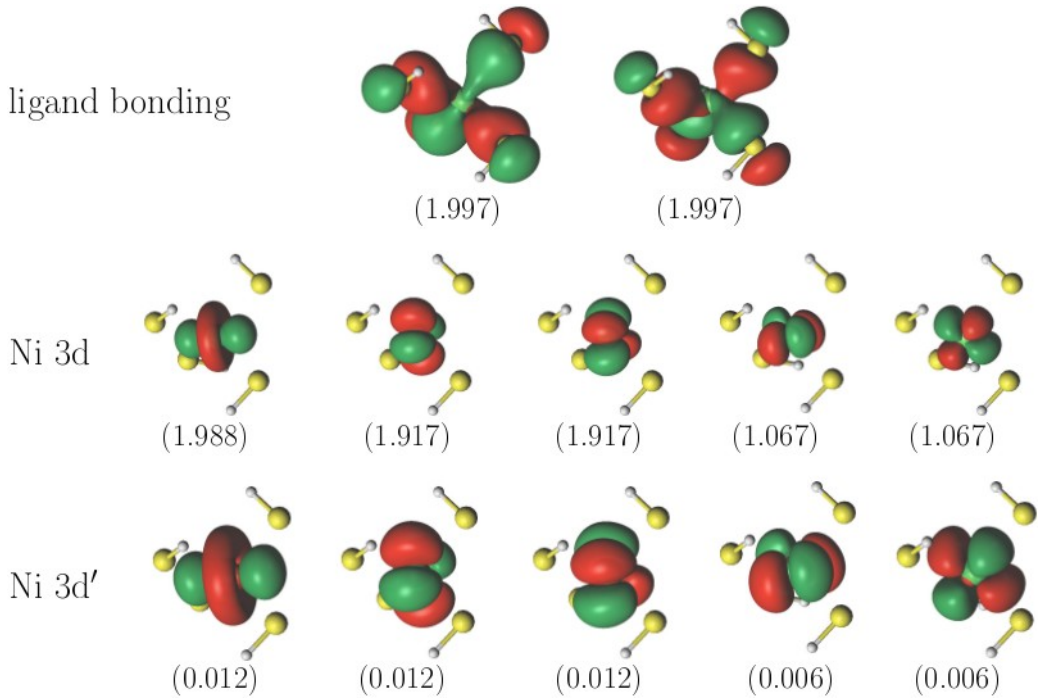
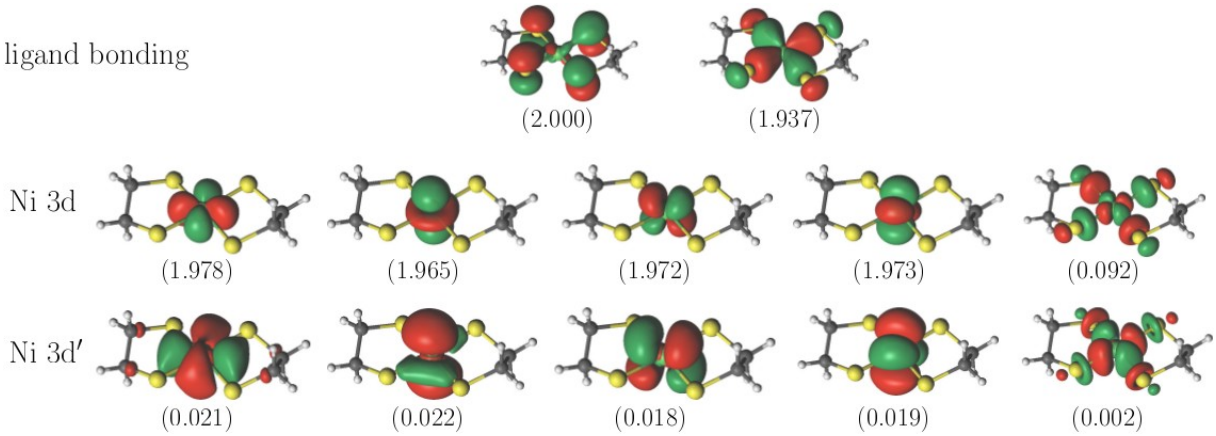


Figure S2. Active natural orbitals and their occupation number resulting from the CAS(12,12) calculation on the (a) singlet and (b) triplet states of $[Ni(edt)_2]^{2-}$.

(a) singlet



(b) triplet

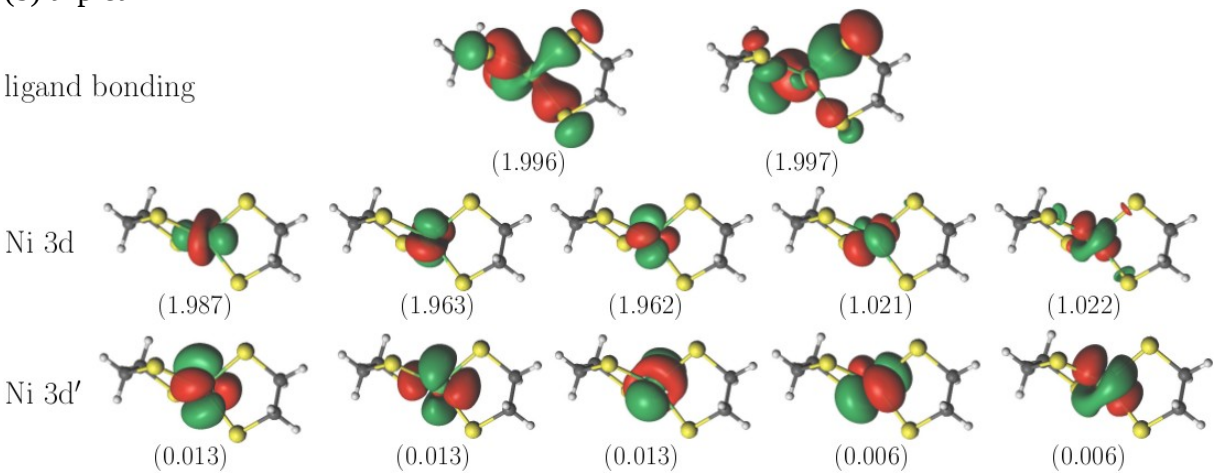


Figure S3. Active natural orbitals and their occupation number resulting from the RAS(20,4,4;9,2,10) calculation on the triplet state of $[(SH)_2Ni(SH)_2Fe(CO)(CN)_2]^{2-}$.