SUPPORTING INFORMATION

For Dalton Transactions

Computational investigation into intramolecular hydrogen bonding controlling the isomer formation and pK_a of octahedral nickel (II) proton reduction catalysts

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Table S1. Single point energies (in a.u.) of the starting catalysts at different spin states (singlet and triplet) using different functionals (B3LYP, B3P86, and M11-L) and 6-311+g(2df,2pd) basis sets in gas phase.

	Single point Energy (a.u.)					
	B3LYP		**B3P86**		**M11-L**	
	Singlet	**Triplet**	**Singlet**	**Triplet**	**Singlet**	**Triplet**
$[Ni(L1)_3]^-$	-3446.4713	-3446.4907	-3450.2148	-3450.2333	-3446.3773	-3446.3936
$[Ni(L2)_3]^-$	-4457.9704	-4457.9942	-4463.3839	-4463.4066	-4457.5641	-4457.5832
$[Ni(L3)_3]^-$	-4457.9881	-4458.0114	-4463.3998	-4463.4222	-4457.5753	-4457.5940
$[Ni(L4)_3]^-$	-4012.4289	-4012.4469	-4017.3341	-4017.3510	-4012.1822	-4012.1963
$[Ni(L5)_3]^-$	-4012.3832	-4012.4655	-4017.2892	-4017.3752	-4012.1388	-4012.2104
$[Ni(L6)_3]^-$	-4825.3524	-4825.3756	-4830.0155	-4830.0379	-4825.1749	-4825.1942
$[Ni(L7)_3]^-$ (*fac*)	-3564.4603	-3564.4799	-3568.6444	-3568.6565	-3564.3476	-3564.3700

Table S2. Gas phase single point energies (in a.u.) of the computationally modeled *fac* and *mer*- isomers of five substituted **$[Ni(PyS)_3]^-$** catalysts in both singlet and triplet spin states.

	Single point Energy (a.u.)			
	fac		***mer***	
	Singlet	**Triplet**	**Singlet**	**Triplet**
$[Ni(L8)_3]^-$	-4463.3715	-4463.3855	-4463.3614	-4463.3853
$[Ni(L9)_3]^-$	-4463.3909	-4463.4115	-4463.3956	-4463.4158
$[Ni(L10)_3]^-$	-3568.6441	-3568.6657	-3568.6501	-3568.6696
$[Ni(L11)_3]^-$	-3568.6362	-3568.6554	-3568.6424	-3568.6601
$[Ni(L12)_3]^-$	-3568.6418	-3568.6615	-3568.6479	-3568.6658

Table S3. Comparison of the different Ni-N and Ni-S bond lengths (in Å) between the X-ray structure[1] and computationally modeled structures (in gas and water solvated phases) of tris(pyridinethiolato)nickel (II), (**$[Ni(L1)_3]^-$**).

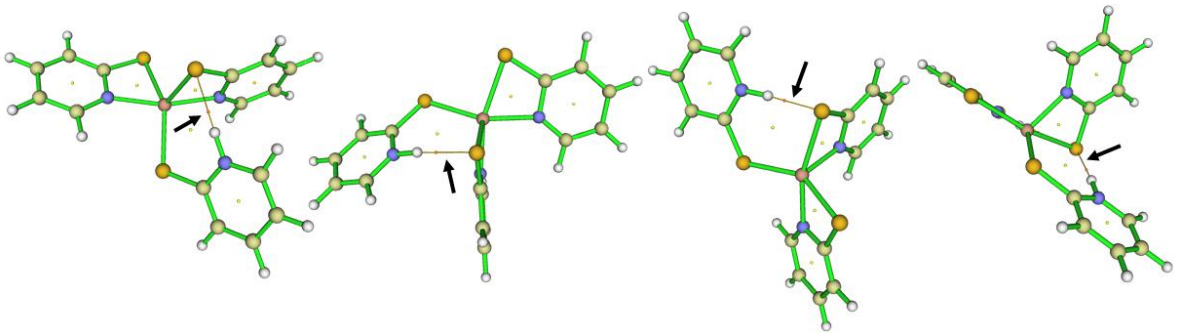
	Bond length (Å)			% Error	
	B3P86/6-311+G(2df,2pd)		**X-ray**		
	Gas	**Water**		**Gas**	**Water**
Ni-N1	2.049	2.055	2.034 (4)	0.74	1.03
Ni-N2	2.054	2.051	2.041 (4)	0.64	0.49
Ni-N3	2.079	2.071	2.081 (4)	0.10	0.48
Ni-S1	2.540	2.534	2.541 (1)	0.04	0.28
Ni-S2	2.503	2.543	2.526 (1)	0.91	0.67
Ni-S3	2.537	2.533	2.518 (1)	0.75	0.60

Table S4. Ni-N and Ni-S bond distances (in Å) of the computationally modeled starting catalysts in water solvated phase.

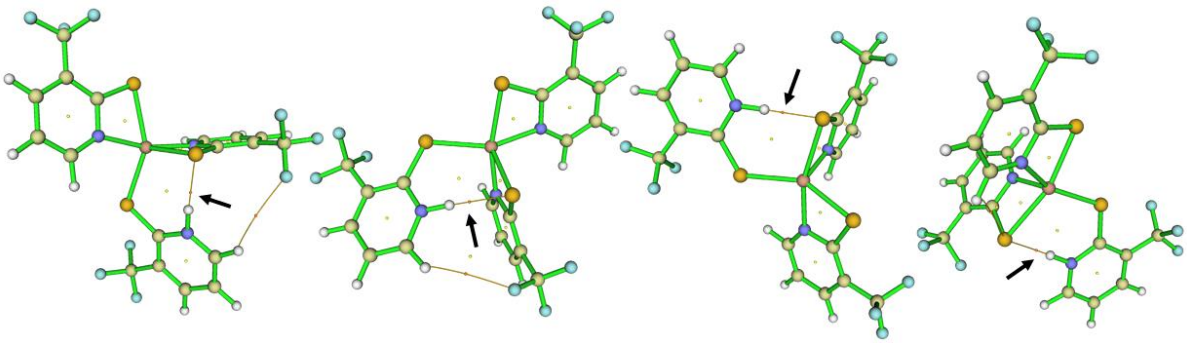
	Ni-N bond length (Å)			**Ni-S bond length (Å)**		
	Ni-N_C	**Ni-N_L**	**Ni-N_R**	**Ni-S_C**	**Ni-S_L**	**Ni-S_R**
$[Ni(L1)_3]^-$	2.071	2.055	2.051	2.533	2.534	2.543
$[Ni(L2)_3]^-$	2.076	2.056	2.055	2.507	2.510	2.508
$[Ni(L3)_3]^-$	2.073	2.056	2.056	2.518	2.522	2.520
$[Ni(L4)_3]^-$	2.073	2.056	2.054	2.518	2.519	2.509
$[Ni(L5)_3]^-$	2.057	2.043	2.042	2.515	2.512	2.528
$[Ni(L6)_3]^-$	2.077	2.058	2.057	2.521	2.522	2.520
$[Ni(L7)_3]^-$ (*fac*)*	2.119	2.116	2.118	2.495	2.496	2.496
$[Ni(L8)_3]^-$ (*fac*)*	2.193	2.204	2.211	2.427	2.427	2.427
$[Ni(L9)_3]^-$	2.072	2.057	2.054	2.521	2.520	2.522
$[Ni(L10)_3]^-$	2.073	2.056	2.051	2.531	2.526	2.545
$[Ni(L11)_3]^-$	2.071	2.055	2.051	2.540	2.538	2.548
$[Ni(L12)_3]^-$	2.069	2.053	2.049	2.540	2.539	2.554

***For the *fac* complexes **$[Ni(L7)_3]^-$** and **$[Ni(L8)_3]^-$**, all three **Ni-N** bonds are equivalent.

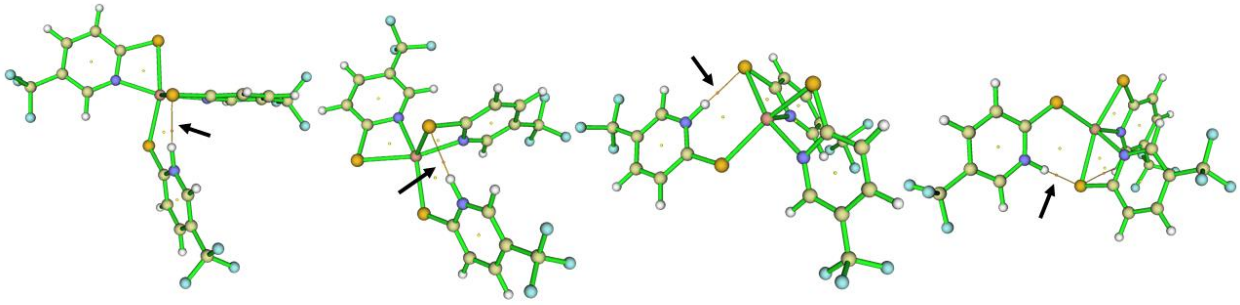
Topology maps of the computationally modeled protonated intermediates (1-H).



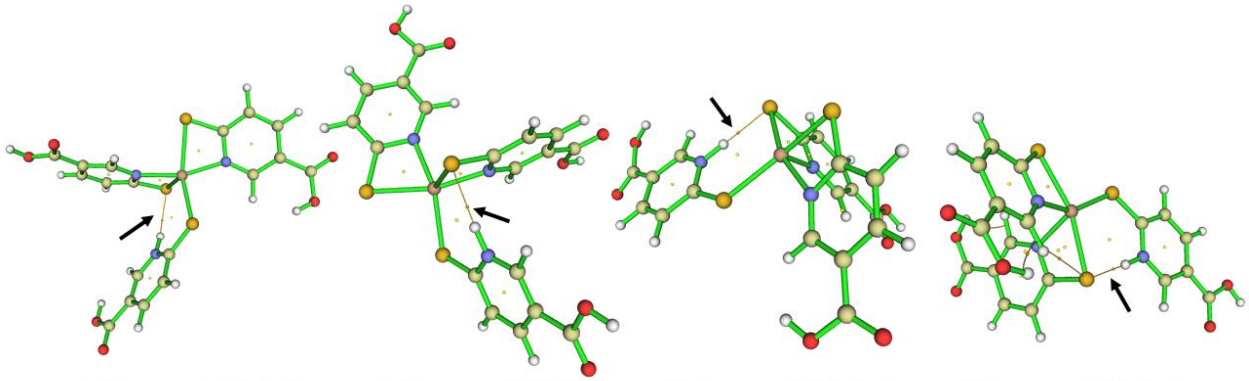
[C] isomer of $[Ni(L1)_3]H$ $[L_C]$ isomer of $[Ni(L1)_3]H$ $[L_R]$ isomer of $[Ni(L1)_3]H$ [R] isomer of $[Ni(L1)_3]H$



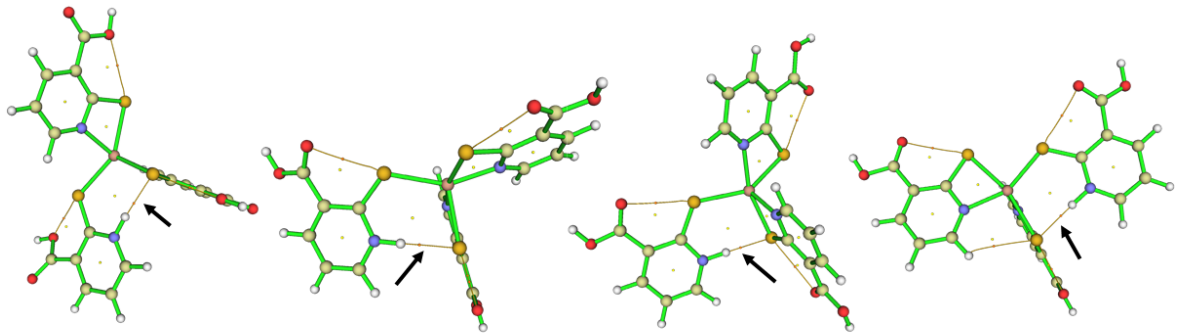
[C] isomer of $[Ni(L2)_3]H$ $[L_C]$ isomer of $[Ni(L2)_3]H$ $[L_R]$ isomer of $[Ni(L2)_3]H$ [R] isomer of $[Ni(L2)_3]H$



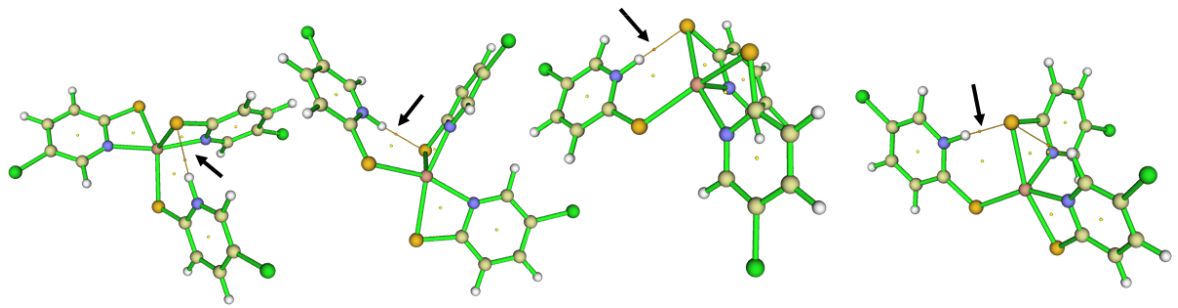
[C] isomer of $[Ni(L3)_3]H$ $[L_C]$ isomer of $[Ni(L3)_3]H$ $[L_R]$ isomer of $[Ni(L3)_3]H$ [R] isomer of $[Ni(L3)_3]H$



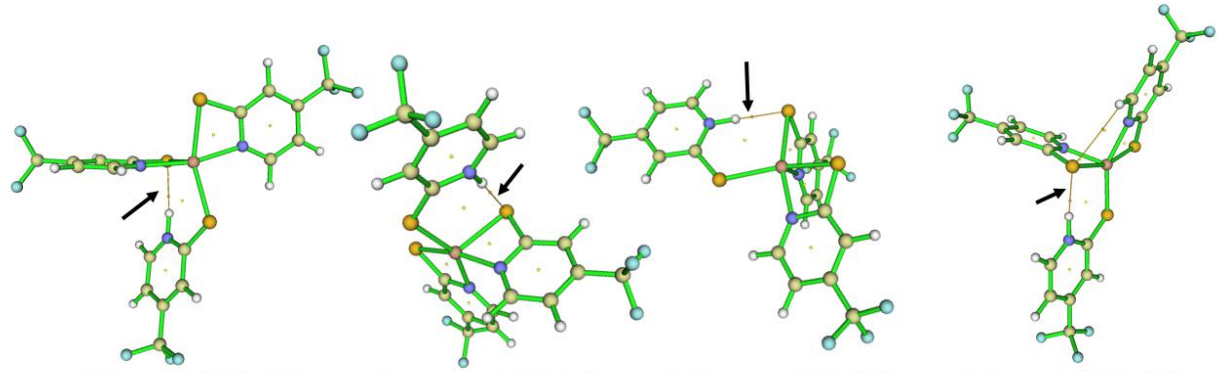
[C] isomer of $[Ni(L4)_3]H$ $[L_C]$ isomer of $[Ni(L4)_3]H$ $[L_R]$ isomer of $[Ni(L4)_3]H$ [R] isomer of $[Ni(L4)_3]H$



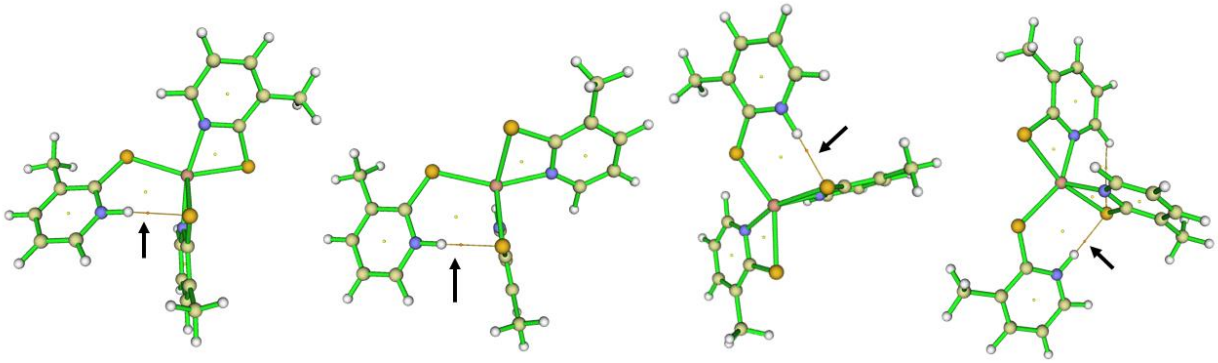
[C] isomer of $[Ni(L5)_3]H$ $[L_C]$ isomer of $[Ni(L5)_3]H$ $[L_R]$ isomer of $[Ni(L5)_3]H$ [R] isomer of $[Ni(L5)_3]H$



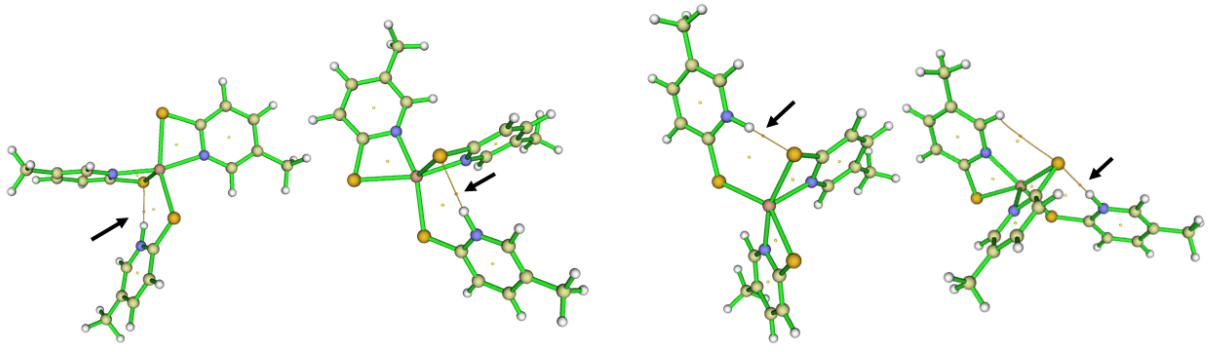
[C] isomer of $[Ni(L6)_3]H$ $[L_C]$ isomer of $[Ni(L6)_3]H$ $[L_R]$ isomer of $[Ni(L6)_3]H$ [R] isomer of $[Ni(L6)_3]H$



[C] isomer of $[Ni(L9)_3]H$ $[L_C]$ isomer of $[Ni(L9)_3]H$ $[L_R]$ isomer of $[Ni(L9)_3]H$ [R] isomer of $[Ni(L9)_3]H$



[C] isomer of $[Ni(L10)_3]H$ $[L_C]$ isomer of $[Ni(L10)_3]H$ $[L_R]$ isomer of $[Ni(L10)_3]H$ [R] isomer of $[Ni(L10)_3]H$



[C] isomer of $[Ni(L11)_3]H$ $[L_C]$ isomer of $[Ni(L11)_3]H$ $[L_R]$ isomer of $[Ni(L11)_3]H$ [R] isomer of $[Ni(L11)_3]H$

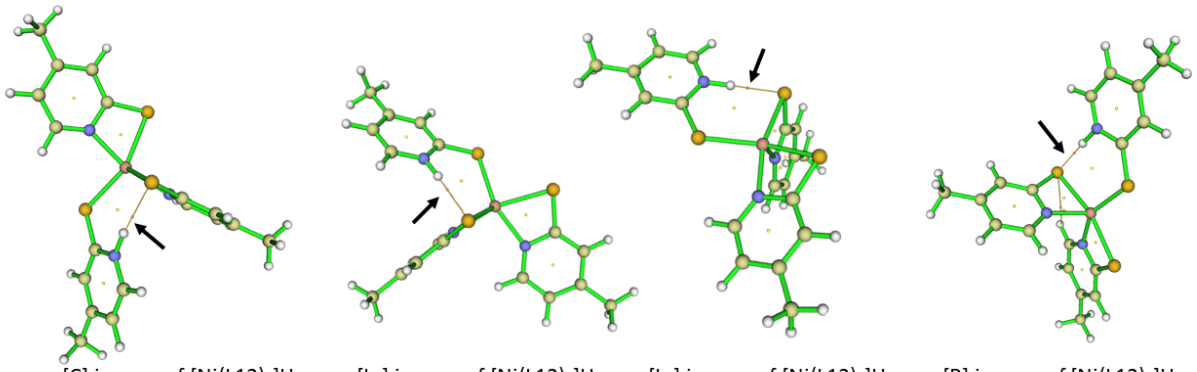
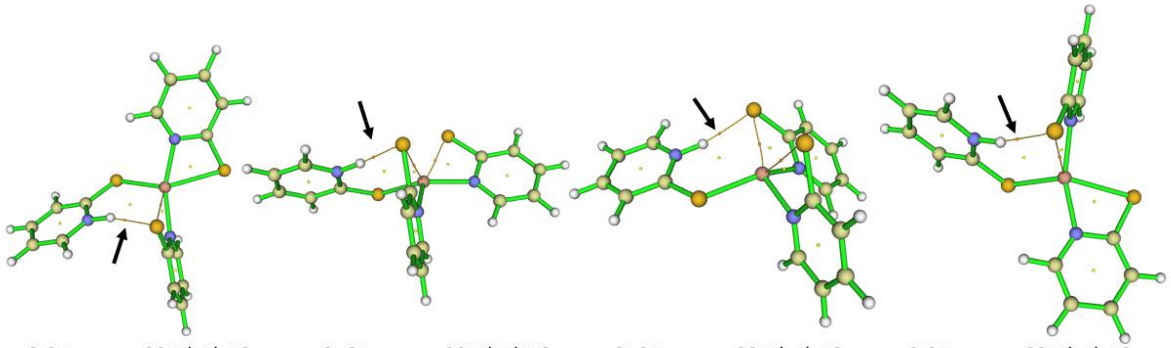
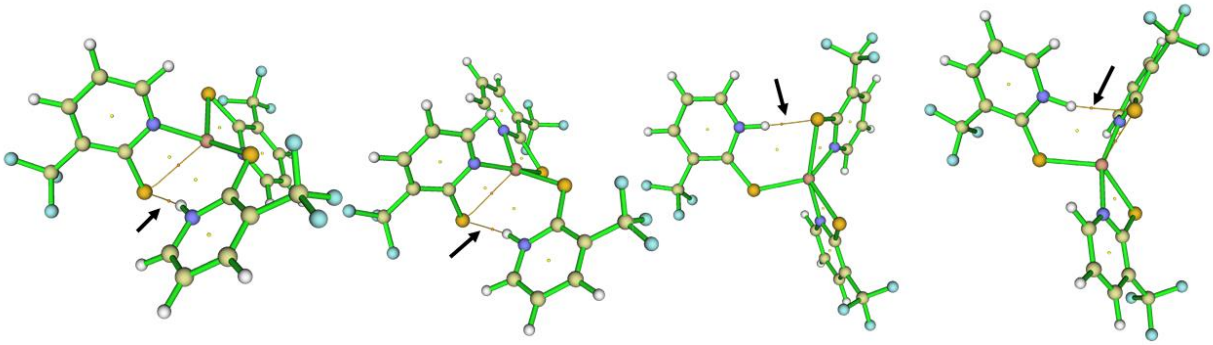


Figure S1. Topology maps of the computationally modeled protonated intermediates (**1-H**) represented using ball-stick drawing method. Blue, White, Light Yellow, Dark Yellow, Pink, Indigo, Red and Green balls represent N, H, C, S, Ni, F, O and Cl atoms respectively. Yellow lines are the bond paths. Black arrows point toward the intra-molecular hydrogen bonding interaction stabilizing the structure.

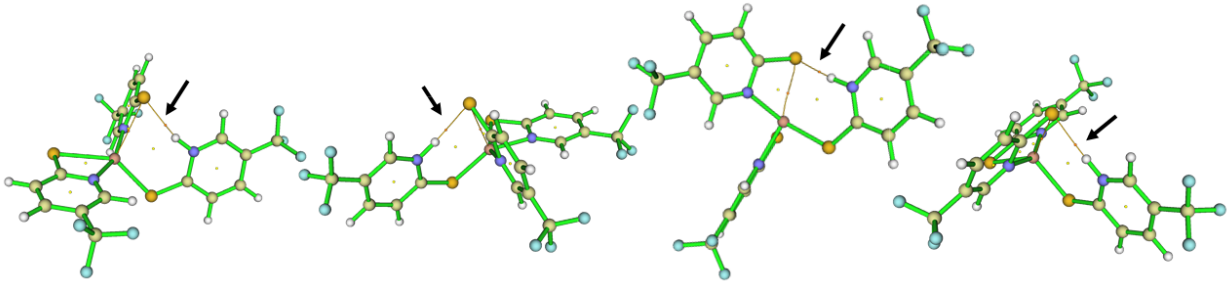
Topology maps of the computationally modeled reduced intermediates (1-H$^-$).



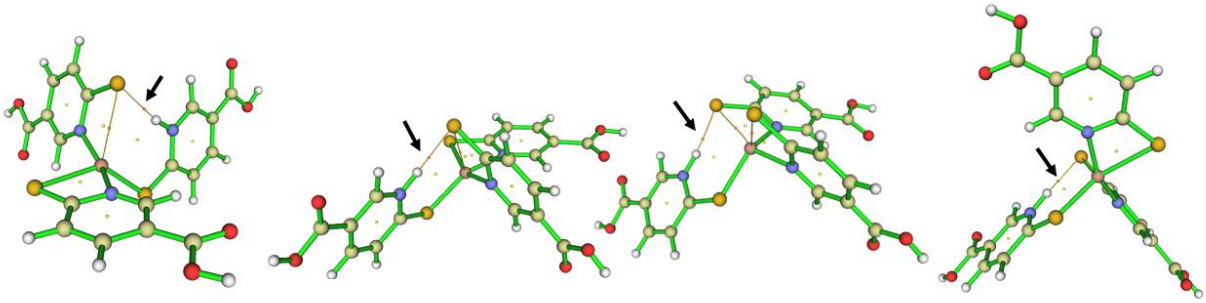
[C] isomer of $[Ni(L1)_3H]^-$ $[L_C]$ isomer of $[Ni(L1)_3H]^-$ $[L_R]$ isomer of $[Ni(L1)_3H]^-$ [R] isomer of $[Ni(L1)_3H]^-$



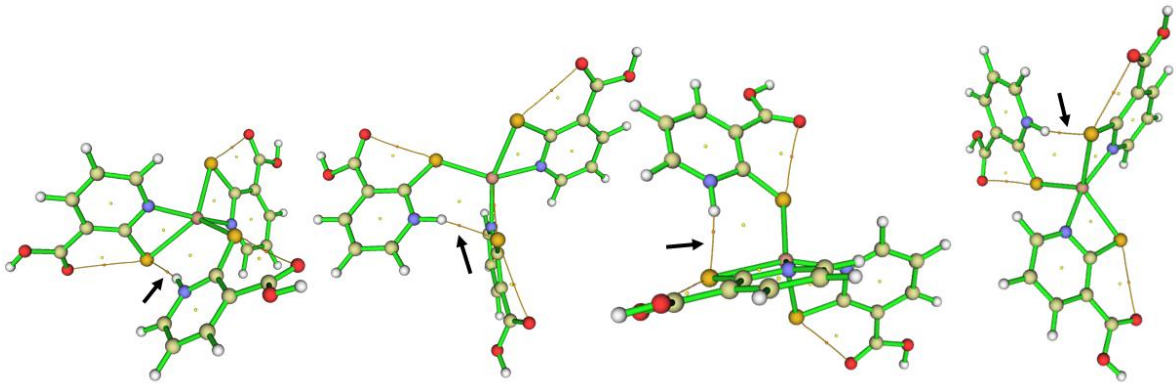
[C] isomer of $[Ni(L2)_3H]^-$ $[L_C]$ isomer of $[Ni(L2)_3H]^-$ $[L_R]$ isomer of $[Ni(L2)_3H]^-$ [R] isomer of $[Ni(L2)_3H]^-$



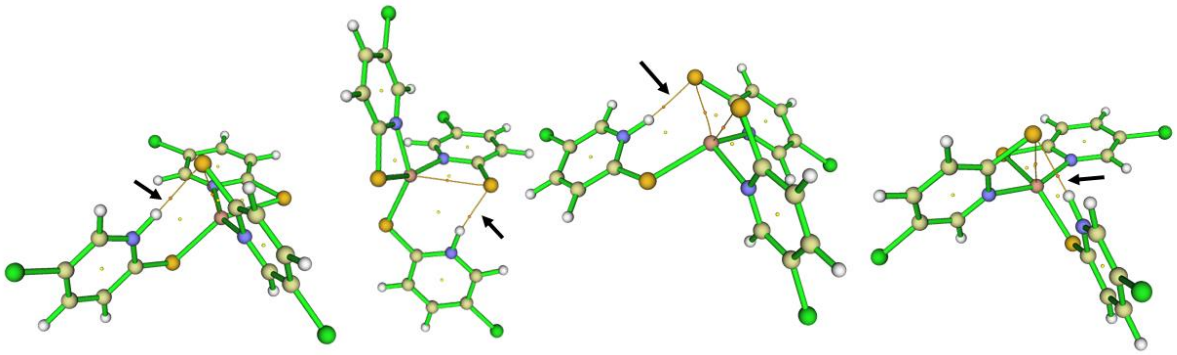
[C] isomer of $[Ni(L3)_3H]^-$ $[L_C]$ isomer of $[Ni(L3)_3H]^-$ $[L_R]$ isomer of $[Ni(L3)_3H]^-$ [R] isomer of $[Ni(L3)_3H]^-$



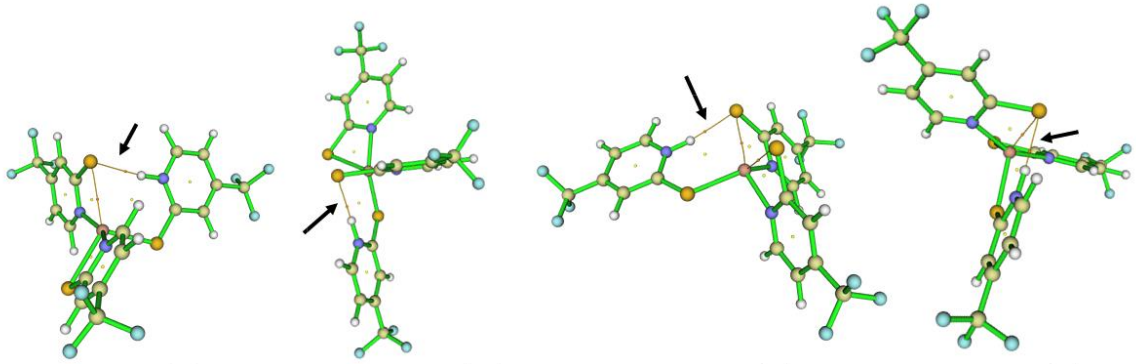
[C] isomer of $[Ni(L4)_3H]^-$ $[L_C]$ isomer of $[Ni(L4)_3H]^-$ $[L_R]$ isomer of $[Ni(L4)_3H]^-$ [R] isomer of $[Ni(L4)_3H]^-$



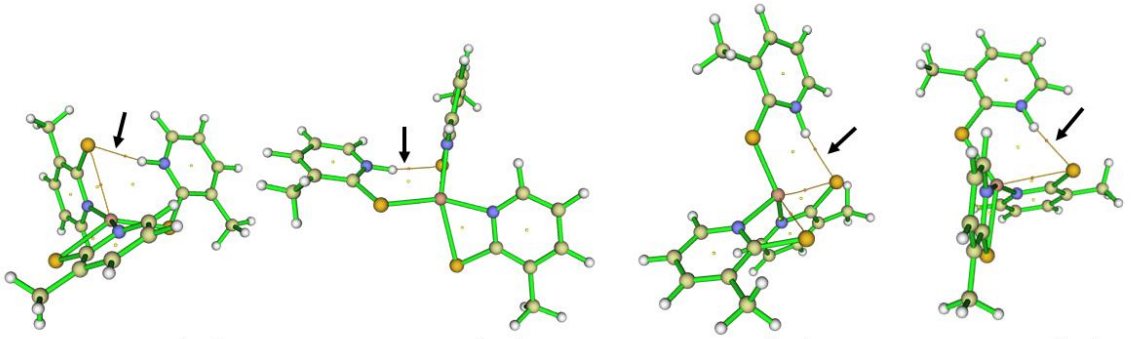
[C] isomer of $[Ni(L5)_3H]^-$ $[L_C]$ isomer of $[Ni(L5)_3H]^-$ $[L_R]$ isomer of $[Ni(L5)_3H]^-$ [R] isomer of $[Ni(L5)_3H]^-$



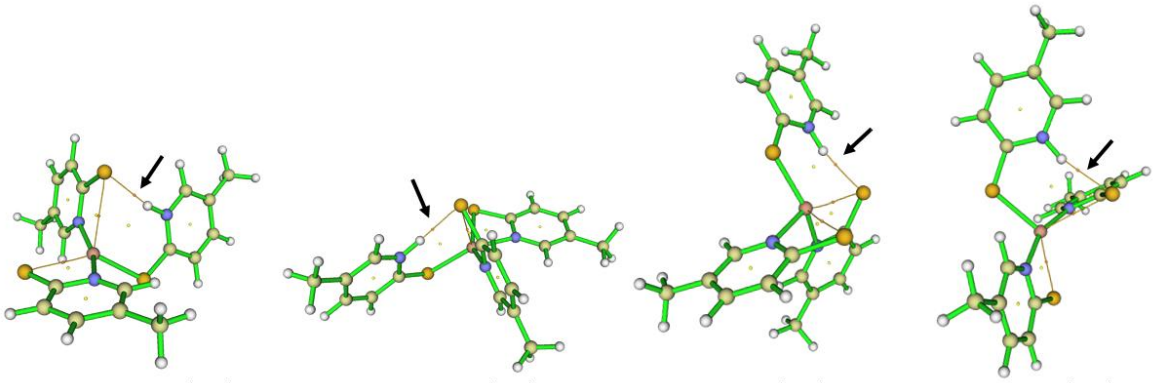
[C] isomer of $[Ni(L6)_3H]^-$ $[L_C]$ isomer of $[Ni(L6)_3H]^-$ $[L_R]$ isomer of $[Ni(L6)_3H]^-$ [R] isomer of $[Ni(L6)_3H]^-$



[C] isomer of $[Ni(L9)_3H]^-$ $[L_C]$ isomer of $[Ni(L9)_3H]^-$ $[L_R]$ isomer of $[Ni(L9)_3H]^-$ [R] isomer of $[Ni(L9)_3H]^-$



[C] isomer of $[Ni(L10)_3H]^-$ $[L_C]$ isomer of $[Ni(L10)_3H]^-$ $[L_R]$ isomer of $[Ni(L10)_3H]^-$ [R] isomer of $[Ni(L10)_3H]^-$



[C] isomer of $[Ni(L11)_3H]^-$ $[L_C]$ isomer of $[Ni(L11)_3H]^-$ $[L_R]$ isomer of $[Ni(L11)_3H]^-$ [R] isomer of $[Ni(L11)_3H]^-$

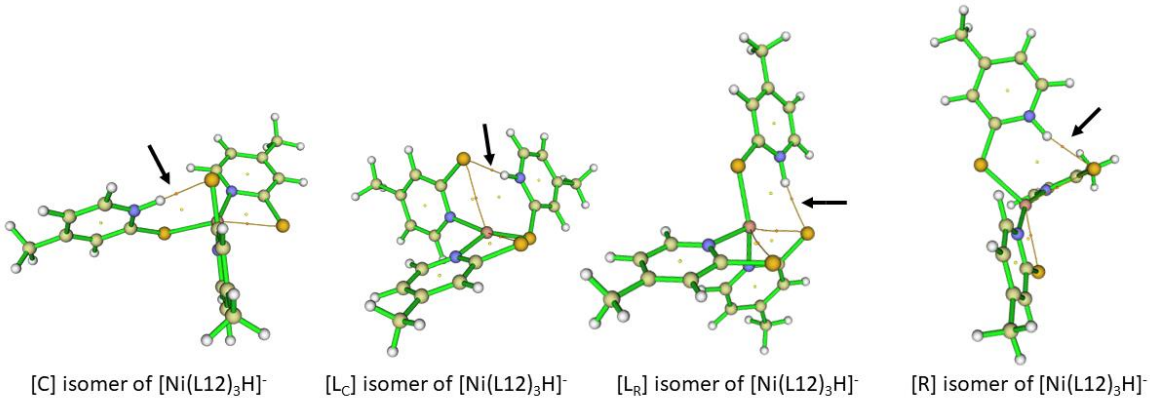


Figure S2. Topology maps of the computationally modeled reduced intermediates (**1-H**$^-$) represented using ball-stick drawing method. Blue, White, Light Yellow, Dark Yellow, Pink, Indigo, Red and Green balls represent N, H, C, S, Ni, F, O and Cl atoms respectively. Yellow lines are the bond paths. Black arrows point toward the intra-molecular hydrogen bonding interaction stabilizing the structure.

References:

1 S. G. Rosenfield, H. P. Berends, L. Gelmini, D. W. Stephan and P. K. Mascharak, *Inorg. Chem.*, 1987, **26**, 2792–2797.