Supplementary Material

How Metal Nuclearity Impacts Electrocatalytic H_2 Production in Thiocarbohydrazone-Based Complexes

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1. Synthesis and NMR Characterization

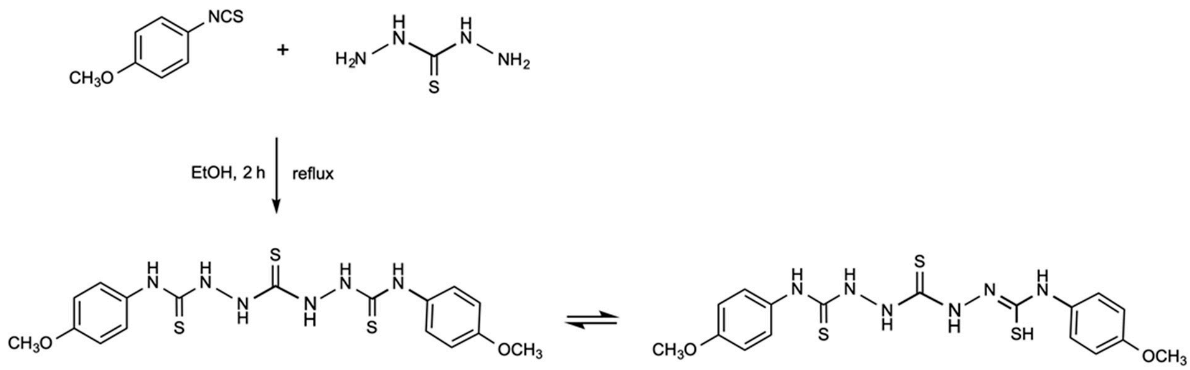


Figure S1. Synthetic protocol used for **H_6L**.

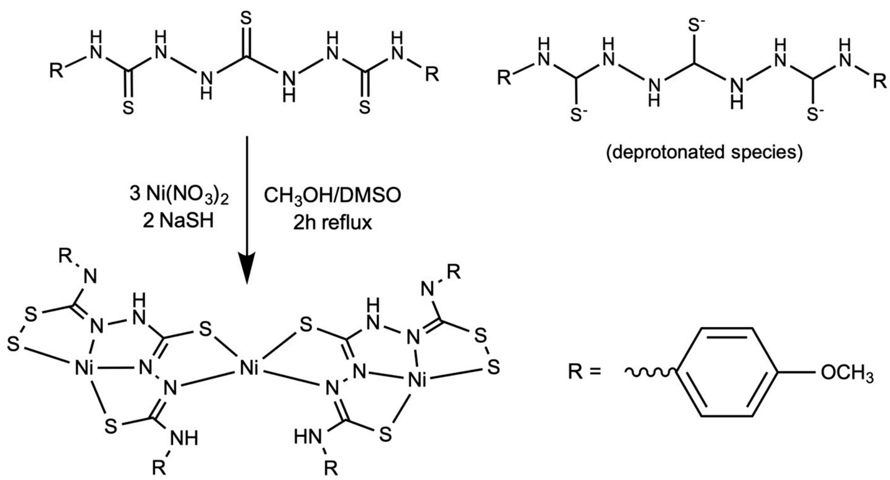


Figure S2. Synthetic protocol used for **Ni_3L_2**.

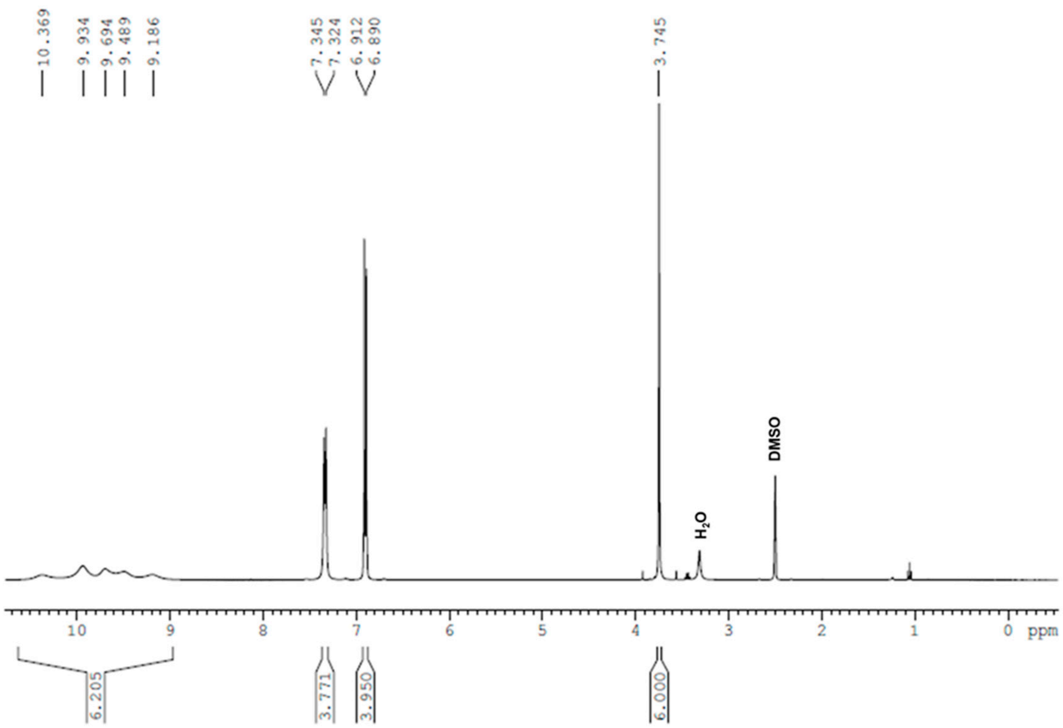


Figure S3. [1]H NMR spectrum and partial assignment for **H_6L** in DMSO at 298 K.

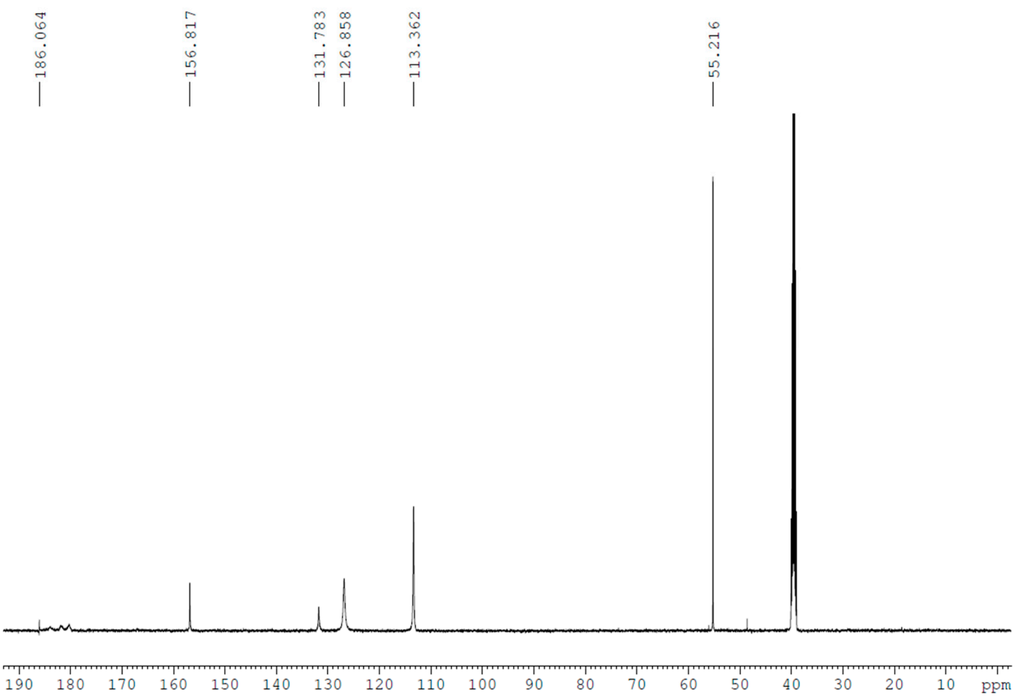


Figure S4. [13]C NMR spectrum and partial assignment for **H_6L** in DMSO at 298 K.

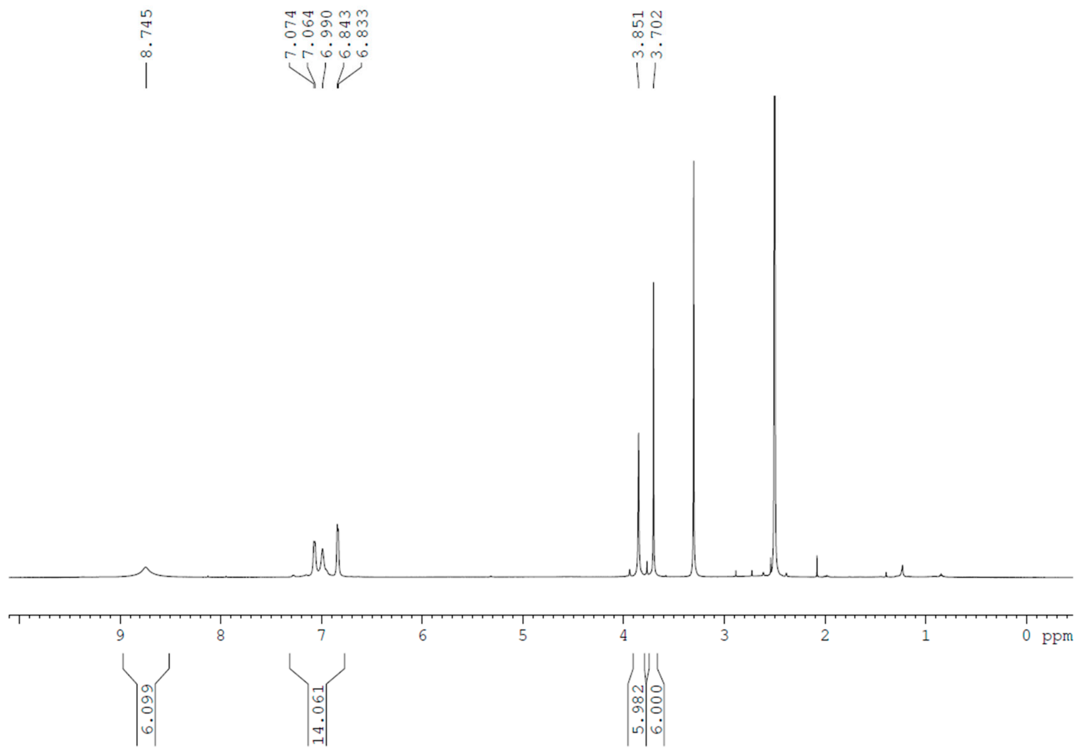


Figure S5. ^{1}H NMR spectrum and partial assignment for **Ni_3L_2** in DMSO at 298 K.

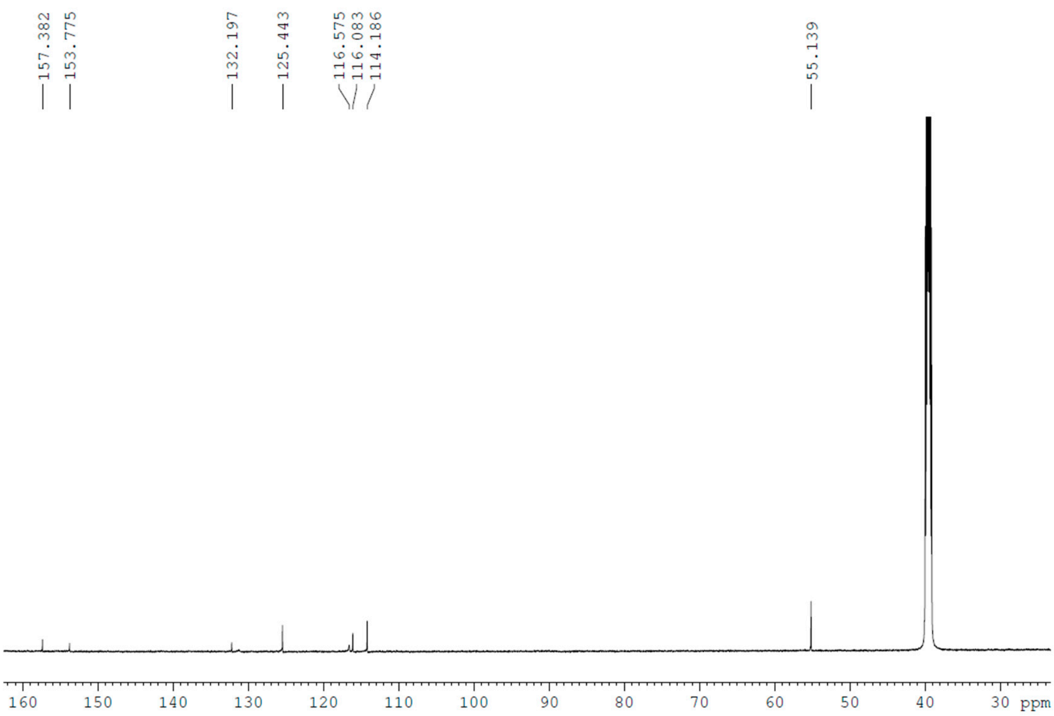


Figure S6. ^{13}C NMR spectrum and partial assignment for **Ni_3L_2** in DMSO at 298 K.

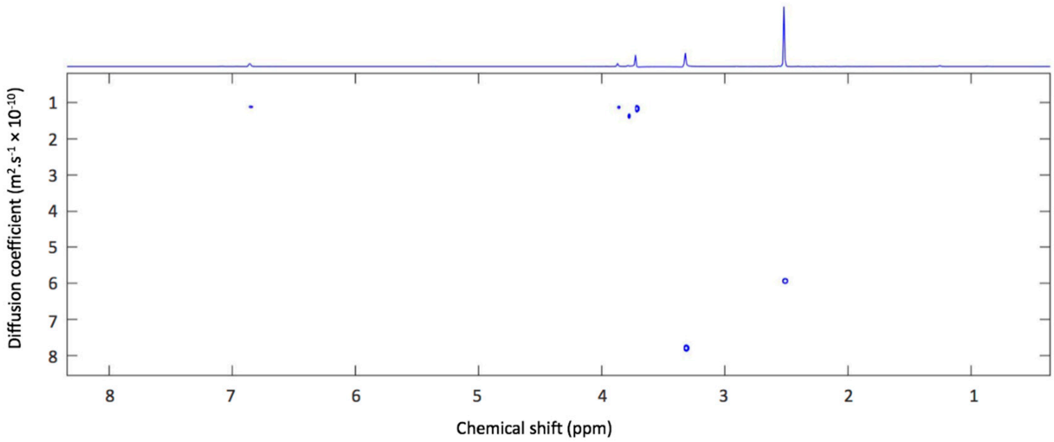


Figure S7. 2D DOSY spectrum for **Ni_3L_2** in DMF at 298 K processed using DOSY Toolbox (GNU General Public License) with 512 points for the self-diffusion axis.

2. Single crystal X-Ray diffraction

Table S1. Crystal data and details of data collection for **Ni_3L_2**.

empirical formula	$C_{41.33}H_{57.33}Ni_3N_{12}O_{8.33}S_{11.67}$
Fw	1405.82
space group	*C*2/*c*
a [Å]	33.688(4)
b [Å]	30.5050(13)
c [Å]	24.913(3)
β [°]	132.81(2)
V [Å^3]	18781(6)
Z	12
λ [Å]	0.71073
ρ_{calcd} [g cm^{-3}]	1.492
crystal size [mm]	0.50 × 0.15 × 0.04
T [K]	293(2)
μ [mm^{-1}]	1.338
R_1[a]	0.0624
wR_2[b]	0.1169
GOF[c]	0.818
CCDC No.	2104371

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table S2. Bond distances (Å) and angles (°) for **Ni_3L_2**.

Ni1-S3	2.387(3)	C13-C14	1.3900
Ni1-S4	2.423(3)	C14-C15	1.3900
Ni1-O5	2.165(8)	C15-C16	1.3900
Ni1-O6	2.176(6)	C16-C11	1.3900
Ni1-N5	2.082(7)	C23-C22	1.3900
Ni1-N11	2.095(7)	C23-C24	1.3900
Ni2-S8	2.142(3)	C22-C21	1.3900
Ni2-S9	2.157(3)	C21-C20	1.3900
Ni2-N2	1.855(8)	C20-C19	1.3900
Ni2-N4	1.822(7)	C19-C24	1.3900
Ni3-S5	2.147(3)	C33-C28	1.3900
Ni3-S6	2.149(3)	C33-C32	1.3900
Ni3-N8	1.863(9)	C28-C29	1.3900
Ni3-N10	1.832(7)	C29-C30	1.3900
S1-O5	1.521(8)	C30-C31	1.3900
S1-C52	1.752(8)	C31-C32	1.3900
S1-C53	1.719(7)	Ni4-S13	2.133(3)
S2-O6	1.522(6)	Ni4-S14	2.145(3)
S2-C54	1.721(9)	Ni4-N15	1.843(8)
S2-C55	1.748(7)	Ni4-N17	1.786(9)
S3-C9	1.720(10)	Ni5-S11	2.392(3)
S4-C26	1.714(9)	Ni5-O9	2.131(6)
S5-C25	1.751(9)	Ni5-N14	2.137(9)
S6-S7	2.077(4)	S11-C43	1.720(10)
S7-C27	1.730(10)	S12-O9	1.511(6)
S8-C10	1.778(8)	S12-C56	1.769(8)
S9-S10	2.057(4)	S12-C57	1.779(7)
S10-C8	1.730(11)	S13-C42	1.773(11)
O1-C1	1.385(11)	S14-S15	2.045(4)
O1-C2	1.367(8)	S15-C44	1.769(10)
O2-C14	1.350(9)	O7-C35	1.402(11)
O2-C17	1.432(11)	O7-C36	1.418(10)
O3-C18	1.432(10)	O8-C48	1.371(7)
O3-C19	1.402(8)	O8-C51	1.440(10)
O4-C31	1.375(8)	N13-C39	1.374(9)
O4-C34	1.411(12)	N13-C42	1.313(11)
N1-C5	1.401(8)	N14-N15	1.384(10)
N1-C8	1.351(11)	N14-C42	1.278(11)
N2-N3	1.436(9)	N15-C43	1.288(11)
N2-C8	1.279(10)	N16-N17	1.412(8)
N3-C9	1.381(10)	N16-C43	1.367(9)
N4-N5	1.382(9)	N17-C44	1.345(10)
N4-C9	1.299(10)	N18-C44	1.356(11)

N5-C10	1.309(10)	N18-C45	1.411(7)
N6-C10	1.307(10)	C39-C38	1.3900
N6-C11	1.384(8)	C39-C40	1.3900
N7-C27	1.356(10)	C38-C37	1.3900
N7-C28	1.454(8)	C37-C36	1.3900
N8-N9	1.369(9)	C36-C41	1.3900
N8-C27	1.303(10)	C41-C40	1.3900
N9-C26	1.351(9)	C49-C50	1.3900
N10-N11	1.423(8)	C49-C48	1.3900
N10-C26	1.286(10)	C50-C45	1.3900
N11-C25	1.312(10)	C45-C46	1.3900
N12-C22	1.355(8)	C46-C47	1.3900
N12-C25	1.355(10)	C47-C48	1.3900
C4-C5	1.3900	S16-O10	1.431(8)
C4-C3	1.3900	S16-C58	1.602(8)
C5-C6	1.3900	S16-C59	1.660(8)
C6-C7	1.3900	S17-O11	1.358(9)
C7-C2	1.3900	S17-C60	1.644(10)
C2-C3	1.3900	S17-C61	1.676(10)
C12-C13	1.3900	S18-O12	1.404(11)
C12-C11	1.3900	S18-C62	1.718(10)

S3-Ni1-S4	100.45(11)	C22-C23-C24	120.0
O5-Ni1-S3	168.0(9)	N12-C22-C23	120.5(7)
O5-Ni1-S4	91.3(8)	N12-C22-C21	119.5(7)
O6-Ni1-S3	86.87(18)	C20-C21-C22	120.0
O6-Ni1-S4	171.97(17)	C21-C20-C19	120.0
O6-Ni1-O5	81.5(8)	O3-C19-C20	124.6(7)
N5-Ni1-S3	83.7(3)	O3-C19-C24	115.4(7)
N5-Ni1-S4	96.1(2)	C24-C19-C20	120.0
N5-Ni1-O5	93.0(7)	C19-C24-C23	120.0
N5-Ni1-O6	87.9(3)	N11-C25-S5	120.7(8)
N5-Ni1-N11	176.4(4)	N11-C25-N12	121.3(9)
N11-Ni1-S3	93.1(2)	N12-C25-S5	117.8(8)
N11-Ni1-S4	82.7(3)	N9-C26-S4	121.0(8)
N11-Ni1-O5	90.5(7)	N10-C26-S4	124.9(8)
N11-Ni1-O6	93.7(3)	N10-C26-N9	114.0(8)
S8-Ni2-S9	97.78(12)	N7-C27-S7	116.5(9)
N2-Ni2-S8	171.0(3)	N8-C27-S7	121.1(9)
N2-Ni2-S9	91.2(3)	N8-C27-N7	122.2(10)
N4-Ni2-S8	85.9(3)	C28-C33-C32	120.0
N4-Ni2-S9	176.3(4)	C33-C28-N7	117.8(9)
N4-Ni2-N2	85.1(4)	C29-C28-N7	122.0(9)
S5-Ni3-S6	96.64(12)	C29-C28-C33	120.0

N8-Ni3-S5	168.8(3)	C28-C29-C30	120.0
N8-Ni3-S6	94.2(3)	C29-C30-C31	120.0
N10-Ni3-S5	88.1(3)	O4-C31-C30	116.9(9)
N10-Ni3-S6	174.5(3)	O4-C31-C32	122.9(9)
N10-Ni3-N8	80.9(4)	C32-C31-C30	120.0
O5-S1-C52	102.0(8)	C31-C32-C33	120.0
O5-S1-C53	109.0(14)	S13-Ni4-S14	97.45(13)
C53-S1-C52	96.0(5)	N15-Ni4-S13	85.7(3)
O6-S2-C54	103.8(4)	N15-Ni4-S14	176.5(4)
O6-S2-C55	105.6(4)	N17-Ni4-S13	169.7(3)
C54-S2-C55	98.3(5)	N17-Ni4-S14	92.8(3)
C9-S3-Ni1	93.2(4)	N17-Ni4-N15	84.0(4)
C26-S4-Ni1	94.8(4)	S11-Ni5-S11^{1}	98.52(17)
C25-S5-Ni3	96.5(4)	O9-Ni5-S11	172.05(19)
S7-S6-Ni3	99.87(15)	O9-Ni5-S11^{1}	88.38(19)
C27-S7-S6	100.9(4)	O9^{1}-Ni5-O9	85.0(4)
C10-S8-Ni2	97.0(4)	N14-Ni5-S11	85.2(3)
S10-S9-Ni2	100.40(15)	N14-Ni5-S11^{1}	94.7(2)
C8-S10-S9	102.0(4)	N14-Ni5-O9	90.4(3)
C2-O1-C1	119.2(10)	N14-Ni5-O9^{1}	89.8(3)
C14-O2-C17	119.7(10)	N14^{1}-Ni5-N14	179.7(5)
C19-O3-C18	114.8(9)	C43-S11-Ni5	92.3(4)
C31-O4-C34	116.9(10)	O9-S12-C56	103.6(4)
S1-O5-Ni1	121.1(6)	O9-S12-C57	105.1(4)
S2-O6-Ni1	124.4(4)	C56-S12-C57	99.9(5)
C8-N1-C5	124.7(9)	C42-S13-Ni4	97.8(5)
N3-N2-Ni2	110.9(6)	S15-S14-Ni4	100.97(16)
C8-N2-Ni2	129.2(9)	C44-S15-S14	101.8(4)
C8-N2-N3	119.9(9)	C35-O7-C36	110.9(10)
C9-N3-N2	112.5(9)	C48-O8-C51	116.5(8)
N5-N4-Ni2	125.4(7)	S12-O9-Ni5	126.9(4)
C9-N4-Ni2	116.4(8)	C42-N13-C39	125.4(9)
C9-N4-N5	118.2(8)	N15-N14-Ni5	112.1(7)
N4-N5-Ni1	116.5(6)	C42-N14-Ni5	133.4(8)
C10-N5-Ni1	130.8(7)	C42-N14-N15	114.5(10)
C10-N5-N4	112.2(8)	N14-N15-Ni4	123.4(7)
C10-N6-C11	125.9(8)	C43-N15-Ni4	115.0(8)
C27-N7-C28	121.8(9)	C43-N15-N14	121.6(10)
N9-N8-Ni3	114.3(6)	C43-N16-N17	110.6(8)
C27-N8-Ni3	123.8(8)	N16-N17-Ni4	114.5(5)
C27-N8-N9	121.9(9)	C44-N17-Ni4	129.8(7)
C26-N9-N8	112.4(8)	C44-N17-N16	115.8(9)
N11-N10-Ni3	121.4(6)	C44-N18-C45	126.2(9)
C26-N10-Ni3	118.1(7)	N13-C39-C38	118.0(8)

C26-N10-N11	120.4(8)	N13-C39-C40	121.8(8)
N10-N11-Ni1	115.4(6)	C38-C39-C40	120.0
C25-N11-Ni1	131.1(7)	C39-C38-C37	120.0
C25-N11-N10	113.3(8)	C38-C37-C36	120.0
C25-N12-C22	125.4(7)	C37-C36-O7	113.0(8)
C5-C4-C3	120.0	C41-C36-O7	127.0(8)
C4-C5-N1	121.4(7)	C41-C36-C37	120.0
C4-C5-C6	120.0	C36-C41-C40	120.0
C6-C5-N1	118.5(7)	C41-C40-C39	120.0
C7-C6-C5	120.0	N13-C42-S13	120.5(10)
C6-C7-C2	120.0	N14-C42-S13	118.5(10)
O1-C2-C7	123.2(7)	N14-C42-N13	120.9(12)
O1-C2-C3	116.7(7)	N15-C43-S11	127.7(8)
C3-C2-C7	120.0	N15-C43-N16	115.6(10)
C2-C3-C4	120.0	N16-C43-S11	116.7(9)
N1-C8-S10	119.2(8)	N17-C44-S15	114.6(9)
N2-C8-S10	117.0(10)	N18-C44-S15	117.8(8)
N2-C8-N1	123.8(10)	N18-C44-N17	127.5(10)
N3-C9-S3	117.8(10)	C50-C49-C48	120.0
N4-C9-S3	127.0(8)	C45-C50-C49	120.0
N4-C9-N3	115.0(10)	N18-C45-C50	122.2(8)
N5-C10-S8	119.1(8)	N18-C45-C46	117.7(8)
N5-C10-N6	122.8(9)	C46-C45-C50	120.0
N6-C10-S8	118.1(9)	C45-C46-C47	120.0
C13-C12-C11	120.0	C46-C47-C48	120.0
C14-C13-C12	120.0	O8-C48-C49	117.2(8)
O2-C14-C13	114.4(10)	O8-C48-C47	122.8(8)
O2-C14-C15	125.6(10)	C47-C48-C49	120.0
C13-C14-C15	120.0	O10-S16-C58	101.7(8)
C16-C15-C14	120.0	O10-S16-C59	112.3(7)
C11-C16-C15	120.0	C58-S16-C59	98.8(8)
N6-C11-C12	119.9(10)	O11-S17-C60	121.6(14)
N6-C11-C16	120.1(10)	O11-S17-C61	106.9(14)
C16-C11-C12	120.0	C60-S17-C61	94.3(16)

Symmetry codes: [1)]2 – *x*, *y*, 1.5 – *z*.

3. UV-vis spectroscopic data

Table S3. Selected features of the electronic absorption spectra of **H_6L** and **Ni_3L_2** in DMF.

Compound	λ (nm)	ε ($M^{-1}cm^{-1}$)	λ (nm)	ε ($M^{-1}cm^{-1}$)	λ (nm)	ε ($M^{-1}cm^{-1}$)	λ (nm)	ε ($M^{-1}cm^{-1}$)
H_6L	270	22829.63	325	13616.20	-	-	-	-
Ni_3L_2	268	55638.60	363	19165.52	518	4203.65	895	1391.34

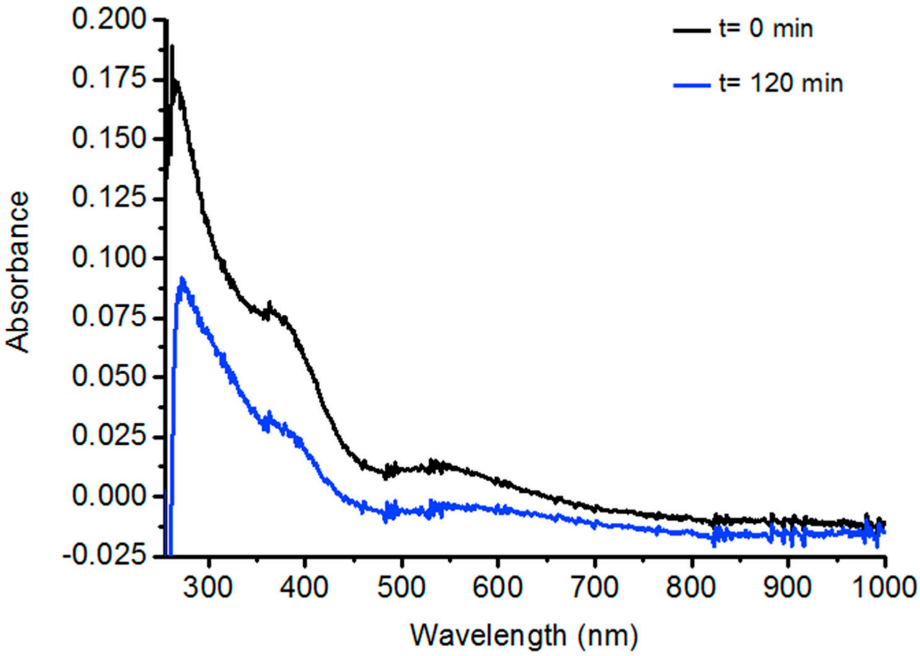


Figure S8. Electronic absorption spectra for the $\mathbf{Ni_3L_2}$ complex (black line), and upon chronoamperometry (-1.7 V vs. $Fc^{+/0}$ with 100 mM of TFA, blue line).

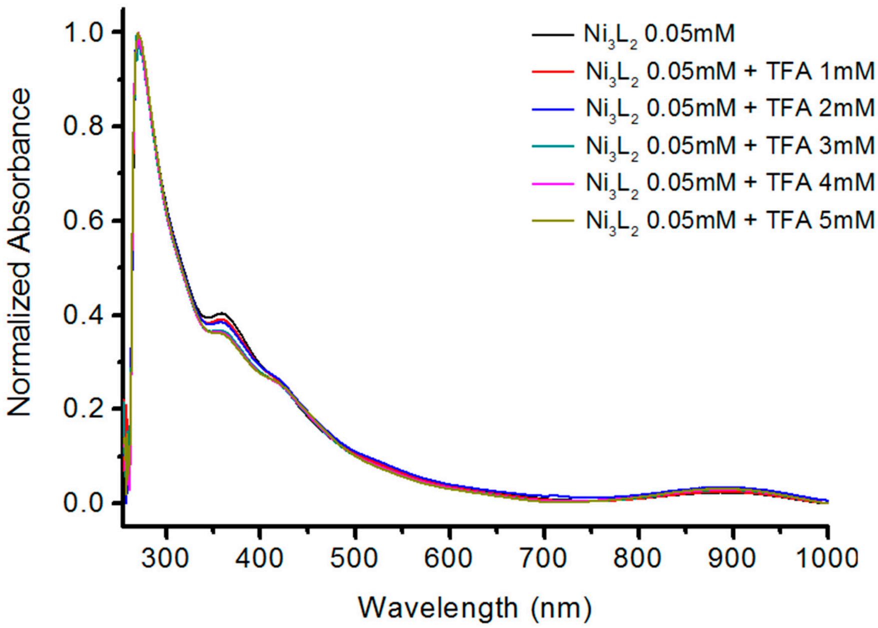


Figure S9. Electronic absorption spectra of 0.5 mM solutions of $\mathbf{Ni_3L_2}$ in DMF in the absence (black line) or in the presence (red, blue green, pink and khaki lines) of TFA.

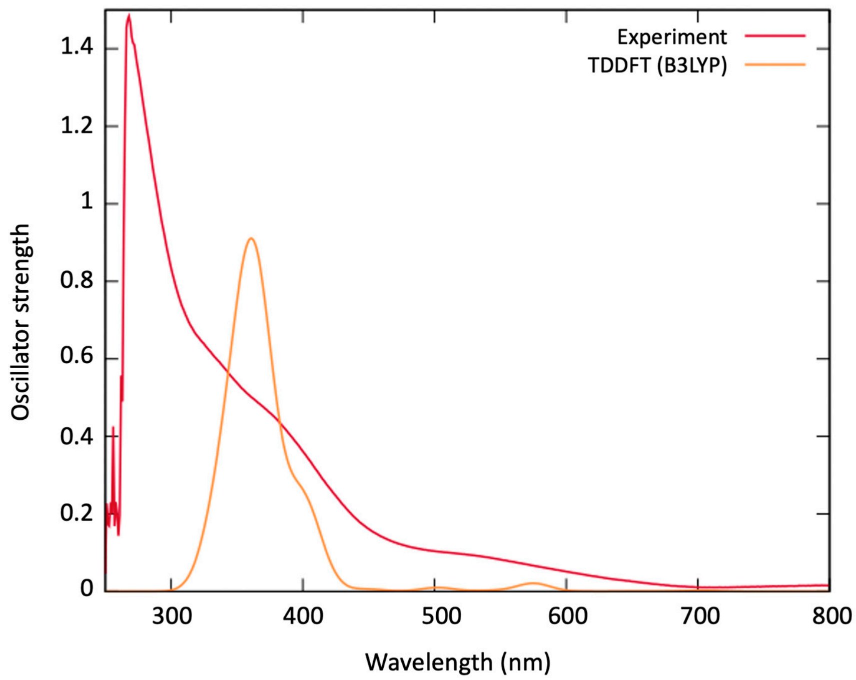


Figure S10. Comparison between experimental and calculated UV-Vis spectra for **Ni_3L_2** in DMF. Calculations performed on the neutral complex in a closed-shell singlet state (B3LYP/def2-TZVP(-f), see Electronic structure section in the main text).

Table S4. Selected intense transitions in the calculated UV-vis spectra of **Ni_3L_2** and their assignment with difference densities (yellow: density loss, red: density gain; CT: charge transfer, MMCT: metal-to-metal CT, LMCT: ligand-to-metal CT, MLCT: metal-to-ligand CT; d → d: local excitation on the metals, L → L: local excitation on the ligands, see Figure S11 for depictions).

State	Wavelength / nm [Energy / cm^{-1}]	Oscillator strength	Assignment
27	575.7 [17370.3]	0.00778	MMCT/LMCT
29	572.9 [17456.4]	0.00262	MMCT/LMCT
39	502.9 [19885.6]	0.00465	LMCT
43	406.9 [24574.0]	0.01930	d → d
47	402.6 [24836.3]	0.02563	L → L

62	381.6 [26208.9]	0.01881	LMCT
67	397.3 [25172.8]	0.04436	MMCT
70	366.2 [27305.3]	0.18733	MMCT
74	371.8 [26893.9]	0.04887	LMCT/MMCT
78	360.6 [27732.2]	0.02336	LMCT/MMCT
80	359.5 [27817.2]	0.03117	LMCT/MMCT
81	356.4 [28057.5]	0.02606	MLCT
87	353.9 [28260.5]	0.15136	MLCT
97	337.7 [29616.3]	0.05810	MLCT
100	334.9 [29860.3]	0.03976	MLCT/MMCT

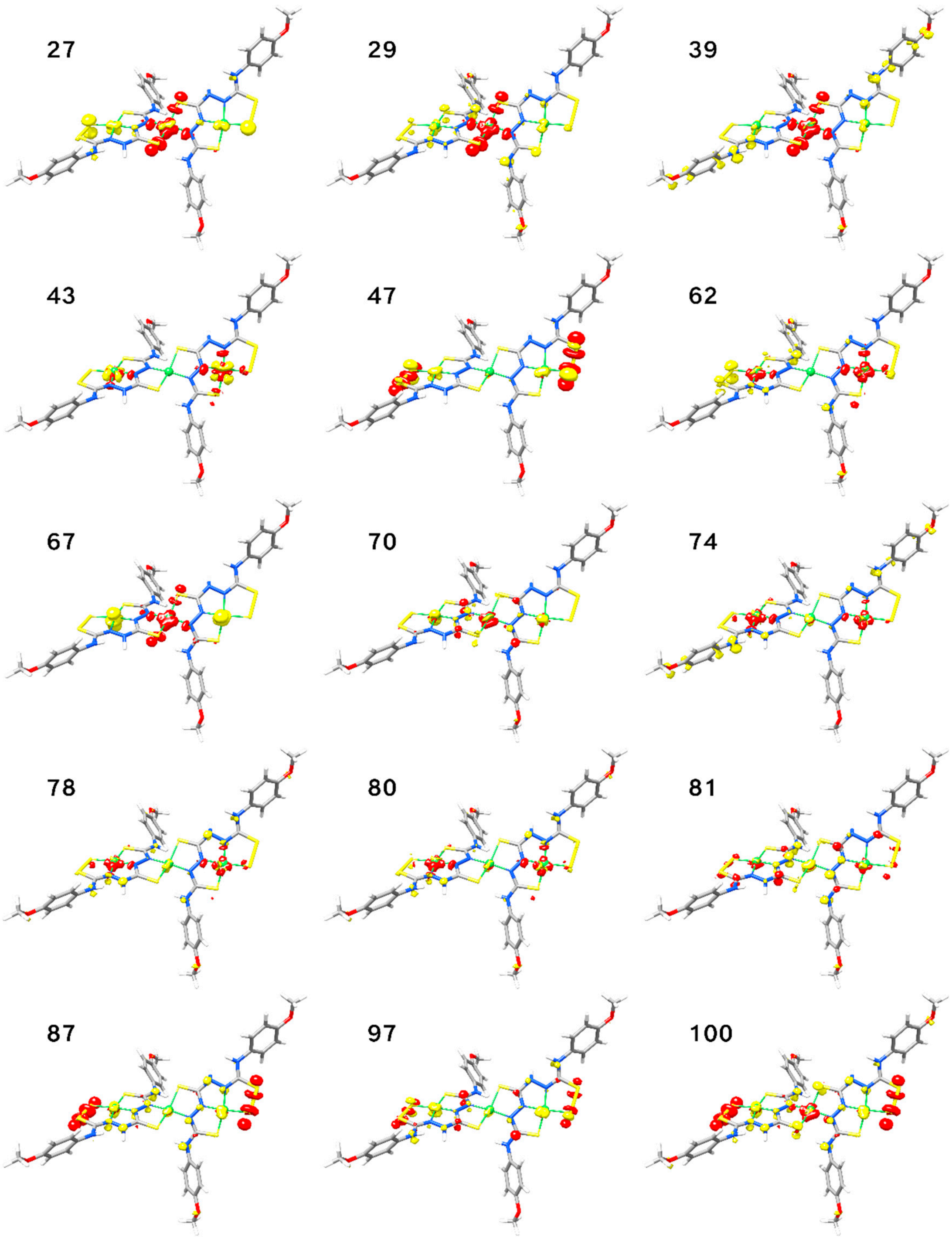


Figure S11. Difference densities of the most important transitions of **Ni_3L_2** predicted with TDDFT (B3LYP/def2-TZVP(-f); yellow: density loss, red: density gain) listed in Table S4.

4. Electrochemical Studies

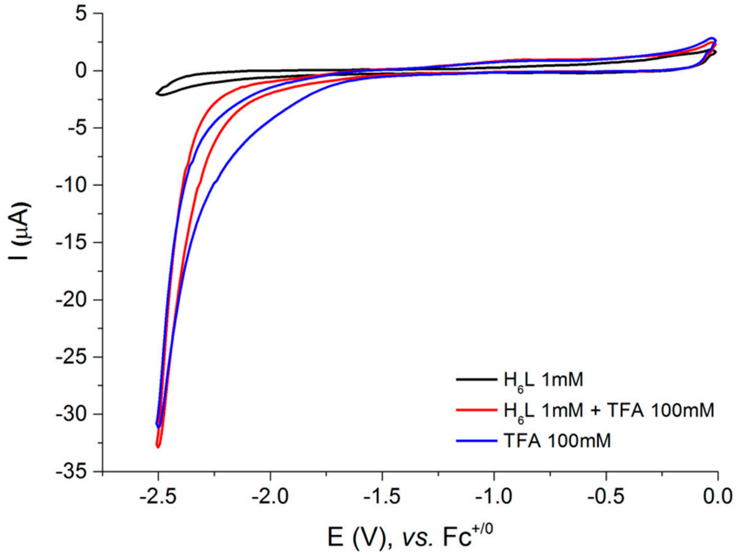


Figure S12. Cyclic voltammogram of a 1 mM solution of **H_6L** (black line) in DMF recorded at a stationary glassy carbon with 0.1 M NBu_4PF_6 as supporting electrolyte. The cyclic voltammograms of a 100 mM of TFA solution in the absence (blue line) and in the presence (red line) of 1 mM **H_6L** are also shown. Scan rate: 500 mV s^{-1}. Potentials are referenced to the $Fc^{+/0}$ electrode.

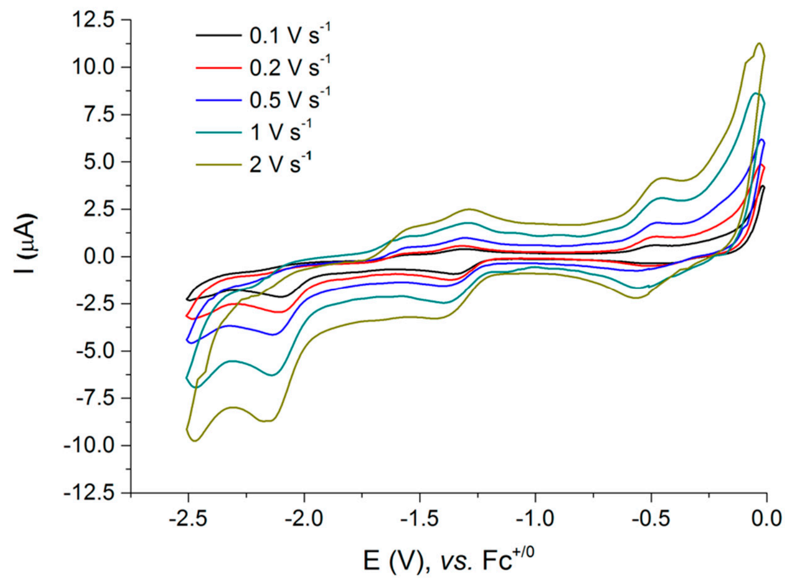


Figure S13. Successive cyclic voltammograms of a 1 mM solution of **Ni_3L_2** in DMF at a stationary glassy carbon electrode at different scan rates (v) in DMF with 0.1 M NBu_4PF_6 as supporting electrolyte. Potentials are referenced to the $Fc^{+/0}$ electrode.

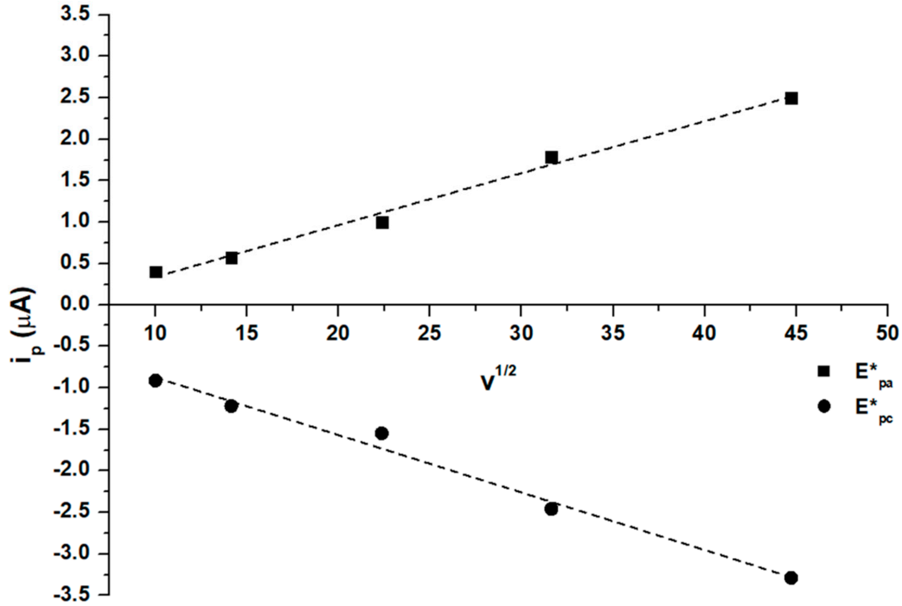


Figure S14. Linear plot of i_p versus the square root of the scan rate $v^{1/2}$ for anodic and cathodic waves of the quasi-reversible redox process of **Ni_3L_2**.

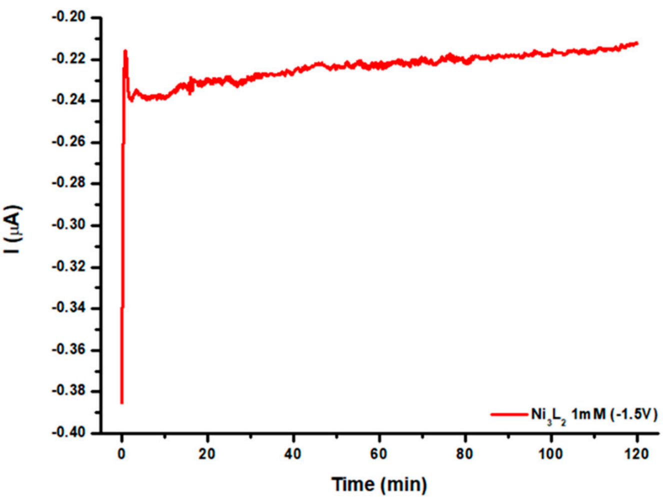


Figure S15. Chronoamperogram of a 1 mM solution of **Ni_3L_2** in DMF recorded at -1.50 V vs. $Fc^{+/0}$ at 1 mm glassy carbon electrode.

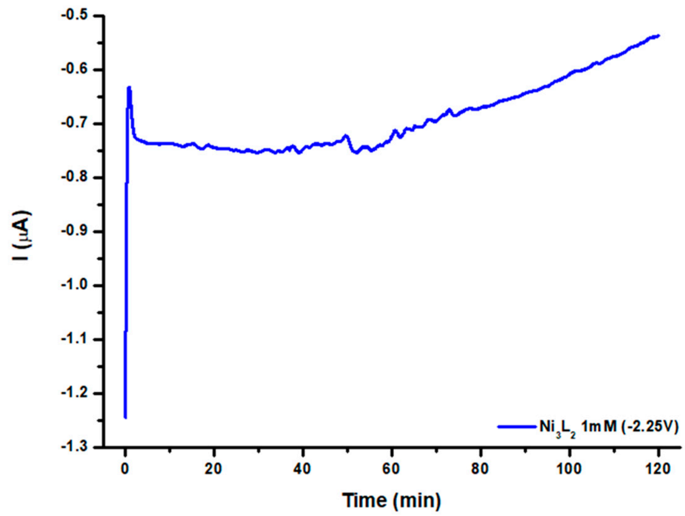


Figure S16. Chronoamperogram of a 1 mM solution of **Ni_3L_2** in DMF recorded at -2.25 V vs. $Fc^{+/0}$ at 1 mm glassy carbon electrode.

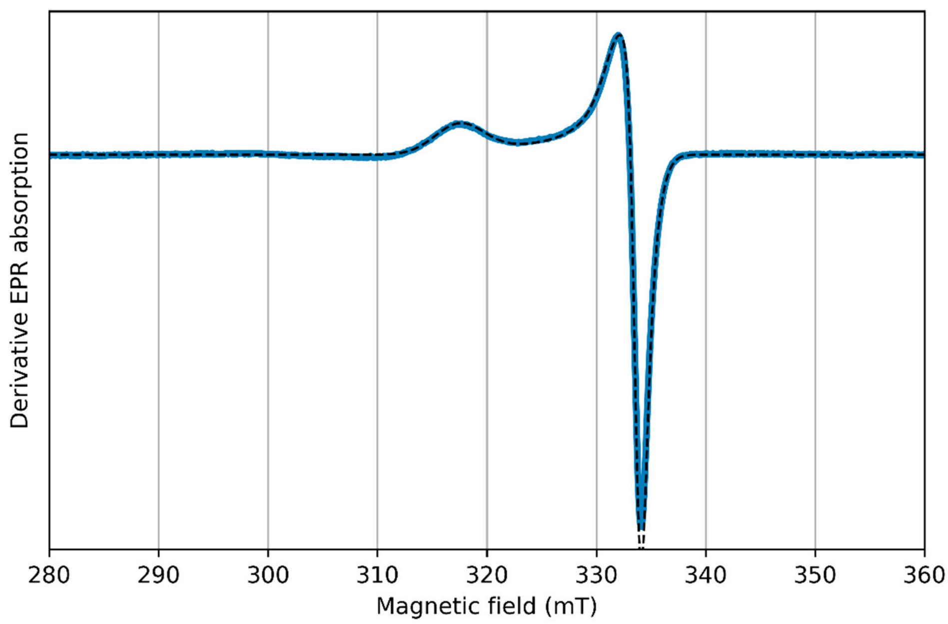


Figure S17. Simulated (blue line) and experimental (dotted line) *cw* X-band EPR spectrum of a 1 mM solution of **Ni_3L_2** in DMF at T=50K recorded upon chronoamperometry at -1.50 V vs. $Fc^{+/0}$ at 1 mm glassy carbon electrode.

5. Electrocatalysis

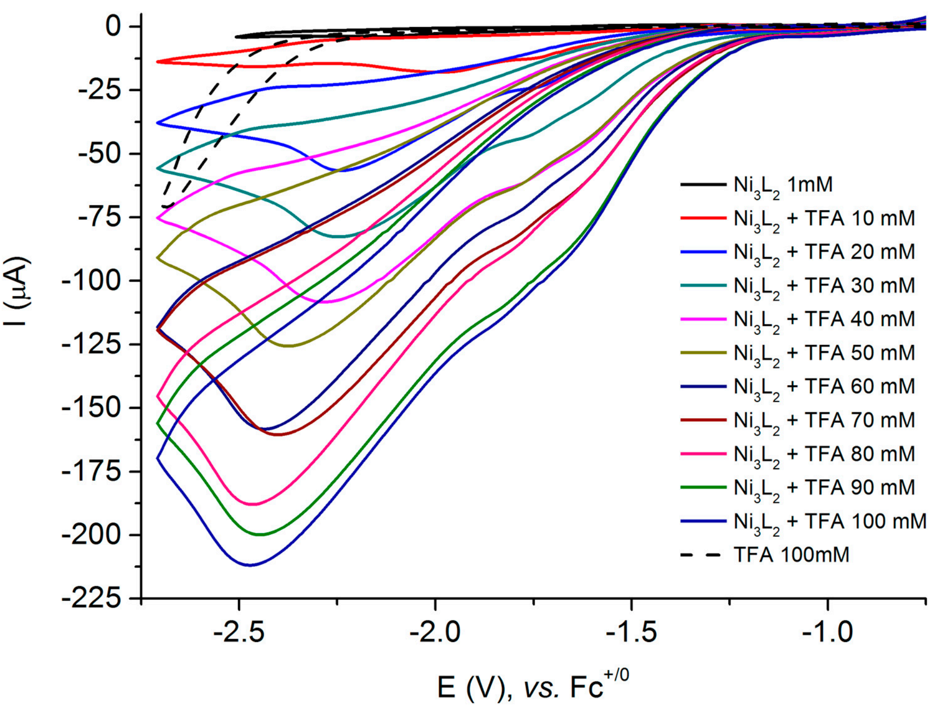


Figure S18. Successive cyclic voltammograms of a 1 mM solution of $\mathbf{Ni_3L_2}$ in DMF (0.1 M NBu_4PF_6) recorded at a glassy carbon electrode with increasing amounts of TFA at 500 mV s^{-1}. Potential are referenced to the $Fc^{+/0}$ electrode.

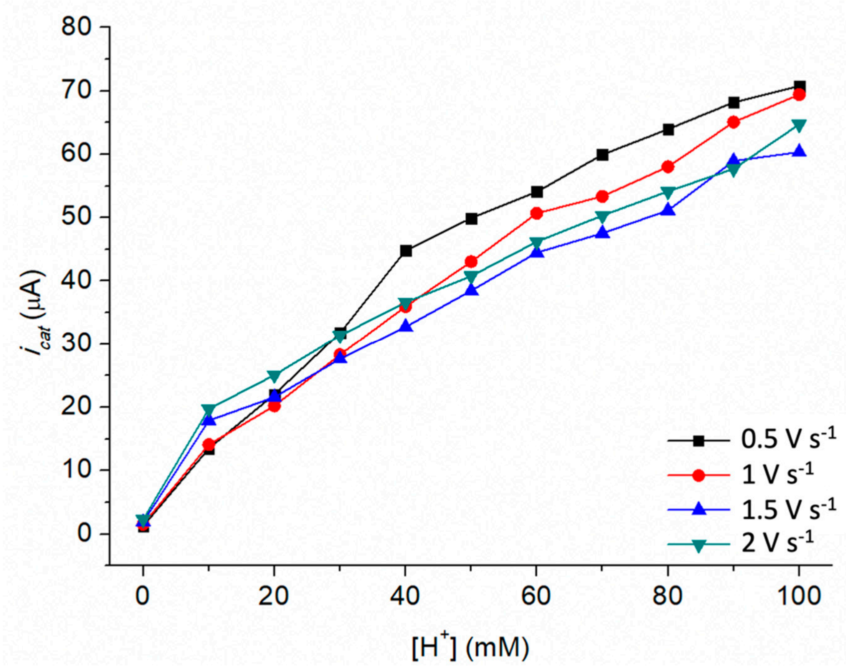


Figure S19. Plot of i_{cat} of $\mathbf{Ni_3L_2}$ for increasing concentrations of TFA at different scan rates.

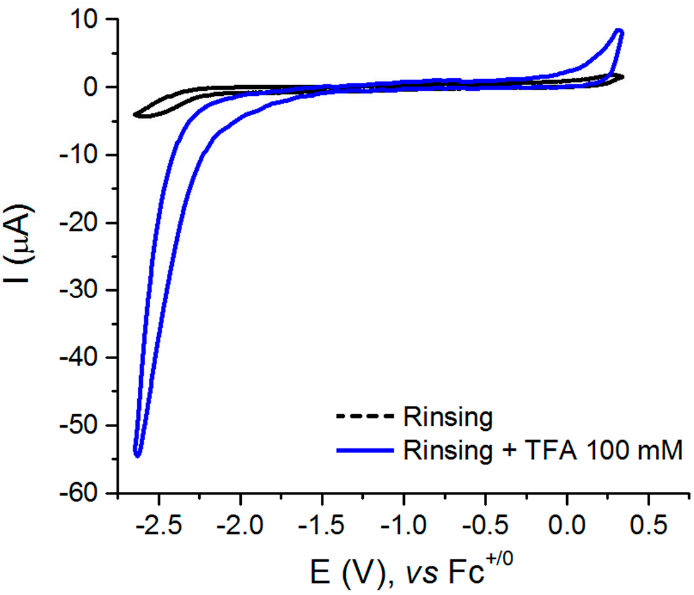


Figure S20. Cyclic voltammograms recorded after electrocatalysis of $\mathbf{Ni_3L_2}$ upon washing the working electrode and immersion into a fresh solution of dry DMF (0.1M NBu_4PF_6, black dashed line) and in the presence of 100 mM of TFA (blue line). Scan rate 500 mV s^{-1}.

6. Gas analysis

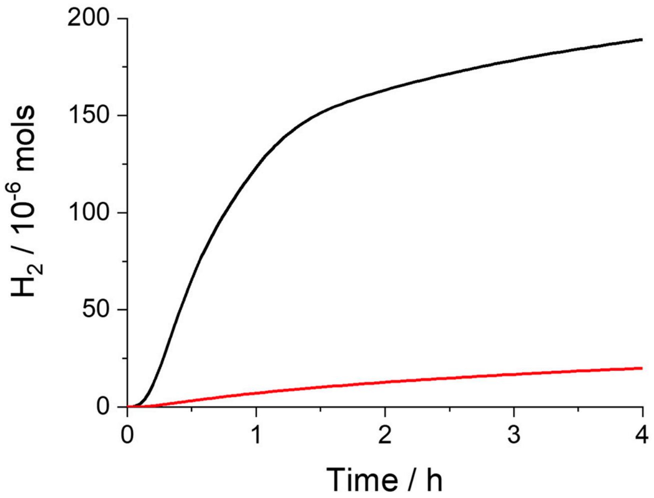


Figure S21. Electrocatalytic hydrogen production vs. time, by applying -1.70 V vs. $Fc^{+/0}$ using a mercury pool working electrode in 0.1 M NBu_4PF_6 solution of DMF containing 100 mM TFA in the absence (red line) and presence of 1 mM of **Ni_3L_2** (black line).

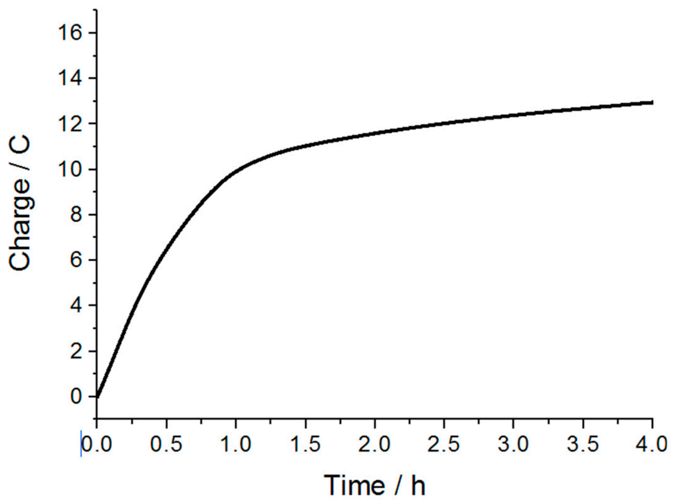


Figure S22. Coulometry during bulk electrolysis experiment at -1.70 V vs. $Fc^{+/0}$ using a mercury pool working electrode. The electrolytic solution contains 0.1 M NBu_4PF_6 in DMF, 100 mM TFA and 1 mM of **Ni_3L_2**.

7. Overpotential calculations

The overpotential value of **Ni_3L_2**, η, was determined following the protocol described by Fourmond et coworkers. This parameter is calculated as the difference between the mid-wave catalytic potential $E^{cat}_{1/2}$ and the theoretical half-wave potential $E^{T}_{1/2}$ such as:

$$\eta = E^{cat}_{1/2} - E^{T}_{1/2} \qquad (1)$$

The value of $E^{T}_{1/2}$ depends on the standard potential for the reduction of protons in DMF $E^{0}_{H^+/H_2}$, the $pK_a$the proton source, the total concentration of the acid C_0, the concentration of dissolved hydrogen $C^{0}_{H_2}$, and the difference in diffusion coefficients between the acid and H_2 ε_D. When homoconjugation is negligible as for the case of trifluoroacetic acid in DMF, the theoretical half-wave potential, $E^{T}_{1/2}$, can be calculated using the following equation:

$$E^{T}_{1/2} = E^{0}_{H^+/H_2} - \left(2.303 \times {RT}/_{F}\right) \times pK_a + \varepsilon_D - \left({RT}/_{2F}\right) \times ln\left(C_0/C^{0}_{H_2}\right) \qquad (2)$$

The relevant values of $E^{0}_{H^+/H_2}$ (-0.62 V), pK_a (6.00 ± 0.3), ε_D (0.04 ± 0.005 V) and $C^{\circ}_{H_2}$ ($1.9.10^{-3}$ M), were obtained from the references listed below. We used R = 8.31 $J.K^{-1}.mol^{-1}$, T = 298 K, F = 96500 $C.mol^{-1}$, C_0= 0.1 M and $E^{cat}_{1/2}$= -1.55V versus $Fc^{+/0}$.

8. Kinetic analysis

The Turnover frequency (TOF) value of **Ni_3L_2** was evaluated using the peak current of the catalyst in the absence i_p and presence of proton source i_{cat}. Without substrate, the peak current is given by the Randles-Sevcik equation (3).

$$i_p = \left(0.4463 \times n_p FA[Cat]\right) \times \sqrt{{F\nu D}/_{RT}} \qquad (3)$$

In (3), n_p is the number of electrons transferred (n_p = 1), F is Faraday's constant, A is the active surface area of the working electrode, [Cat] is the concentration of the catalyst, ν is the scan rate, D is the diffusion coefficient, R is the universal gas constant and T is temperature.

In the presence of substrate, the peak current is given by equation (4):

$$i_{cat} = (n_{cat} FA[Cat]) \times \sqrt{D k_{H_2} [H^+]} \qquad (4)$$

In (4), n_{cat} is the number of electrons required for the catalytic reaction (n_{cat}= 2), k_{H_2} is the rate constant of the catalytic reaction and $[H^+]$ is the acid concentration.

Thus, the ratio of ${}^{i_{cat}}/_{i_p}$ is given by equation (5):

$$ {}^{i_{cat}}/_{i_p} = \left({}^{n_{cat}}/_{0.4463 n_p}\right) \times \sqrt{{}^{RT}/_{F}} \times \sqrt{{}^{k_{H_2}[H^+]}/_{v}} \qquad (5) $$

Under pseudo first-order conditions where $k_{obs} = k_{H_2} \times [H^+]$, we obtain equation (6):

$$ {}^{\mathrm{i_{cat}}}/_{\mathrm{i_p}} = 4.484 \times \sqrt{{}^{\mathrm{RT}}/_{\mathrm{F}}} \times 0 \qquad (6) $$

When at scan rate independent conditions, we can derive equation (7) to estimate the observed rate constant or the maximum TOF value:

$$ TOF_{max} = k_{obs} = 1.938\ x\ v \left[{}^{i_{cat}}/_{i_p}\right]^2 \qquad (7) $$

The above equations are used to estimate TOF values in the case of electrocatalysts under pure kinetic conditions where plateau current is easily observable and is scan rate independent. In the case of **Ni_3L_2**, the peak current i_{cat} plateaus for concentration and scan rates higher than 100 mM and 2 V.s^{-1}, respectively. In addition, the ratio $\left({}^{i_{cat}}/_{i_p}\right)$ varies linearly with the inverse of the square root of scan rate $\sqrt{v}$ which confirms the validity of the approach.

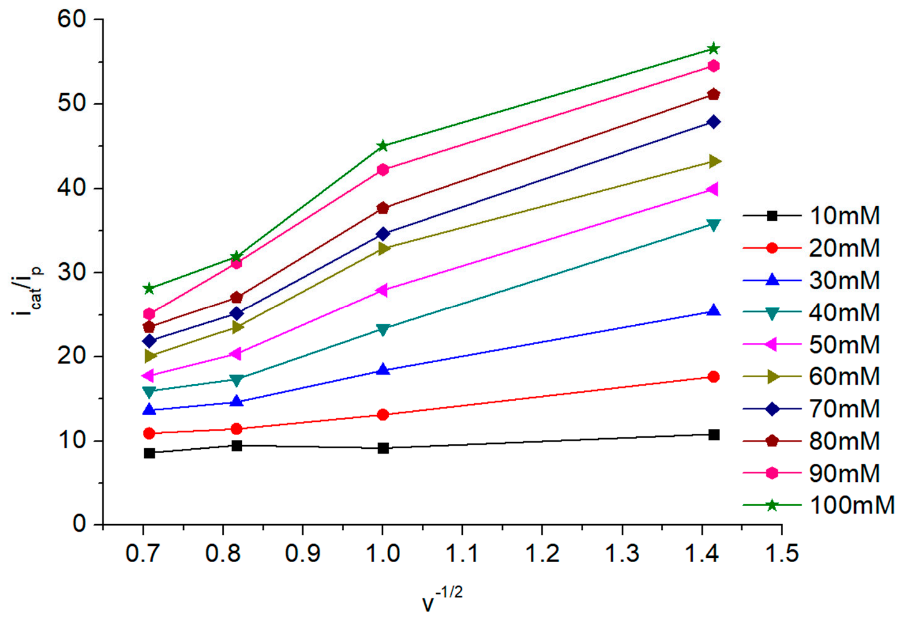


Figure S23. Plot of ${}^{i_{cat}}/_{i_p}$ versus inverse of the square root of the scan rate ($v^{-1/2}$) for **Ni_3L_2** in DMF in the presence of different amounts of TFA. The plots were derived from the voltammograms recorded at different scan rates in the absence and presence of proton source.

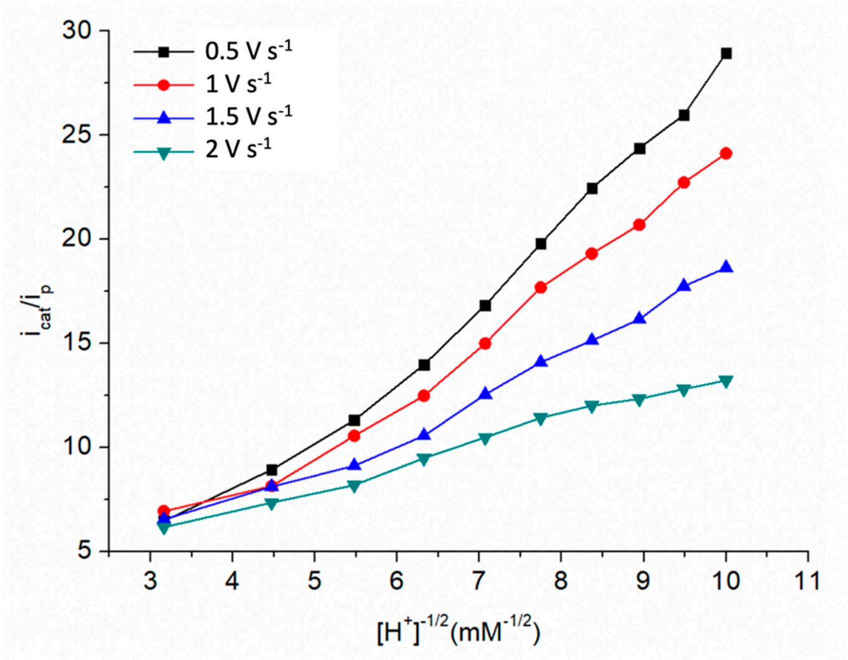


Figure S24. Plot of i_{cat}/i_p versus the square root of the acid concentration ($[H^+]^{-1/2}$) for **Ni_3L_2** in DMF at different scan rates. The plots were derived from the voltammograms recorded at different scan rates in the absence and presence of proton source.

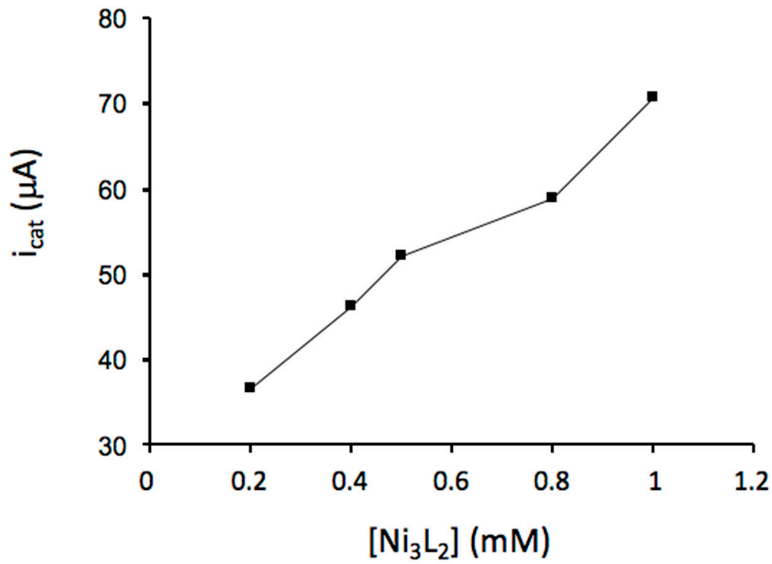


Figure S25. Plot of i_{cat} versus the **Ni_3L_2** concentration in DMF in the presence of 100 mM TFA at 500 mV s^{-1}.

9. DFT calculations

Table S5. Top: Comparison of free energies for each oxidation state of $\mathbf{Ni_3L_2}$ for up to three reduction events. Bottom: Comparison of free energies for the neutral state of $\mathbf{Ni_3L_2}$ including 2 bound DMSO molecules.

Oxidation state	**Gibbs free energy (Eh)**	**Relative free energy (kcal/mol)**
	Ni_3L_2 (no DMSO)	
Q = 0, S = 0	-9986.413809	0
Q = 0, S = 1	-9986.410978	1.8
Q= (-1), S = 1/2	-9986.553718	-
Q= (-2), S = 0	-9986.649992	10.4
Q= (-2), S = 1	-9986.666662	0
Q= (-2), Ms = 0	-9986.665499	0.7
Q = (-3), S = 1/2	-9986.766808	0
Q = (-3), S = 3/2	-9986.766474	0.2
Q= (-3), Ms =1/2	-9986.766344	0.3

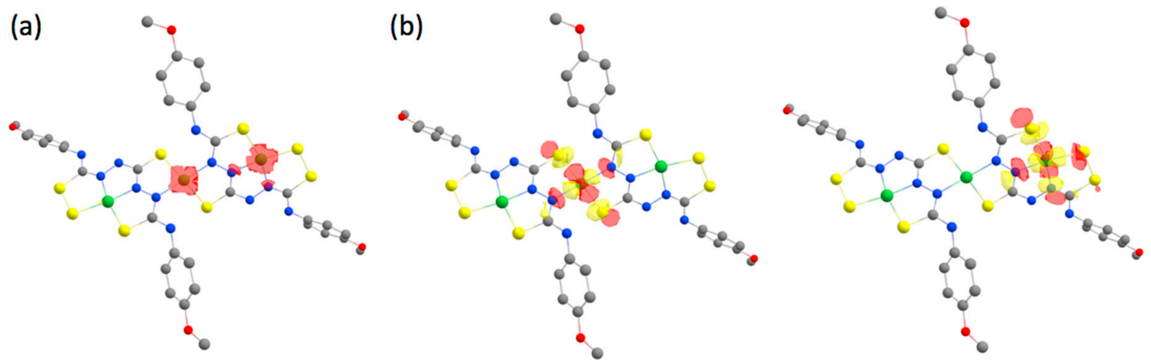
Oxidation state	**Gibbs free energy (Eh)**	**Relative free energy (kcal/mol)**
	Ni_3L_2 (2 DMSO included)	
Q = 0, S = 0	-11092.960417	0
Q = 0, S = 1	-11092.954677	3.6

Table S6. Redox potentials of Ni_3L_2, considering three successive one-electron as well as two-electron reduction events for the deprotonated complex, and redox processes including protonation of the complex. We are considering Nic as our protonation site (see Mechanistic considerations section in the main text). All results are reported vs. $Fc^{+/0}$ electrode, where the reference was calculated to be -4.87 V using the same level of theory (BP86/def2-TZVP(-f), CPCM(DMF)).

Process	Oxidation state	E^0(V)
1-electron	Q = 0, S =0 → Q= (-1), S = ½	-1.06
1-electron	Q= (-1), S = 1/2→ Q= (-2), S = 1	-1.83
1-electron	Q= (-2), S = 1→ Q= (-3), S = ½	-2.11
2-electron	Q = 0, S =0 → Q= (-2), S = 1	-1.45
2-electron	Q = (-1), S = ½ → Q= (-3), S = ½	-1.97
1-electron 1-proton	Q = 0, S = 1/2 → Q = (-1), S = 1 (Ni_cH)	-1.19
1-electron 1-proton	Q = (-1), S = 1 → Q = (-2), S = ½ (Ni_cH)	-1.47

Table S7. Mulliken spin densities of the Ni centers (central, c and side, s and s') in the one-, two-, and three-electron reduced complex Ni_3L_2.

Charge – spin state	Atom	Spin density
Q= (-1), S = ½	Ni_c	0.843
	Ni_s	0.002
	Ni_s'	0.002
Q= (-2), S = 1	Ni_c	0.837
	Ni_s	0.753
	Ni_s'	0
Q= (-3), S = ½	Ni_c	0.848
	Ni_s	0.786
	Ni_s'	0.785



Supplementary figure S26. Spin density plot (a) and localized Singly Occupied Molecular Orbital (SOMO, b) for **Ni_3L_2** after two subsequent one-electron reduction reactions. The complex is in a triplet dianionic state.

Table S8. Relative *pK$_a$* values for **Ni_3L_2** before reduction steps. Values are relative to the free energy of protonating the Ni_c atom. 'X' corresponds to cases where geometry optimization of the protonated complex showed cleavage of the complex. Cleavage cases are not considered, as they will affect the ability to restore the catalyst at the end of the catalytic cycle.

Proton site	$Ni_3L_2^+$
Ni_c	0.0
Ni_s	[a]
S_c	8.2
S_{sc}	4.4
S_s	9.7
S_d	-1.9
N_c	2.8
N_{sc}	1.3
N_s	5.0

[a] Attempting to protonate Ni_s leads to a proton transfer to S_s

Prior to reduction, S_s is the first protonation site. Nevertheless, this preference changes to Ni_c being the first protonation site upon the first reduction. For the unreduced case, we started by putting TFAH in H-bonding position with S_s, our best candidate in terms of pK_as, and S_c, the second best. Geometry optimization of the system in the product state, i.e. with the proton attached to the complex, resulted in the proton moving back to form TFAH. This suggests that a proton transfer between TFAH and **Ni_3L_2** in its neutral state would yield a high-energy intermediate, thus being unlikely to occur.

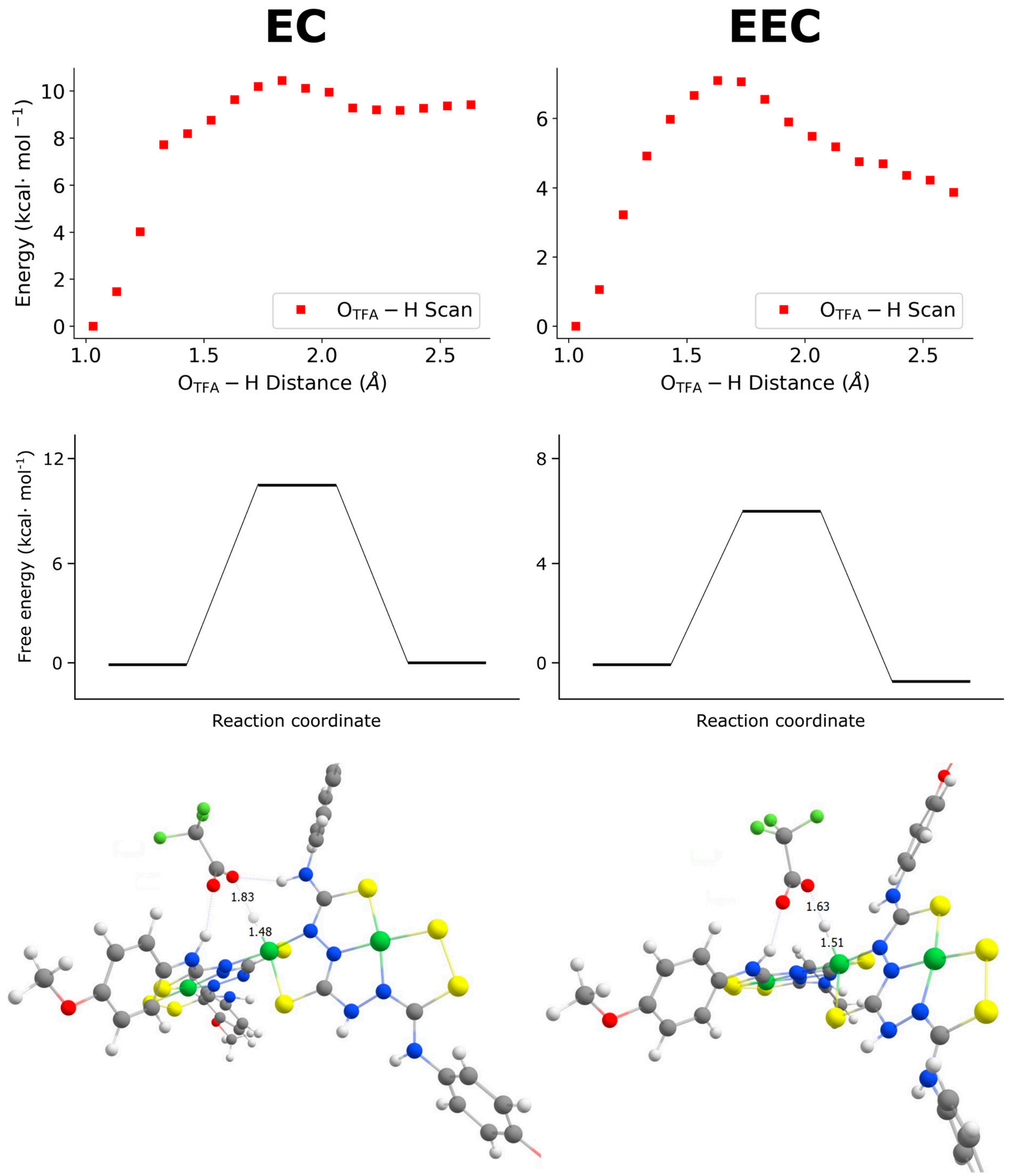


Figure S27. Potential energy surface scans for the proton transfer between TFAH and **Ni_3L_2** after the first (left) and second (right) reductions (top), free energy diagrams of the proton transfer, where the transition state was taken as the highest point in the PES scan (middle) and transition state geometries, with Ni-H and O_{TFA}-H distances displayed in Å (bottom). Their cartesian coordinates are provided in Tables S14 and S15.

Table S9. Cartesian coordinates of **Ni_3L_2** used as the reference for the study including 2 DMSO.

Ni	24.71490184937175	24.85884870163864	-4.20768747495596
Ni	23.24819073957001	26.06593765098960	0.18492882280339
S	21.67870765797588	24.75359056101595	-0.51663099686504
S	22.49593852411109	26.37919101826877	2.19197878913501
S	26.13171120582073	26.40967323950533	-3.10868155574816
S	23.76480228916352	27.95558556357658	2.84171884986062
S	24.14460537385856	22.20352084133381	-6.11745454896985
N	23.55780973913461	24.96407384522050	-2.45513868860566
O	23.49644470930579	23.20013117324775	-5.12031951154328
N	24.06608977273711	25.78747284986621	-1.45540068204475
N	24.67111796564826	27.23215873669706	0.46802730517512
C	25.17325203478966	26.48556835310603	-1.68639936997785
N	25.51266522873205	27.37062325470522	-0.66240142212206
H	26.51297345174814	27.39841851572551	-0.43871092297953
N	21.79811379630602	23.53603033332017	-2.94123268254470
H	22.34655573785427	23.25483868134226	-3.77056552292819
O	27.26314061791858	32.43489810117588	5.64633173474919
C	20.49321676786332	22.99353091094821	-2.80067180161566
C	22.40264875040073	24.41173068642158	-2.09545133667961
C	24.85640768894903	28.07093873050741	1.47664651794374
N	25.82869814895759	29.03142442813951	1.43792008410985
H	26.04301252229300	29.37448583206255	0.49901933743233
C	26.62030503356213	32.16196303027934	3.29332842324703
H	26.67774429191760	33.22780574819122	3.07954745565034
C	26.90154114614416	31.66296481747892	4.57447705876885
C	23.54531549949663	22.68299400601144	-7.75945405751576
H	22.45101464434128	22.75277529409726	-7.73970248754515
H	23.88727245600113	21.92079771652941	-8.47177074016547
H	24.00403721557764	23.65079711364448	-7.99534670538578
C	23.19024464600200	20.67349601845576	-5.94329484914183
H	23.40064666001929	20.26756762694045	-4.94724357252495
H	23.54292080665786	19.97456902371204	-6.71251222492853
H	22.12314193730061	20.89445772057566	-6.06653346195741
O	16.62674631711296	21.41290801272485	-2.54585551474976
C	26.16391634746009	29.90596331491010	2.50836174856483
C	17.91750494563320	21.86319266544967	-2.64336786837440
C	20.30872014905234	21.61207635114023	-2.93209109739312
H	21.17550862299203	20.96565622618540	-3.07858997402653
C	26.82734904495018	30.27848036388917	4.80948264154623
H	27.07039213327503	29.89504481595077	5.80143062040570
C	26.24482895858308	31.28291269419043	2.27324799522495
H	26.01113038854085	31.67706593807321	1.28246420048964
C	19.03247337611440	21.04207579920137	-2.86571088672389
H	18.92529058240497	19.96409326960273	-2.97428110226028
C	26.47792517952350	29.40639408259640	3.78405341202751
H	26.46607008580941	28.33214531032715	3.96943957549650
C	18.09596071560052	23.25248028535194	-2.51208517655080
H	17.22138511376695	23.88646014228532	-2.35783638999030
C	19.36560768947851	23.81149125815899	-2.60295906589126
H	19.48581749838571	24.89234563126018	-2.53115871475840
C	27.35763273366662	33.85622287142805	5.43578209239572
H	26.38696616769196	34.27555006240620	5.13043498886643

H	28.11976418221576	34.09339103378763	4.67793174259508
H	27.65445453160032	34.27702831830938	6.40204179080760
C	16.40952377141574	19.99623386866129	-2.67930050872209
H	16.73576003237233	19.63727288743717	-3.66738299466048
H	15.32914998165296	19.85312482499783	-2.57285614447026
H	16.93707427251607	19.43961232128895	-1.88975298681841
Ni	26.18074864730576	26.06693323912438	-8.60010603525622
S	27.74977898832554	24.75290699612223	-7.90083776026362
S	26.92845321884239	26.37650048193859	-10.60939336903393
S	23.30866133686920	26.42353265634711	-5.29804126427633
S	25.66107141297449	27.95443024629849	-11.25768226661106
S	25.28472619996971	22.20029573455308	-2.29421199904149
N	25.87392484548478	24.96579429804283	-5.95935836004939
O	25.91901231202277	23.18362492202414	-3.31276096727988
N	25.36564206271922	25.79048015177015	-6.95806410908223
N	24.75948774365337	27.23593584472981	-8.88076508617310
C	24.26184382617299	26.49281671482828	-6.72415578470380
N	23.92170778295111	27.37764330469097	-7.74812996279901
H	22.92066444763807	27.40720083823027	-7.96822307674411
N	27.63197906165799	23.53411636308392	-5.47680246847508
H	27.08225494345885	23.24891568467554	-4.64979731281983
O	22.15017420444171	32.42969438866240	-14.06001271019738
C	28.93568158901106	22.98961401680870	-5.61890670905437
C	27.02764976545730	24.41163995483067	-6.32102755395121
C	24.57268796548271	28.07318547933179	-9.89036391576363
N	23.60216727275714	29.03550616830747	-9.85009285615579
H	23.39280369193241	29.38174123250055	-8.91124121798068
C	22.80065544179974	32.16144666677200	-11.70857353972218
H	22.74248204529360	33.22755483650820	-11.49638048620172
C	22.51594881275257	31.65995824245501	-12.98795190710737
C	25.91461283377090	22.69179125494122	-0.66725738526946
H	27.00843108986524	22.75990328012432	-0.70774246068078
H	25.58476163366300	21.93583900350891	0.05729659421275
H	25.46099474581112	23.66178537782649	-0.43080423044432
C	26.22883046403194	20.66444227363332	-2.47132101504883
H	26.00080345739053	20.25232927227815	-3.46093681951572
H	25.88500602702853	19.97311822049103	-1.69129613521643
H	27.29876253490721	20.88110411741611	-2.36653072492219
O	32.79924782647863	21.40225365038082	-5.87816926592740
C	23.26259632602939	29.90736785503814	-10.92118838171008
C	31.50936322723069	21.85485918006198	-5.77888330205952
C	29.11835778803871	21.60817505696046	-5.48436493801857
H	28.25088842081427	20.96347878815068	-5.33431261725244
C	22.59112517832057	30.27515555813998	-13.22077554095205
H	22.34539032045488	29.88969524865344	-14.21127567870794
C	23.18058239513647	31.28462837342224	-10.68823183541751
H	23.41700351482646	31.68082297478406	-9.69890148831339
C	30.39359831961793	21.03609751833799	-5.55202182196741
H	30.49935832055823	19.95824368697360	-5.44091047241306
C	22.94504767757294	29.40524410670339	-12.19502897822548
H	22.95771862837304	28.33071983472194	-12.37872052332832
C	31.33276144604788	23.24408498823697	-5.91315966549282
H	32.20797032482261	23.87634830644220	-6.07083704538524
C	30.06418921896179	23.80533193248050	-5.82090417574663

H	29.94562690345168	24.88619930042387	-5.89506816552492
C	22.05479477121483	33.85125287362377	-13.85149384406259
H	23.02602699754401	34.27222417183208	-13.55021450820776
H	21.29503672031934	34.08883159644125	-13.09139108463715
H	21.75412630180149	34.27013397922092	-14.81740552959846
C	33.01441229004392	19.98551648762350	-5.74221199340899
H	32.68966406438908	19.62913353671766	-4.75270067678358
H	34.09433071893552	19.84040268660390	-5.85059498857089
H	32.48431749322700	19.42810307082404	-6.52949818181980

Table S10. Cartesian coordinates of **Ni_3L_2** in its neutral form (Q = 0, S = 0).

Ni	24.68703987323967	26.18011852907187	-4.19880923676987
Ni	23.18655037526463	26.35128226791460	0.16870177775400
S	21.55869126964408	25.44015523588120	-0.93480307812059
S	22.31151783667053	26.29969583436859	2.14653977461572
S	26.34306082691130	26.70324180133583	-2.80522525449846
S	23.81812692716051	27.29868949145121	3.26456270181850
N	23.55465873599899	25.98304927588155	-2.66636771647811
N	24.06558326819511	26.41643549289664	-1.44537655851981
N	24.78903207776548	27.05134733570931	0.82349307729534
C	25.32769554599680	26.78948247715828	-1.41012721572069
N	25.76198968300947	27.27348736040724	-0.18808771439427
H	26.71576549203155	27.00642222694134	0.07715402857241
N	21.77528830975878	24.77641135864670	-3.55508858074739
H	22.39055212988690	24.60672063194523	-4.35334254741589
O	27.81763862711571	29.90971731859171	7.39289034943464
C	20.44136566772480	24.30463308618535	-3.66949168040876
C	22.34695059172887	25.41886028695587	-2.50667788276700
C	25.03859399918724	27.53663579458038	2.03309741510313
N	26.18391955267527	28.22272526837587	2.31099476737672
H	26.57341897013661	28.74222240287673	1.52166023856206
C	27.36428472610335	30.46049173362750	5.04519878922519
H	27.63751234429306	31.50756214393727	5.16350132019258
C	27.42449916418324	29.56844303990324	6.12722264346509
O	16.52147973919831	22.93556574756451	-4.14063630843393
C	26.57633732592392	28.66766130466229	3.60558986806928
C	17.82892762702638	23.32496718621795	-4.02194550116658
C	20.22348006070188	23.05836815689221	-4.26874921071815
H	21.07702211221094	22.46077192984977	-4.59371775446059
C	27.07391154558963	28.22016712343208	5.93394050446608
H	27.14545818158116	27.52771947273223	6.77377577391132
C	26.93242888581553	30.00691113023602	3.79556060540072
H	26.87175171529577	30.70669534453318	2.96014223519037
C	18.92778954131871	22.56777662435423	-4.45533597249646
H	18.79127535677754	21.59603037659884	-4.92674926362762
C	26.66873781956478	27.76958173683572	4.68243698637200
H	26.43985556835367	26.71379767262513	4.53612719396921
C	18.04564350655459	24.58129636418660	-3.42760485666183
H	17.18552001159741	25.17423545899495	-3.11316954857491
C	19.33578827153790	25.07302417654051	-3.26528639292153
H	19.48452844007056	26.06238128535008	-2.83390465388482
C	28.18598118871922	31.28262257894077	7.62431008419905

H	27.33993455345037	31.95710305674618	7.42331963692604
H	29.04709501462409	31.57081057034196	7.00251143100910
H	28.45953479493006	31.33849097280902	8.68298883744700
C	16.26490079885210	21.65862762247330	-4.75443118329783
H	16.63727840366321	21.63650428094753	-5.78983486651032
H	15.17592708605734	21.54467359397297	-4.75093906346226
H	16.72538214114042	20.84301672301649	-4.17650164544927
Ni	26.18623381185975	26.41019392104813	-8.56430146494189
S	27.80810863499056	25.46981824302908	-7.47686798683753
S	27.05904468302547	26.38226805192117	-10.54362695834902
S	23.03489610459543	26.74046970401007	-5.58246338502905
S	25.56002115922343	27.41150108420765	-11.64422096995363
N	25.81744010441250	25.99991675080521	-5.73504030818705
N	25.30895474187632	26.45653371693516	-6.94854871931211
N	24.58890495173040	27.13332178788923	-9.20657729306275
C	24.04991242194387	26.84038443235596	-6.97683908444279
N	23.61864720056247	27.34737717792320	-8.19066150261552
H	22.66250792271791	27.09243394320467	-8.45932583421774
N	27.58901082210730	24.76694395984792	-4.86708479214280
H	26.97313833023263	24.58942376489465	-4.07101144373761
O	21.58066003347964	30.11827309498090	-15.72854890682996
C	28.91916160719769	24.28259500637398	-4.76161559481480
C	27.02104064779862	25.42973983773181	-5.90477431420949
C	24.34237568357878	27.63955493022425	-10.40814568633156
N	23.20225635954520	28.33898119336504	-10.67432451632641
H	22.81844449479148	28.85027399464389	-9.87686720237110
C	22.04107962523982	30.62915046353002	-13.37323359486156
H	21.77753638058502	31.68039313286002	-13.47539340763818
C	21.97164003620136	29.75420154429873	-14.46857818772623
O	32.82815111331406	22.87404655431946	-4.31683453562375
C	22.81320222668574	28.80741224044306	-11.96167582763422
C	31.52384963124607	23.27614954085806	-4.42761326778526
C	29.12750799983837	23.02593868616003	-4.18095531503139
H	28.26950566731365	22.43075921731069	-3.86336659421683
C	22.30973364018548	28.39991149092216	-14.29608515582225
H	22.23108312633885	27.72094026390203	-15.14622264431543
C	22.46963007815696	30.15268156258653	-12.13098331099663
H	22.53743287725406	30.83912751479270	-11.28511075162076
C	30.41932285506207	22.52191307177811	-4.00356878196239
H	30.54840549868628	21.54228631548072	-3.54660962457694
C	22.71159342214508	27.92666219661320	-13.05190265969070
H	22.93078346496893	26.86670770387691	-12.92176853936777
C	31.31677009869568	24.54282227643500	-5.00311064832294
H	32.18133555502872	25.13314144532820	-5.31019845021814
C	30.03053816163651	25.04760089927031	-5.15619109694303
H	29.88946287680389	26.04433879873806	-5.57285349718525
C	21.22527932687096	31.49797378372496	-15.93888393269857
H	22.07777571037293	32.16124282913960	-15.72813013473243
H	20.36721312135282	31.78484283105653	-15.31227836018057
H	20.95180519998872	31.57252937411847	-16.99643355982261
C	33.07488580322246	21.58598545429550	-3.72256141047296
H	32.70420436786235	21.55161224342629	-2.68688007812250
H	34.16283547077366	21.46280010277548	-3.72981581480326
H	32.60639826326238	20.78300898106907	-4.31163820678306

Table S11. Cartesian coordinates of **Ni_3L_2** in its monoanionic form (Q = (-1), S = 1/2).

Ni	24.77459216598267	27.06943183866915	-4.27354579545575
Ni	23.62684402940488	26.10942829955895	0.17805366504186
S	21.96016845231384	25.33667932457990	-0.97880890860590
S	22.97189851197035	25.45662900724755	2.13979141172611
S	26.42666923229676	27.71099157002383	-2.78728040295930
S	24.42688698483403	26.40209767015061	3.36755803644928
N	23.74164075086195	26.46543998351954	-2.67632192911436
N	24.33653676875346	26.66072677212547	-1.43673303323149
N	25.17735365690374	26.87635392336038	0.87846320374740
C	25.53049281263028	27.23804932893232	-1.39556161864898
N	26.00115430763245	27.48312352692250	-0.10446754339912
H	27.00137550858553	27.29540173122664	0.02088616790239
N	21.87667368740592	25.61005920520917	-3.71406614477053
H	22.24815494663536	26.14641456814269	-4.51457496146921
O	28.48868055996754	28.62428840075175	7.70546468850945
C	20.64542671203558	24.95621816582799	-3.91954816586322
C	22.57824791843881	25.82669311119282	-2.56080693471465
C	25.47974421504793	27.09410884687899	2.14956720502617
N	26.54774650700976	27.86936846728249	2.50755176669818
H	26.77592923487633	28.60674929204878	1.83729991492128
C	27.74549138939769	29.60066463053671	5.57947134105615
H	27.91567527569696	30.62452728464550	5.90786785753443
C	28.00889909018421	28.51386454135551	6.42722156698784
O	16.97094488814082	23.15721511222660	-4.85063753853732
C	27.01259748607974	28.07127942391544	3.83594802854095
C	18.18613901816334	23.69356847570187	-4.50037787758989
C	20.24675835297198	23.80829865551651	-3.21939738186606
H	20.89697316406718	23.37863562163868	-2.45892438733800
C	27.78660342150762	27.20507121789315	5.96340809040698
H	28.01623503166644	26.36373621900805	6.61881490175596
C	27.24092227611009	29.37303428360876	4.29566233340315
H	27.02156531343828	30.22220543198015	3.64582393325007
C	19.02201184176302	23.18858361518551	-3.49524621605156
H	18.74417848382160	22.30125206565532	-2.92837992188810
C	27.30868526159319	26.98401795177856	4.67625309626859
H	27.18136353837949	25.96314516937509	4.31563075052285
C	18.59424603135449	24.82586386095761	-5.22711454426818
H	17.94721746476444	25.21472036016679	-6.01505560776591
C	19.80111796672215	25.44948871224323	-4.93562406078902
H	20.10088305834677	26.33534621604311	-5.49954704627297
C	28.73122469906556	29.95162412064775	8.20773985755278
H	27.80339004070968	30.54333468359631	8.22342359127303
H	29.49176287988266	30.46963543421707	7.60386844229342
H	29.10041702339900	29.81618667862724	9.22960789547369
C	16.53433235301394	21.99331311158697	-4.12741907031564
H	17.23288848355795	21.15411023322428	-4.26819526147191
H	15.55705139873212	21.73362859575547	-4.54796869020736
H	16.42966604121708	22.21024502434463	-3.05307276392813
Ni	25.71102838109348	26.29467744624847	-8.80414557913448
S	27.37928533096557	25.38853247520687	-7.75231037572429
S	26.22918677042054	25.66140394745436	-10.81245933425083

S	23.16672821255473	27.99728005212224	-5.66758753182294
S	24.79920411400931	26.75375930743277	-11.94354678608733
N	25.75409588605994	26.57058258861787	-5.93843727347497
N	25.11351163750115	26.83922710999820	-7.14154076711711
N	24.19317860684031	27.19527185182609	-9.40952963673818
C	23.96416506984084	27.50124996904164	-7.11146768636391
N	23.45738140293109	27.82348502129153	-8.37178626086117
H	22.44215284787751	27.70751995324039	-8.45774934357464
N	27.55618859819390	25.49341313541613	-5.00864273490294
H	27.08325670185507	25.78420598137542	-4.13991149380904
O	20.73932169866519	29.41549543574247	-16.02494179976719
C	28.81239882682770	24.87671520779421	-4.84563161098846
C	26.87045450675895	25.86688533105054	-6.12939837510533
C	23.85318450071665	27.47786645847892	-10.65815039050045
N	22.83055954614850	28.33943166837277	-10.94303895659709
H	22.68379066272254	29.06602158758007	-10.23906952416097
C	21.62916346661713	30.26020015984995	-13.89866876003599
H	21.51510412520091	31.30477010552603	-14.18329145918314
C	21.25994251675175	29.22586529595311	-14.77227179339076
O	32.54171657020980	23.07541501324933	-4.16446486951171
C	22.32598671510380	28.62126652078508	-12.24199746515813
C	31.30089316147989	23.64381279241253	-4.32022719958401
C	29.02964485703996	24.16032256812036	-3.65660674538485
H	28.21994792077722	24.07137325581393	-2.92955089429365
C	21.41079849546517	27.88879355770709	-14.36380234505751
H	21.09903664798428	27.08962029252169	-15.03778030157814
C	22.16772325393336	29.95167045201134	-12.64592112194324
H	22.46930447530460	30.75959751374203	-11.97674104287193
C	30.25913927859980	23.55470391200549	-3.38534793644828
H	30.38530478411268	23.01030955743272	-2.45083183765228
C	21.92300936143471	27.58843823829509	-13.10623002320719
H	21.99420044122438	26.54853035450523	-12.78695766249741
C	31.09407481233981	24.36441065185967	-5.50799981079426
H	31.91203747447922	24.44900724328681	-6.22548355986879
C	29.87390358871782	24.98323079951508	-5.76487711082771
H	29.75267284729297	25.56262880366541	-6.67868598009797
C	20.56397879345720	30.77372804474033	-16.46915037821119
H	21.52709576075868	31.30515260246844	-16.50469519887015
H	19.86452082051726	31.31594357986666	-15.81483595452447
H	20.14484351349034	30.70106308023379	-17.47806824946025
C	32.77982937831628	22.34159089680946	-2.95064892540155
H	32.67762221503708	22.99149641571352	-2.06783618543155
H	33.81023680543696	21.97774963590697	-3.02284191383973
H	32.09101537959901	21.48730336262819	-2.86189775371226

Table S12. Cartesian coordinates of **Ni_3L_2** in its dianionic form (Q = (-2), S = 1).

Ni	24.76417642587210	27.12481476930367	-4.29205501010271
Ni	23.57403615122540	26.17516402511446	0.20304128476351
S	21.92675562067776	25.35239950826962	-1.02832987423509
S	22.97784914710880	25.56316792294645	2.23009182807066
S	26.40371879877485	27.79007813592962	-2.79840673757217
S	24.50440306346597	26.46446325869929	3.39766930568159
N	23.73207955835466	26.52339612708957	-2.68810632352098
N	24.30323639776039	26.75097090506526	-1.44423414288218
N	25.16843453445433	26.99181850342810	0.88623547562208
C	25.48856795944761	27.33293545456484	-1.40557432168576
N	25.95638365827420	27.60914857065902	-0.11344819879451
H	26.96561912472410	27.47164874057800	0.00370621577343
N	21.91711410586454	25.63821120591241	-3.77058115180995
H	22.31023141666348	26.19373509237907	-4.54846403279968
O	28.78904963048573	28.51118172240468	7.61497957551980
C	20.73693696779821	24.93282043446824	-4.05713771286754
C	22.57688247796560	25.85796545445965	-2.58623602226391
C	25.52175941729205	27.17410070216659	2.14137792491023
N	26.61767770640211	27.93592763680347	2.48165306471791
H	26.78020097521769	28.72572050858532	1.85297356339396
C	27.95205643436764	29.56117019452818	5.55821960773240
H	28.14076504260478	30.57318511158329	5.91271544228455
C	28.24966119773680	28.44626542096568	6.35544280890061
O	17.22031160118867	22.97645880944554	-5.27342437580933
C	27.13294703494242	28.09381090724891	3.79564373945959
C	18.38039357794778	23.56699114950336	-4.82645211349714
C	20.29313030645288	23.80684685366628	-3.34550398824417
H	20.86585386374091	23.44131495669786	-2.49514787315155
C	27.99995844853286	27.15491797949997	5.85786172364902
H	28.25465551164504	26.29098253910981	6.47366480777021
C	27.38734239010669	29.37790918791475	4.29147708042297
H	27.14161703455153	30.25006393936513	3.68240713190218
C	19.12124074486911	23.13626131728594	-3.71810626564302
H	18.80878841223750	22.26840669115191	-3.13880071750429
C	27.46253729581649	26.97891510607551	4.58729512154084
H	27.31118077722723	25.97121998468300	4.20003214863064
C	18.83171657639047	24.67753578050030	-5.56027133485124
H	18.26004245134920	25.01109222321183	-6.42801684043370
C	19.98603946434838	25.35008899687215	-5.17789442354673
H	20.32038365113855	26.21752328023304	-5.75168247774701
C	29.06002292334288	29.81964445889396	8.14884151326645
H	28.13645838573989	30.41316298622355	8.22891778333617
H	29.79277602255978	30.35687617371746	7.52727809351491
H	29.47719131836362	29.64982696579949	9.14696805257529
C	16.74520771219514	21.83341756637183	-4.54325896061876
H	17.47737102271878	21.01138614003758	-4.57146759604402
H	15.82339066268778	21.52246356234454	-5.04650937899912
H	16.52529722978293	22.09406593571360	-3.49615313062623
Ni	25.74657674007804	26.31583442630913	-8.86655468785558
S	27.36677430352867	25.32199349078499	-7.72286130220179
S	26.20117441245257	25.72737048715168	-10.93947196924501

S	23.18032003346633	28.07574813789673	-5.70274594638155
S	24.71799461993881	26.80333571710215	-12.01033838049431
N	25.73613833953322	26.59260133827383	-5.95825441440727
N	25.13192734480456	26.89894289278701	-7.16890607985225
N	24.20382749583354	27.29899322096739	-9.45716406294143
C	24.00228016335548	27.58169896382243	-7.14308267713526
N	23.51233015343794	27.94440823618834	-8.40579673500478
H	22.49112341237170	27.89758498031259	-8.48504350053288
N	27.45735708295583	25.45980896791407	-4.96640106667577
H	26.96529185534977	25.81782131717810	-4.13230995083318
O	20.49441475408591	29.41327050039171	-15.97634015284723
C	28.67915461287493	24.82171531228878	-4.70199258540530
C	26.83097282858983	25.83983289926239	-6.12789733866482
C	23.81946747719157	27.55715804727344	-10.68916443622777
N	22.78431923178390	28.42598916976084	-10.95796198864909
H	22.71822853217120	29.20136773805236	-10.29465779178583
C	21.48474990087745	30.29459780437411	-13.90825755391679
H	21.36809081584164	31.33409211907437	-14.21035309536396
C	21.06859005016217	29.24609049681099	-14.74167609158583
O	32.30385383529585	22.94637985494500	-3.67832119483546
C	22.23882422044467	28.68490092279528	-12.24310193083745
C	31.09655394115416	23.55241193050438	-3.94334499287309
C	28.86770911280876	24.32715418814406	-3.39710510729592
H	28.06326959625535	24.43045990379746	-2.66579374249479
C	21.22633399207922	27.91707292901847	-14.31015164825802
H	20.88000716382299	27.10623321972742	-14.95285685201849
C	22.07519067211143	30.00712718023125	-12.67297747973218
H	22.41288325575151	30.82722254815715	-12.03619706528351
C	30.05816217817904	23.70544064880272	-3.01324445145528
H	30.15721381914033	23.34031179667783	-1.99204593292028
C	21.78990041351764	27.63885360623655	-13.06944040017328
H	21.86910095989531	26.60519633138474	-12.73243028489398
C	30.92137714722886	24.04647929207723	-5.24535572027783
H	31.73446234199648	23.93962907107349	-5.96586553951967
C	29.73816209730019	24.67807207208148	-5.62170381392414
H	29.63655580092614	25.06679454832532	-6.63303868086475
C	20.31356918150606	30.76295398596632	-16.44111953705718
H	21.27936432887551	31.28349935133785	-16.53012915539430
H	19.64932540061300	31.32732867197917	-15.76875431886930
H	19.84965917751883	30.67463056074764	-17.42910542455413
C	32.50098565672117	22.43594467905503	-2.34945556685178
H	32.44505989686738	23.24200547852528	-1.60115113952586
H	33.50566843401104	21.99971892622562	-2.34544394463133
H	31.75953198287865	21.65831814073392	-2.10822055563851

Table S13. Cartesian coordinates of **Ni_3L_2** in its dianionic form (Q = (-3), S = 1/2).

Ni	24.61047796692693	27.13542616141584	-4.27206955650259
Ni	23.43153672311021	26.17933831103739	0.30568559058823
S	21.86590204418020	25.20087520642356	-1.01502495251065
S	22.98381909164061	25.62294958370009	2.40813186339795
S	26.19496368591949	27.96185034120612	-2.78294471500989
S	24.52927440914396	26.61549855127625	3.48221682687486

N	23.61169319556101	26.52224126584214	-2.64417145010039
N	24.15256612998686	26.81724471811681	-1.40061215726777
N	25.05108165709716	27.17331791518271	0.93642836365955
C	25.29559006916111	27.46575787307864	-1.37943458088585
N	25.76110030170091	27.80925320269781	-0.09832992267398
H	26.78172632663070	27.77690340718278	-0.00359796544446
N	21.88130712692008	25.52858928550901	-3.75559990731585
H	22.26846528447888	26.11113401288933	-4.51746099201156
O	29.15013373560504	28.64608133038265	7.40446539168073
C	20.81720796114953	24.69399186396228	-4.11819231989092
C	22.50381501600212	25.77041818004403	-2.54823719430325
C	25.46554377387136	27.35755888176860	2.16473153625843
N	26.55645924148186	28.16284946455391	2.45747240549286
H	26.61008770269889	28.99914660288840	1.87129762807741
C	28.13695518926912	29.73176173905423	5.44523962806341
H	28.35470880470423	30.73791837656776	5.80009865860796
C	28.50301228816786	28.60404812636931	6.19306288833367
O	17.64226024302106	22.35620860529525	-5.60060649891012
C	27.16989427583439	28.29513942669064	3.72774660998227
C	18.68938636498590	23.07500818971421	-5.06348721155562
C	20.40458588663838	23.55457069568537	-3.40599762009519
H	20.91015056526551	23.28559621222735	-2.48062406259768
C	28.21129328426138	27.32209975556674	5.69416033830384
H	28.51727145024414	26.44719538103938	6.27012134266064
C	27.46550087317664	29.56985375567918	4.22778128912401
H	27.16905121494633	30.45345700627857	3.65861712558962
C	19.34806633914455	22.75864402321204	-3.86874251162801
H	19.05890559492143	21.88526661434150	-3.28521413953949
C	27.56690177860497	27.16766137278240	4.47136026246412
H	27.38092695133705	26.16660707382802	4.08237460113458
C	19.10675568274010	24.20104728448596	-5.79349949713625
H	18.59960839373789	24.44920608341411	-6.72767259534393
C	20.14680941083700	24.99545276936326	-5.32661943683845
H	20.45677883749183	25.87153153332986	-5.90161366688152
C	29.47429867378932	29.94446861652510	7.93075995741321
H	28.56506300630480	30.54024753127001	8.10531783411837
H	30.14862295976453	30.49008556756628	7.25264282519351
H	29.98130106353526	29.75865291956153	8.88357461149266
C	17.21032680857874	21.19447340234486	-4.87515021564096
H	18.02074191204813	20.45338191466714	-4.79070103330386
H	16.38418514531090	20.77091231133937	-5.45661030006188
H	16.85352416712248	21.46323587110356	-3.86827794358457
Ni	25.84978816557652	26.44124056117087	-8.88143043852021
S	27.40052786093106	25.39215587011814	-7.59833453896191
S	26.35658739620895	26.04868272876103	-11.00677493554715
S	23.02590727531140	28.01195223813810	-5.73256294888363
S	24.82785382857791	27.10868245293385	-12.04318773497987
N	25.62431847683698	26.60793698805156	-5.92073191848545
N	25.09912461733257	26.97290948541436	-7.15202005111000
N	24.22940682002533	27.45436058269272	-9.47667960679015
C	23.94982367407614	27.61018829369620	-7.15082565928275
N	23.49818704241093	28.02648059487640	-8.41601448344624
H	22.47951008668772	27.97781397379084	-8.52453404082396
N	27.34414714366167	25.55871891828432	-4.84465046936813

H	26.95799435151006	26.10893272978376	-4.05850554703884
O	20.53766746798611	29.77010711213841	-15.95043639860981
C	28.40517784571788	24.70480308654126	-4.52008555466451
C	26.73681770985317	25.86760992205249	-6.04426187772328
C	23.86159084374006	27.75443383236889	-10.69770164464182
N	22.79565813709880	28.60231099256358	-10.95314199831426
H	22.70815224899271	29.35406611106839	-10.26509576761397
C	21.43761794910476	30.57340914343729	-13.80852855046955
H	21.26162528282275	31.62153969829810	-14.04529447401521
C	21.10131216677726	29.55863836727115	-14.71546552026123
O	31.53097136284635	22.14833667942542	-3.32314806211774
C	22.26485149906474	28.90761136683069	-12.23096483866792
C	30.51577482413856	23.02193575309882	-3.65168575976804
C	29.08515263066087	24.94694680901778	-3.31057059100515
H	28.79133626865747	25.80337815109521	-2.69878475342534
C	21.33506014710936	28.21692038094125	-14.36567996515075
H	21.05115891449968	27.42943470957552	-15.06572594436663
C	22.02515744188530	30.24241065272482	-12.58213800658639
H	22.30064078703669	31.03952486490375	-11.88837092633097
C	30.12290698249705	24.11940382655127	-2.87268221588931
H	30.61794251061425	24.34745247620535	-1.92973901097356
C	21.89505624282677	27.89332167063403	-13.13422367884759
H	22.03508495844275	26.84664045726631	-12.86411071433724
C	29.84038557333234	22.76566566046316	-4.85552224228177
H	30.13591511839885	21.90155304550345	-5.45389889055644
C	28.79778502740611	23.58451464250385	-5.28353036465837
H	28.28174922994029	23.35862774197597	-6.21470102909774
C	20.28370175622469	31.13344680587544	-16.33120301524409
H	21.21721724168794	31.71611338544581	-16.36492104137216
H	19.57413875522103	31.61292184611234	-15.63919386131084
H	19.84419729902375	31.08335297128407	-17.33305673998024
C	32.22658501237751	22.39225109660996	-2.09048050592961
H	32.72258872813157	23.37566162756318	-2.10055440121806
H	32.98081372159900	21.60156650687113	-2.01310945044561
H	31.54267196608533	22.33574386960822	-1.22889096236371

Table S14. Cartesian coordinates of TS for the proton transfer between $\mathbf{Ni_3L_2}$ and TFAH after the first reduction (Q = (-1), S = 1/2).

Ni	24.47860279737442	25.49469859435335	-4.15697574664078
Ni	23.28455052920804	26.18126181108256	0.28750555045533
S	21.75878650243560	24.85964424160477	-0.48455874139151
S	22.55212780290958	26.33147951473838	2.31798135713489
S	26.05603045999013	26.80885972831520	-3.03636554199203
S	23.82157510245750	27.85456326163377	3.07984374895359
N	23.56568215467486	25.31255401023413	-2.44521488135722
N	24.06049609672744	26.06936711463702	-1.38462233895386
N	24.70318527036887	27.33591950946556	0.64473938459162
C	25.15858031572565	26.78942669118192	-1.57335032087979
N	25.51751187329802	27.58392004113431	-0.48754436290336
H	26.52306355637050	27.60551346405995	-0.28843471458345
N	21.81431703214580	23.88527787621127	-3.00125477276400

H	22.28182677526879	23.76263616038890	-3.90994117632746
O	27.28975937410144	32.20250652848417	6.14874857745620
C	20.63888803310634	23.10867010955542	-2.76977752243779
C	22.44077510327989	24.66824603127285	-2.09584743455648
C	24.88773137486935	28.10022287607930	1.71238566572182
N	25.83982162856328	29.07887229292371	1.73416216039767
H	26.04826645711110	29.48491541249618	0.81953810170315
C	26.63727518390674	32.08086897985228	3.78582066625811
H	26.69313273171212	33.15825435160319	3.64079004154156
C	26.92409954101916	31.50076316312521	5.03116898500426
O	17.15812650717764	20.84260323459616	-2.33975980949714
C	26.17900153946514	29.87981646266170	2.85909059783581
C	18.32829496711701	21.54708289154690	-2.42977337674865
C	20.59385657807427	22.11619478200668	-1.78484112264647
H	21.46657763121351	21.93488842970685	-1.15766836455596
C	26.85150529134887	30.10402780918272	5.17660230047105
H	27.09890230604560	29.65743112603512	6.14062384867813
C	26.25839184081371	31.26919767395732	2.71285236069374
H	26.02069047753989	31.72611826859440	1.75042496087029
C	19.44312847930301	21.34404858062182	-1.60130016848581
H	19.43432814501706	20.58058434778526	-0.82529569855783
C	26.49839604905104	29.29933337416849	4.09855917485267
H	26.48936456712226	28.21548221906596	4.21515857097484
C	18.37970347940457	22.52754298241265	-3.43680117809717
H	17.51050353498048	22.67539996310795	-4.07927185880501
C	19.52261572475165	23.30332273570552	-3.59885056367086
H	19.55449703487908	24.07067106228418	-4.37383194687808
C	27.38536319722467	33.63429047461197	6.02872684404848
H	26.41374369259876	34.07357031221704	5.75622883775969
H	28.14362289108112	33.91816820941592	5.28323523322653
H	27.68819380114112	33.99226517105958	7.01815836440178
C	17.07420033571798	19.82382995024597	-1.32527556845199
H	17.83213958296334	19.04258521511072	-1.48719819541105
H	16.07256973936977	19.39282711223560	-1.42434461159376
H	17.19499564160828	20.25640822141016	-0.32062679524816
Ni	26.02206399835821	26.12956193425090	-8.47668967794827
S	27.45978483313781	24.77314540539380	-7.57425894311760
S	26.91093466025654	26.25825696974635	-10.44518302122467
S	22.95112421329133	26.76259335405659	-5.40837433951264
S	25.74489346583750	27.82002145999156	-11.29279123005955
N	25.53389037209477	25.32315480411156	-5.77957241370470
N	25.10086756134826	26.03892812991750	-6.87890480815208
N	24.64903958174023	27.30231103363269	-8.94674706390410
C	23.98511195554298	26.75256746078199	-6.78409417340022
N	23.72455477245650	27.54003098798466	-7.89871993464999
H	22.74303500262699	27.56567168565647	-8.19424197865037
N	26.98899753369586	23.66568007329640	-5.10230261601085
H	26.20860498482318	23.18955872928348	-4.61508217538572
O	22.57190293223070	32.15174838552309	-14.67469754941579
C	28.25319249502366	23.04179054968791	-5.01397558159451
C	26.61294958605925	24.59001224027407	-6.03485586351884
C	24.56189334086041	28.06801026184896	-10.02585865022820
N	23.61908876939922	29.05000089100579	-10.13250931829301
H	23.33665386737378	29.46301591867373	-9.24120220150607

C	23.03586958009013	32.04440504510615	-12.26717529799264
H	22.98671832940776	33.12400918270491	-12.13696088921817
C	22.83777616775023	31.45589457320050	-13.52574375046246
O	32.00598237324424	21.22182141814481	-4.61689305095369
C	23.38298345384566	29.84615665288914	-11.28745717208330
C	30.74578272258223	21.75572914474613	-4.72569685492444
C	28.32378672259368	21.68406833439295	-4.67114341359199
H	27.40011807970480	21.12259777171190	-4.52092433929101
C	22.89838928451526	30.05664868863513	-13.65251645679273
H	22.72002516474423	29.60425460537105	-14.62900132192527
C	23.31590698009938	31.23793960750864	-11.16035476859751
H	23.48492456371337	31.70092962397147	-10.18643323261338
C	29.55667481437863	21.04157079573704	-4.51932421907825
H	29.57379166886359	19.98644132850241	-4.25094365781727
C	23.15233687489071	29.25776737155406	-12.54280078681221
H	23.15348502942601	28.17268087787405	-12.64789546384654
C	30.68035237513255	23.11972813502844	-5.06036549368369
H	31.60851279752505	23.67655862497418	-5.19897224355473
C	29.45195270076311	23.75842063561705	-5.19027342747929
H	29.42244863280672	24.82346698877780	-5.41949487894684
C	22.49156379218276	33.58605677982996	-14.57535186773391
H	23.44663226380835	34.01213577323595	-14.23252789329262
H	21.68311125148012	33.88980829824665	-13.89312463205995
H	22.27211493184782	33.93872115640635	-15.58840470547519
C	32.10233493257048	19.82854781657440	-4.27194315283915
H	31.65344302258612	19.63231883224926	-3.28603917239212
H	33.17412834812728	19.60610319807040	-4.23973154073033
H	31.61551624719316	19.19789622159059	-5.03169792747480
H	23.82485808917841	24.29671498529669	-4.71773747825414
O	23.14315397398779	22.71288415273238	-5.33064615271698
C	23.89339835390567	21.79352165818570	-4.89502309330334
C	23.47406605749256	20.33307051901545	-5.30637805688026
O	24.92810780027192	21.85324003121841	-4.19694108722470
F	24.40703765676665	19.78498094080659	-6.14086286658269
F	23.38637313626839	19.51902829540332	-4.21503854299060
F	22.27988516846332	20.26692228539235	-5.94811808970221

Table S15. Cartesian coordinates of TS for the proton transfer between **Ni_3L_2** and TFAH after the second reduction (Q = (-2), S = 1).

Ni	24.495371	25.923147	-4.134223
Ni	23.235009	26.176584	0.414062
S	21.554285	25.186395	-0.633634
S	22.587264	26.109675	2.516710
S	26.123336	27.020881	-2.842744
S	24.113672	27.243335	3.450375
N	23.471367	25.750551	-2.464075
N	24.031753	26.261761	-1.306549
N	24.834505	27.113086	0.904170
C	25.199832	26.871697	-1.393162
N	25.647306	27.449426	-0.200608
H	26.654652	27.353442	-0.035345

N	21.600427	24.736576	-3.334876
H	22.082613	24.956626	-4.214173
O	28.333956	30.241540	7.122003
C	20.354774	24.096435	-3.477663
C	22.258480	25.211675	-2.238615
C	25.171077	27.597333	2.082179
N	26.276334	28.401235	2.246044
H	26.469272	29.004079	1.443135
C	27.580309	30.739011	4.837914
H	27.788796	31.804114	4.924131
C	27.826215	29.863052	5.905467
O	16.668166	22.263453	-4.301125
C	26.765711	28.881985	3.489974
C	17.876664	22.828987	-3.971277
C	19.761730	23.279615	-2.504259
H	20.263326	23.112488	-1.553490
C	27.554221	28.492141	5.750688
H	27.769079	27.812370	6.576589
C	27.043259	30.245235	3.644454
H	26.837840	30.934472	2.822997
C	18.529146	22.659379	-2.743054
H	18.099337	22.033777	-1.962102
C	27.044770	28.003674	4.552268
H	26.876425	26.933159	4.434148
C	18.478355	23.624653	-4.961636
H	17.975788	23.752555	-5.921688
C	19.693952	24.250234	-4.714803
H	20.145216	24.874499	-5.489347
C	28.627485	31.638003	7.307743
H	27.718908	32.250572	7.203011
H	29.389805	31.980678	6.591399
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C	16.036386	21.440403	-3.305603
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S	22.884094	26.949379	-5.523354
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N	24.428842	27.119648	-9.169198
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H	22.541707	27.326638	-8.357234
N	27.235962	24.355095	-4.876542
H	26.533874	23.983700	-4.216019
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C	28.565791	23.935040	-4.669578
C	26.751006	25.081945	-5.927474
C	24.177229	27.638017	-10.355173
N	23.086128	28.446265	-10.575058

H	22.832391	29.023767	-9.770599
C	21.974126	30.861529	-13.184970
H	21.771679	31.929008	-13.254516
C	21.807990	30.017937	-14.293307
O	32.511340	22.724723	-3.912362
C	22.688128	28.964042	-11.836946
C	31.195393	23.061667	-4.124147
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H	27.948483	22.092182	-3.734477
C	22.067880	28.642452	-14.159598
H	21.914629	27.987883	-15.018886
C	22.422052	30.331705	-11.970469
H	22.565643	30.995738	-11.115814
C	30.099070	22.274983	-3.744824
H	30.239435	21.319585	-3.241314
C	22.487881	28.117760	-12.941985
H	22.647028	27.043870	-12.843429
C	30.968490	24.293975	-4.761663
H	31.823825	24.913731	-5.036436
C	29.673758	24.730916	-5.020534
H	29.518851	25.700670	-5.491947
C	21.116675	31.835749	-15.699335
H	22.016103	32.440521	-15.507217
H	20.302230	32.161469	-15.034295
H	20.809245	31.953075	-16.743748
C	32.769518	21.474393	-3.251314
H	32.330538	21.461370	-2.241580
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H	32.375859	20.627889	-3.835092
H	24.126901	24.495172	-4.475398
O	23.813593	22.918769	-4.746857
C	24.536012	22.239911	-3.955260
C	24.053381	20.749426	-3.813462
O	25.525685	22.575388	-3.278068
F	24.991465	19.943467	-3.251884
F	22.941507	20.680689	-3.021074
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