Electronic Supplementary Information (ESI)

for

Nickel Complexes of Ligands Derived from (*o*-Hydroxyphenyl) Dichalcogenide: Delocalised Redox States of Nickel and *o*-Chalcogenophenolate Ligand

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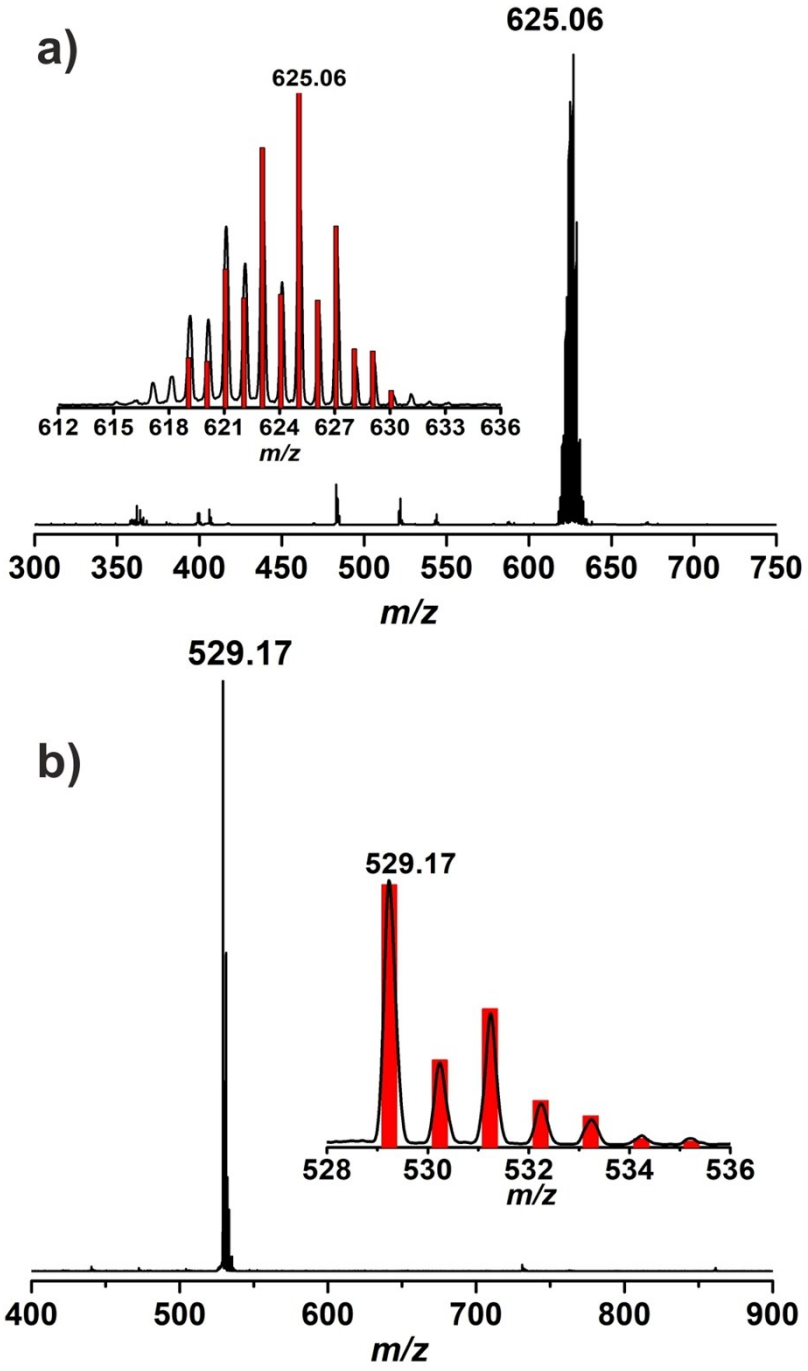


Figure 1. ESI-mass spectra (negative ion mode in acetonitrile) of complex (a) **1** and (b) **2**. Insets: ion peaks along with the isotope distribution patterns. The red bards indicate the calculated isotope distribution patterns.

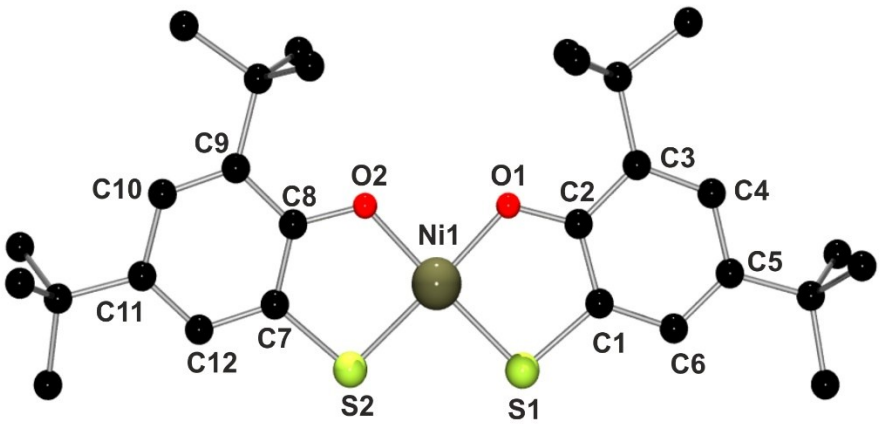


Figure S2. Crystal structures of the complex anion of $Bu_4N[Ni(L^{SO})_2]$ **(2)**. The counter cations, solvent molecules and all the hydrogen atoms have been omitted for clarity.

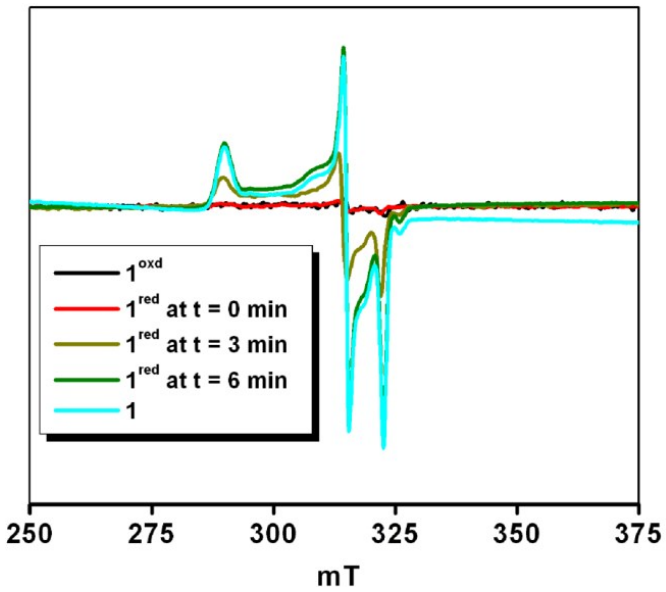


Figure S3. X-band EPR spectral changes during the conversion of $\mathbf{1}^{red}$ to **1**. Temperature = 77 K, microwave frequency = 9.14 GHz, microwave power = 0.998 mW, modulation amplitude = 0.1 mT.

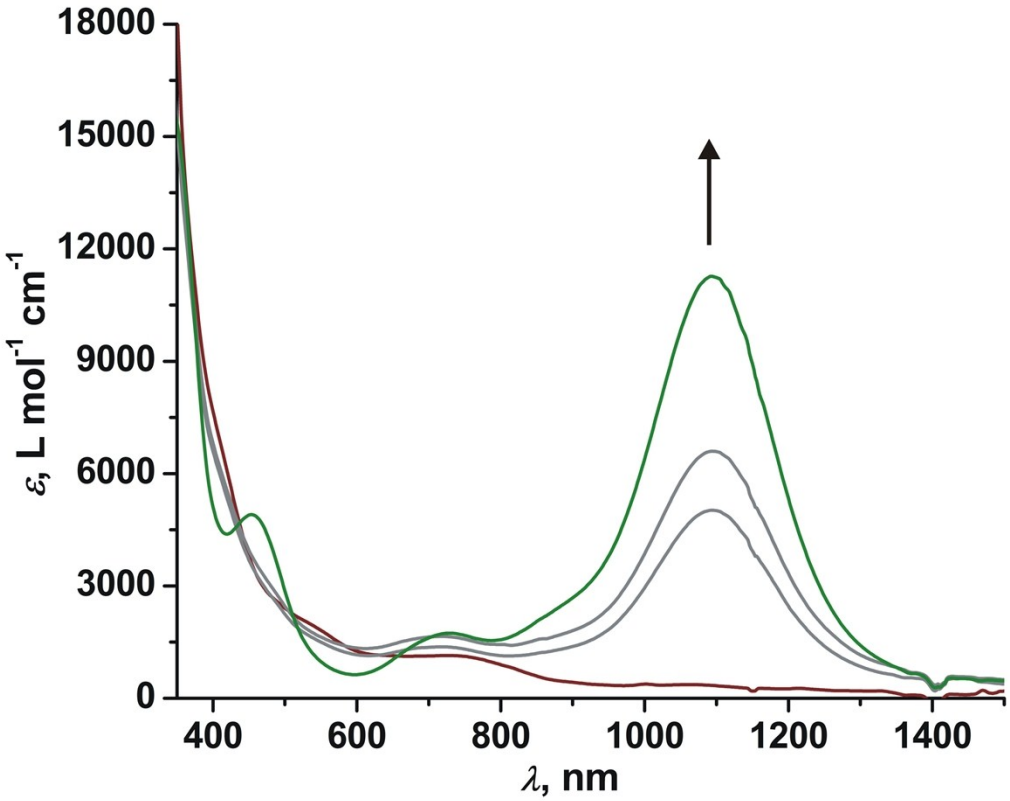


Figure S4. Optical spectral changes during the conversion of **1**^{red} to **1** upon exposure to air in dichloromethane at 298 K.

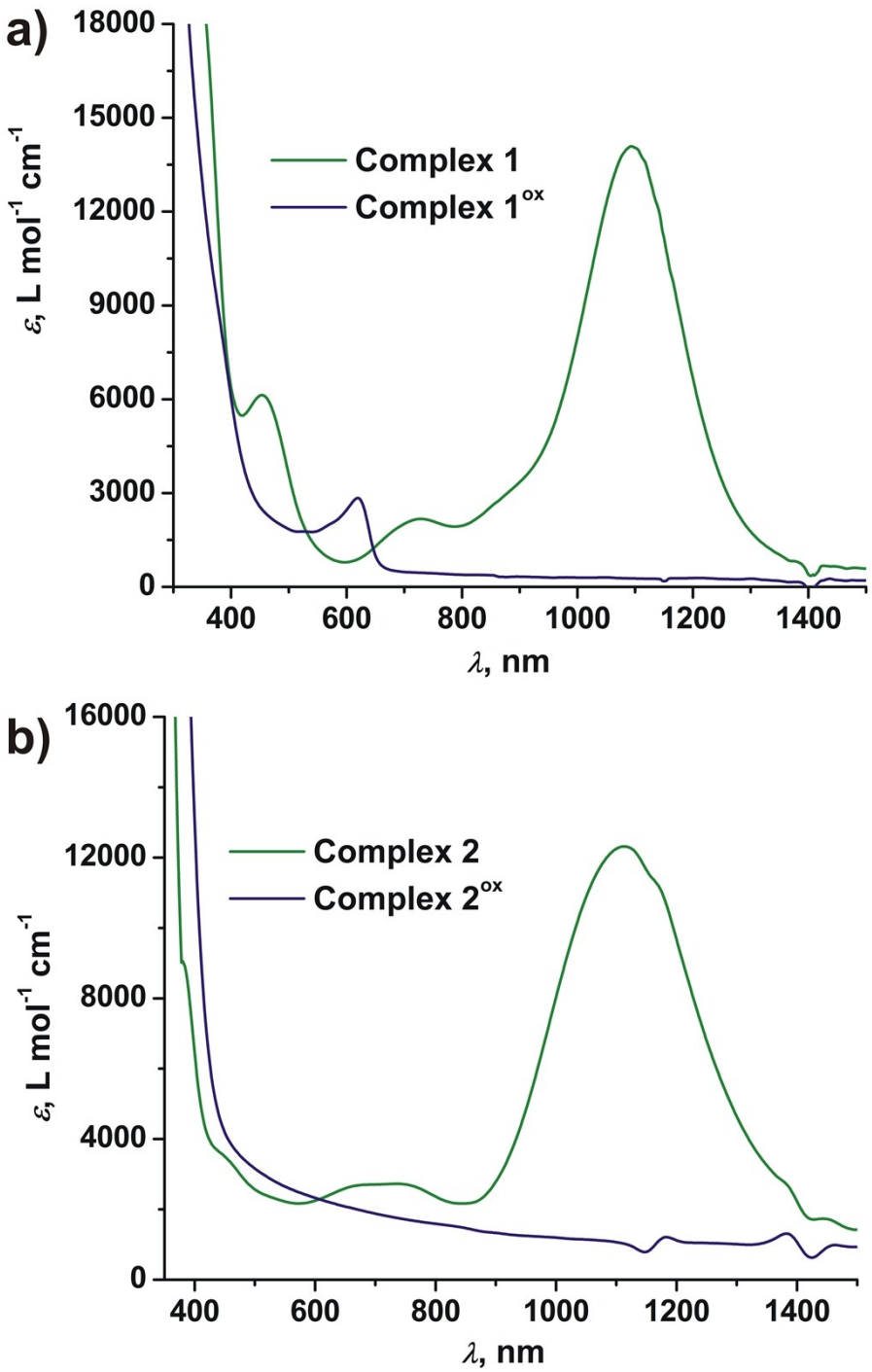
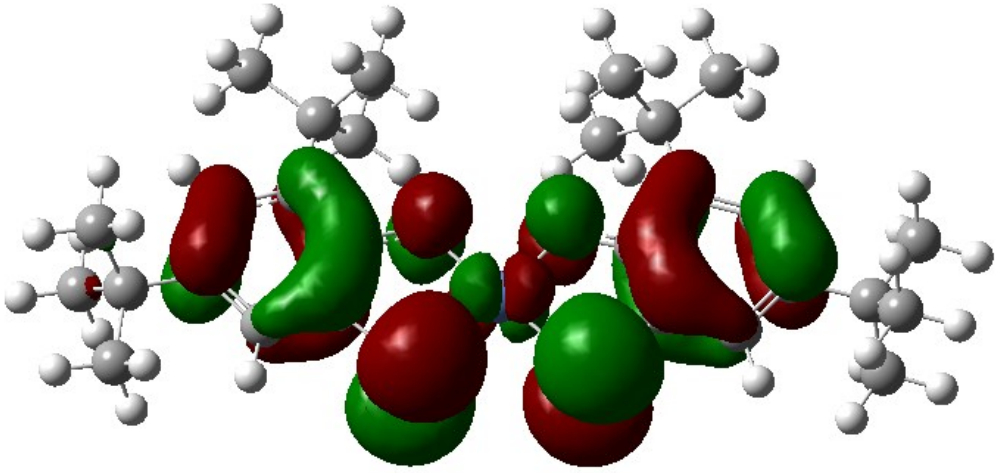
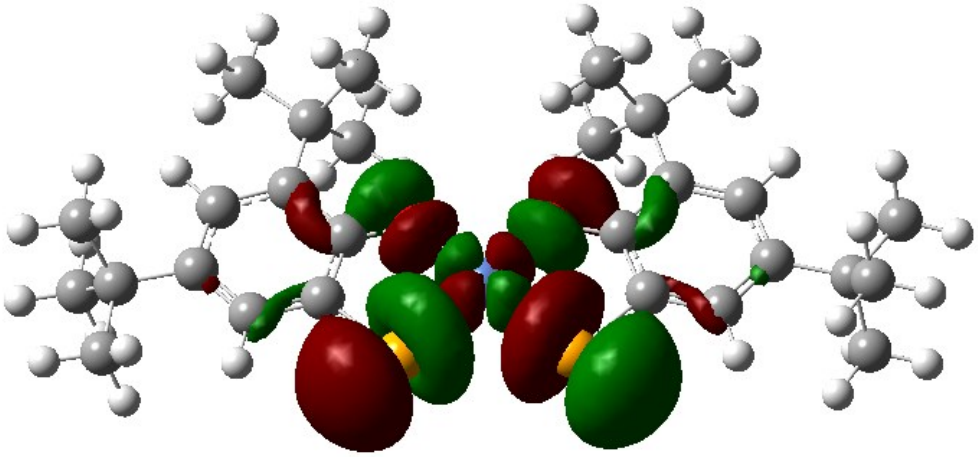


Figure S5. One-electron oxidation of (a) **1** and (b) **2** in dichloromethane with ferrocenium hexafluorophosphate (1.5 equiv) at 298 K.

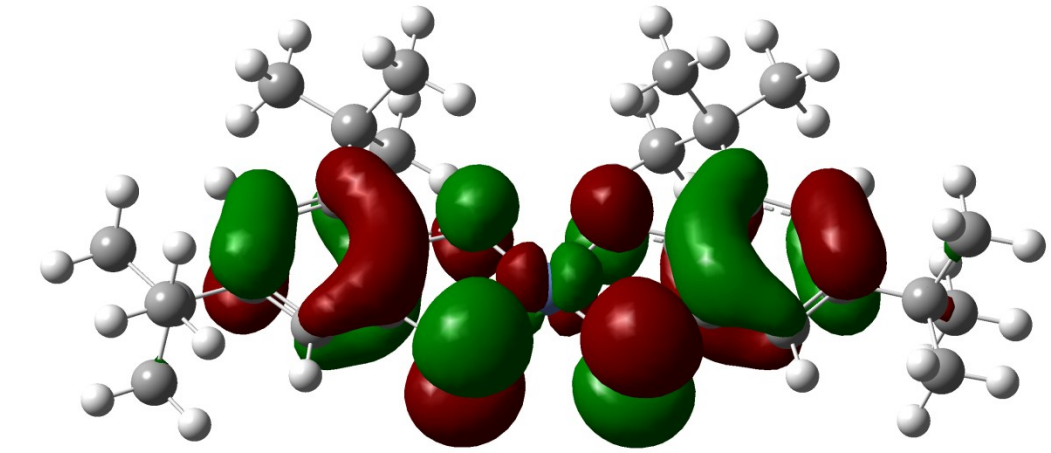


HOMO

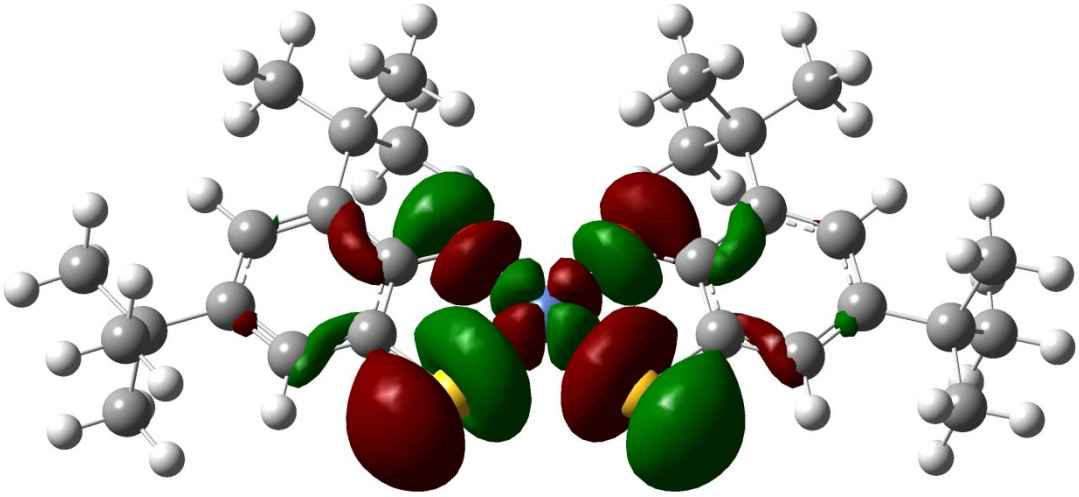


LUMO

Figure S6. Frontier orbitals of complex **1** ([$(L^{SeO})_2Ni]^-$). Isosurface cut off value: 0.02. In HOMO, % contribution of Ni = 32 and of ligand = 68. In LUMO, % contribution of Ni = 46 and of ligand = 54.



HOMO



LUMO

Figure S7. Frontier orbitasl of complex **2** ($[(L^{SO})_2Ni]^-$). Isosurface cut off value: 0.02. In HOMO, % contribution of Ni = 18, ligand = 82. In LUMO, % contribution of Ni = 47, of ligand = 53.

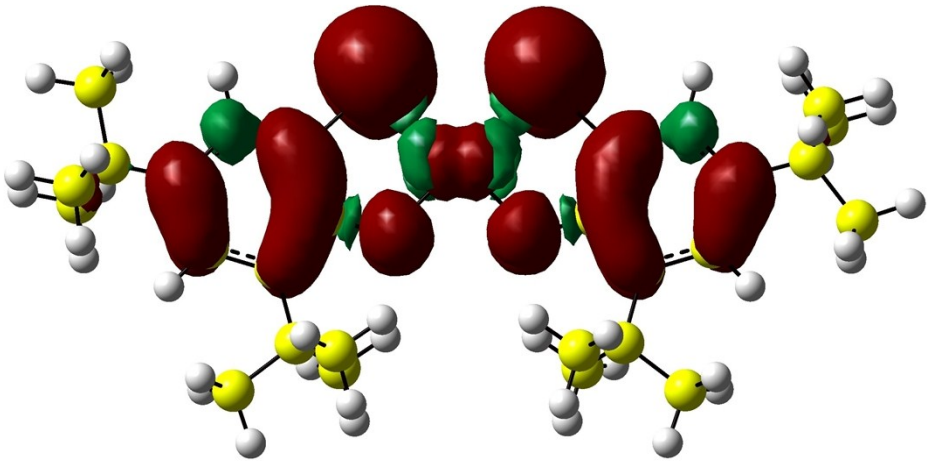


Figure S8. Spin density plot for complex **1** ($[(L^{SeO})_2Ni]^-$). 37.4% of total spin density is on the Ni centre and 62.6% is on the ligands.

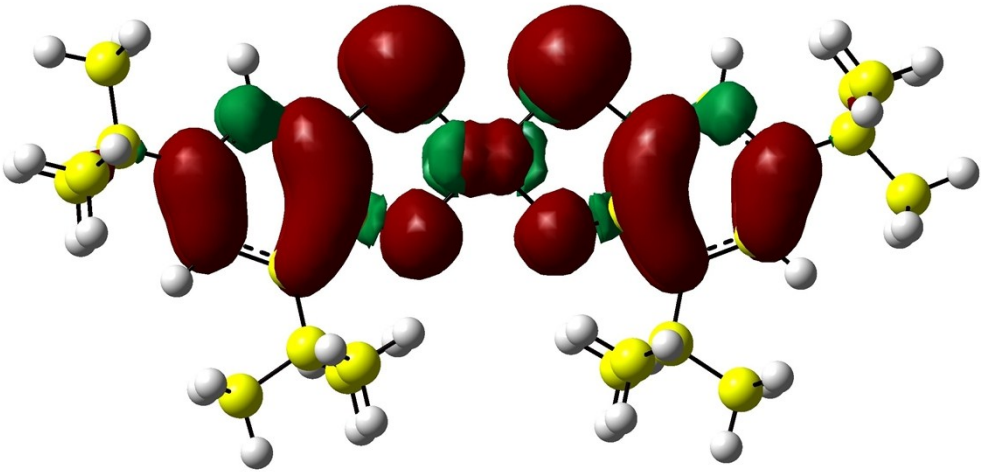


Figure S9. Spin density plot for complex **2** ($[(L^{SO})_2Ni]^-$). 36.3% of total spin density is on the Ni centre and 63.7% is on the ligands.

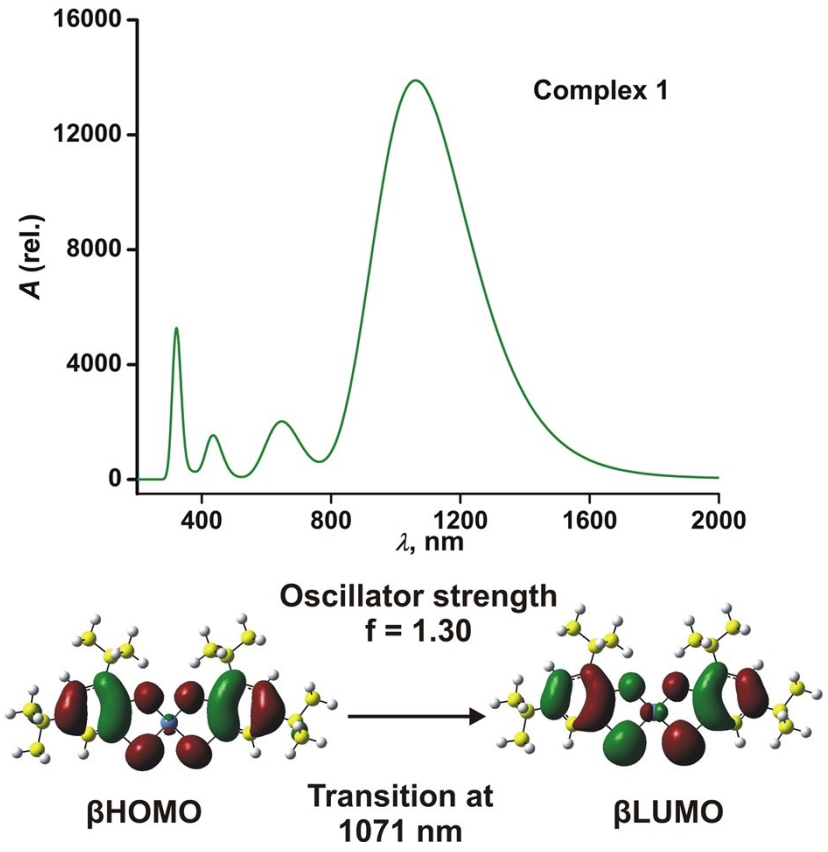


Figure S10. Optical transition predicted for complex **1** ($[(L^{SeO})_2Ni]^-$) by TDDFT calculations and assignment of the lowest energy transition.

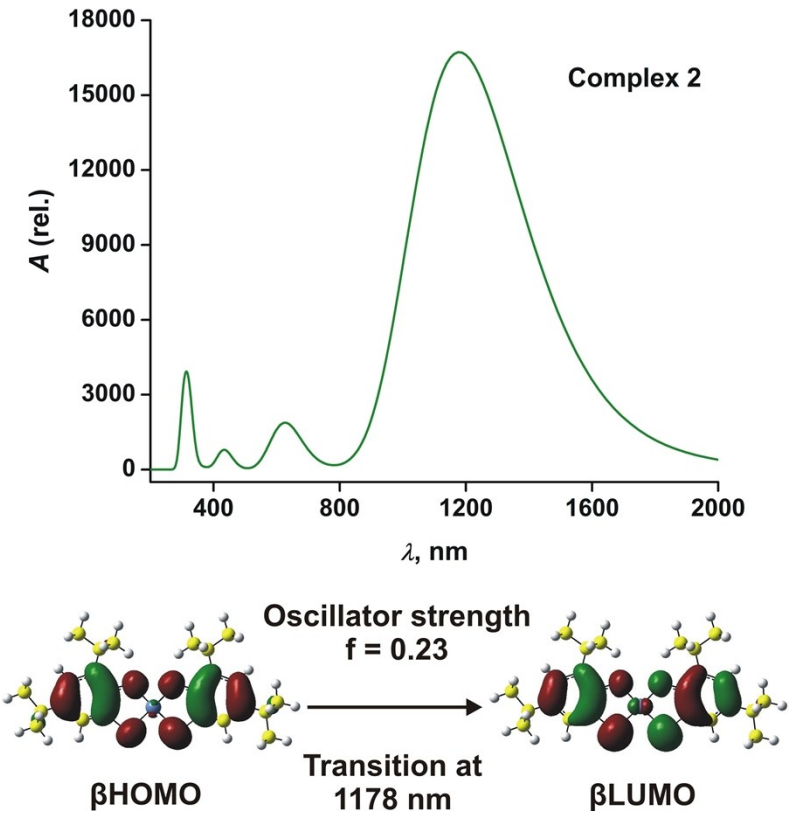
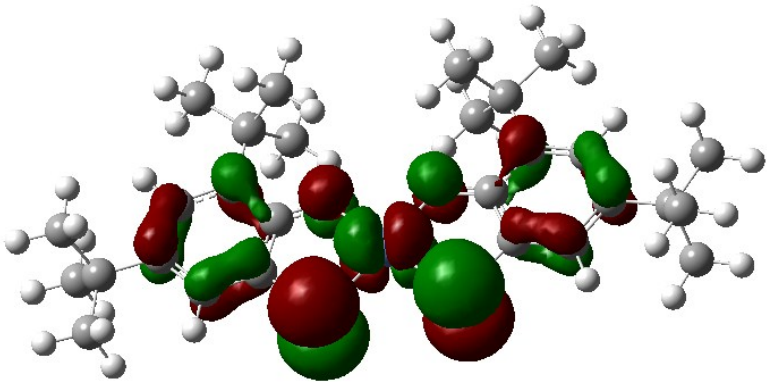
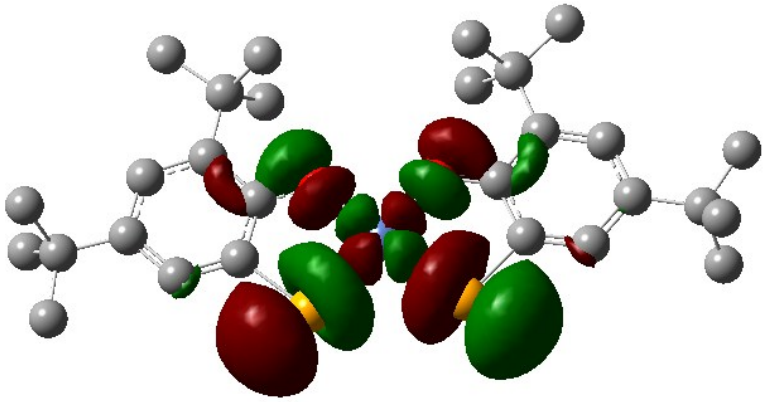


Figure S11. Optical transition predicted for complex **2** ($[(L^{SO})_2Ni]^-$) by TDDFT calculations and assignment of the lowest energy transition.

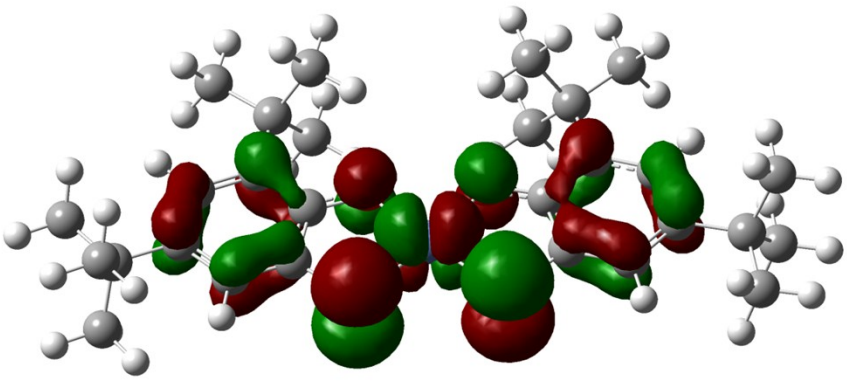


HOMO

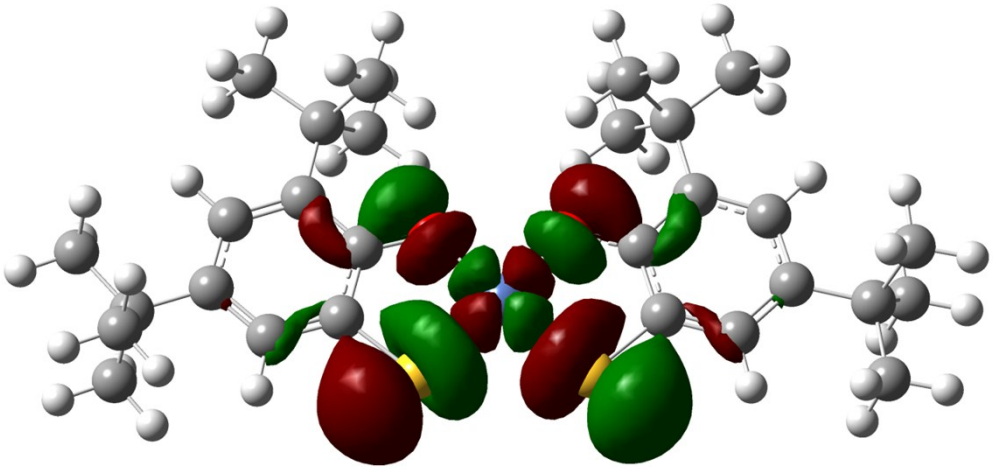


LUMO

Figure S12. Frontier orbitals of **1^{red}** ([(L^{SeO})$_2$Ni]$^{2-}$). Isosurface cut off value: 0.02. In HOMO, % contribution of Ni = 39 and of ligand = 61. In LUMO, % contribution of Ni = 48, and of ligand = 52.



HOMO



LUMO

Figure S13. Frontier orbitals of **2^{red}** ([$(L^{SO})_2$Ni]$^{2-}$). Isosurface cut off value: 0.02. In HOMO, % contribution of Ni = 61 and of ligand = 39. In LUMO, % contribution of Ni = 55 and of ligand = 45.

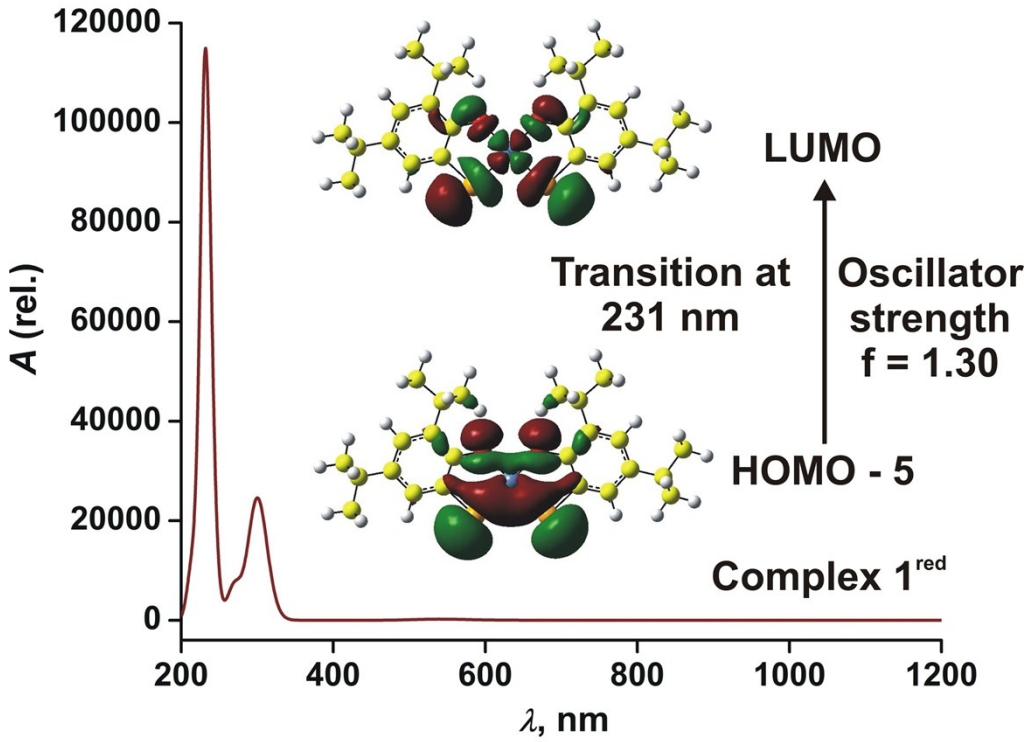


Figure S14. Optical transition predicted for complex **1**^{red} ([$(L^{SeO})_2Ni]^{2-}$) by TDDFT calculations and assignment of the transition with highest oscillator strength (f).

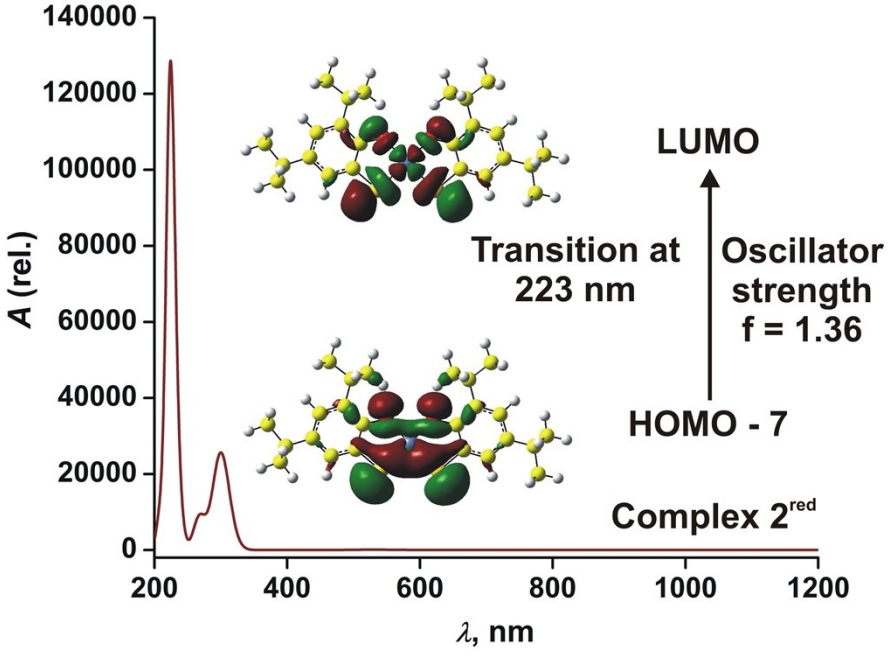


Figure S15. Optical transition predicted for complex **2**^{red} ([$(L^{SO})_2Ni]^{2-}$) by TDDFT calculations and assignment of the transition with highest oscillator strength (f).

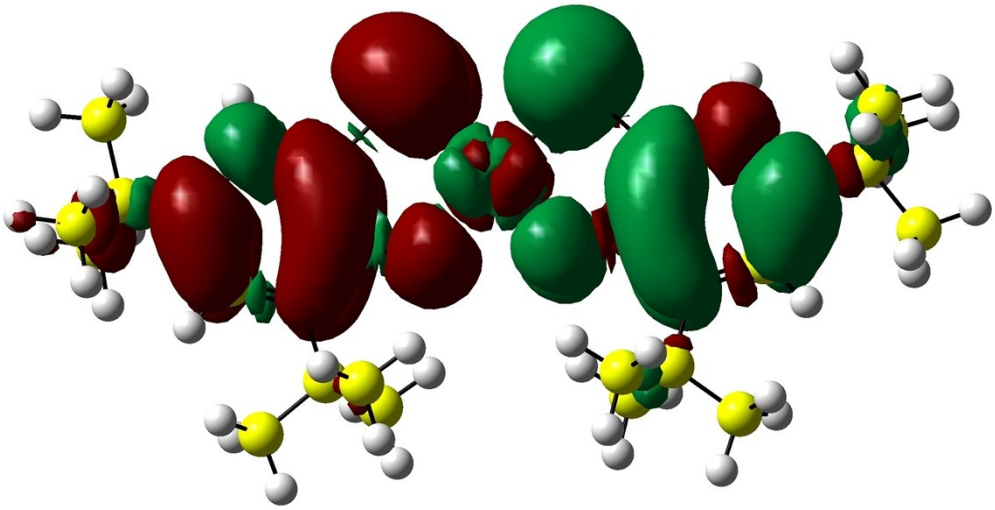


Figure S16. Spin density plot for the open shell singlet configuration of complex **1^{ox}** ([(L^{SeO})$_2$Ni]).

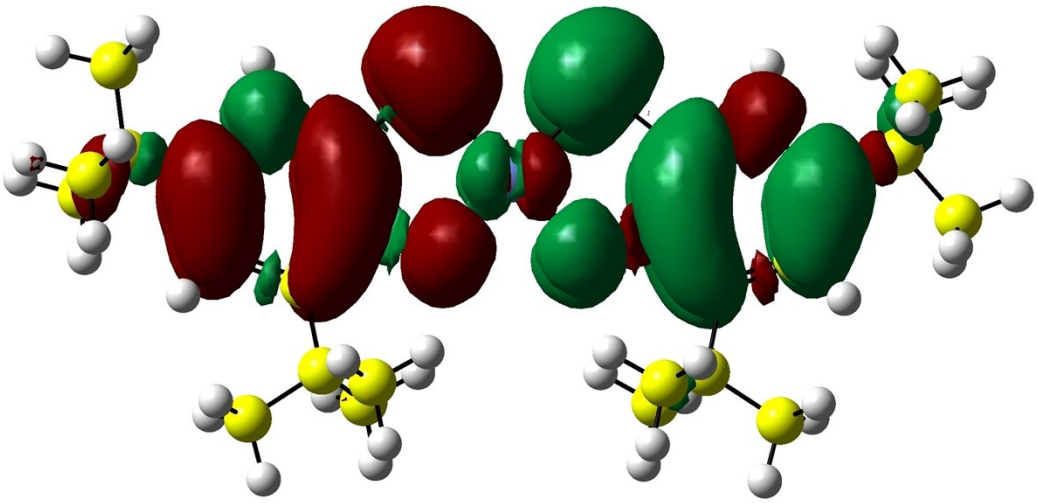


Figure S17. Spin density plot for the open shell singlet configuration of complex **2^{ox}** ([(L^{SO})$_2$Ni]).

Table S1. Crystallographic data for **1** and **2**.

Parameters	**1**	**2**
Empirical formula	$C_{44}H_{76}NNiO_2Se_2$	$C_{92}H_{158}N_2Ni_2O_5S_4$
Formula weight	867.68	1617.85
Crystal system	'Triclinic'	'Triclinic'
Space group	'P-1'	'P-1'
a, Å	12.2167(9)	11.7642(12)
b, Å	17.5848(13)	17.6359(15)
c, Å	22.4459(17)	24.949(2)
α, deg	102.464(3)	102.301(3)
β, deg	92.731(3)	96.756(3)
γ, deg	101.164(3)	103.944(3)
Volume, Å^3	4599.1(6)	4829.8(8)
Z	4	2
$D_{calcd.}$, Mg/m^3	1.253	1.112
μ Mo Kα, mm^{-1}	2.038	0.523
F(000)	1836	1768
Temperature/K	293(2)	100(2)
θ range, deg	1.21 – 22.85	2.52-27.088
Reflections collected	42950	13155
Reflns unique	12543	9682
R(int)	0.0528	0.0893
Data ($I>2\sigma(I)$)	8169	8469
Parameters refined	933	975
Goodness-of-fit on F^2	1.023	1.016
w*R*2	0.1211	0.2145

Table S2. Selected bond lengths (Å) and angles (°) for **2**.

Ni(1)-O(1)	1.841(5)	C(1)-C(2)	1.398(11)
Ni(1)-O(2)	1.839(5)	C(2)-C(3)	1.411(10)
Ni(1)-S(1)	2.125(2)	C(3)-C(4)	1.386(11)
Ni(1)-S(2)	2.142(2)	C(4)-C(5)	1.427(12)
C(2)-O(1)	1.326(9)	C(5)-C(6)	1.370(11)
C(8)-O(2)	1.322(8)	C(6)-C(1)	1.403(11)
C(1)-S(1)	1.764(8)	C(7)-C(8)	1.393(11)
C(7)-S(2)	1.762(8)	C(9)-C(10)	1.380(11)
O(1)-Ni(1)-S(2)	176.92(19)	C(10)-C(11)	1.425(12)
O(2)-Ni(1)-S(1)	175.77(17)	C(11)-C(12)	1.369(12)

Table S3. DFT optimised bond lengths (Å) and angles (°) for **1**, **1**^{red} and **1**^{ox}.

	1	**1**^{red}	**1**^{ox}
Ni(1)-O(1)	1.88906	1.87618	1.91936
Ni(1)-O(2)	1.89264	1.88052	1.91893
Ni(1)-Se(1)	2.29461	2.27145	2.32323
Ni(1)-Se(2)	2.29593	2.27236	2.32348
C(1)-C(2)	1.42183	1.43736	1.44833
C(2)-C(3)	1.43400	1.44212	1.45147
C(3)-C(4)	1.39873	1.41000	1.38276
C(4)-C(5)	1.41370	1.42693	1.42987
C(5)-C(6)	1.39720	1.41002	1.39448
C(6)-C(1)	1.39764	1.40104	1.39578
C(7)-C(8)	1.42035	1.43767	1.44599
C(8)-C(9)	1.43894	1.44602	1.45272
C(9)-C(10)	1.39302	1.41266	1.37923
C(10)-C(11)	1.41946	1.43288	1.43526
C(11)-C(12)	1.39205	1.42006	1.38828
C(12)-C(7)	1.40282	1.40609	1.40212
Bond Angle			
O(1)-Ni(1)-Se(2)	178.51083	179.51154	177.46252
O(2)-Ni(1)-Se(1)	178.67870	179.70017	177.58533
O(1)-Ni(1)-Se(1)	88.85806	89.16748	88.05161
O(2)-Ni(1)-Se(2)	88.69007	88.97882	88.00807

Table S4. Cartesian coordinates for the optimized structure for complex **1** ([$(L^{SeO})_2$Ni]$^-$).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	34	0	-1.596603	-2.308027	-0.000215
2	34	0	1.630459	-2.288978	-0.000148
3	28	0	0.007524	-0.735363	-0.000216
4	6	0	4.407158	-1.317276	0.000004
5	1	0	4.700150	-2.378235	-0.000055
6	6	0	3.568841	1.410380	0.000202

7	6	0	5.382118	-0.301404	0.000102
8	6	0	4.926014	1.039982	0.000208
9	1	0	5.673222	1.841621	0.000322
10	6	0	3.044564	-0.992811	-0.000007
11	6	0	2.588278	0.358487	0.000057
12	8	0	1.284850	0.615822	0.000018
13	8	0	-1.287212	0.599867	-0.000350
14	6	0	-3.025862	-1.030387	-0.000008
15	6	0	-3.581275	1.366758	-0.000181
16	6	0	-4.387214	-1.377007	0.000199
17	1	0	-4.660963	-2.440546	0.000302
18	6	0	-3.157419	2.850249	-0.000468
19	6	0	-2.586371	0.324009	-0.000170
20	6	0	-5.369970	-0.374397	0.000256
21	6	0	-6.882315	-0.680857	0.000498
22	6	0	-4.368665	3.808946	-0.000427
23	1	0	-5.003861	3.672376	-0.898737
24	1	0	-4.005830	4.856437	-0.000649
25	1	0	-5.003587	3.672675	0.898125
26	6	0	-4.928413	0.976203	0.000054
27	1	0	-5.694111	1.764068	0.000069
28	6	0	-2.309740	3.147787	-1.267353
29	1	0	-1.422270	2.491739	-1.297349
30	1	0	-1.972186	4.205321	-1.264059
31	1	0	-2.907039	2.979647	-2.186049

32	6	0	-2.309301	3.148189	1.266021
33	1	0	-2.906249	2.980268	2.184984
34	1	0	-1.971814	4.205743	1.262312
35	1	0	-1.421781	2.492199	1.295865
36	6	0	-7.172881	-2.198263	0.000706
37	1	0	-6.751095	-2.694088	0.896959
38	1	0	-6.751442	-2.694270	-0.895606
39	1	0	-8.267966	-2.372646	0.000929
40	6	0	-7.541178	-0.066536	-1.264028
41	1	0	-8.635066	-0.256923	-1.269995
42	1	0	-7.107181	-0.506370	-2.183194
43	1	0	-7.385846	1.028376	-1.310976
44	6	0	3.126568	2.888893	0.000350
45	6	0	2.275243	3.177076	-1.266311
46	1	0	2.874819	3.017406	-2.185061
47	1	0	1.924171	4.230274	-1.262298
48	1	0	1.396108	2.509911	-1.297400
49	6	0	7.207102	-1.516637	-1.264021
50	1	0	7.004067	-0.933938	-2.183865
51	1	0	6.592251	-2.435564	-1.308192
52	1	0	8.275723	-1.818751	-1.272095
53	6	0	7.207013	-1.517058	1.263951
54	1	0	8.275654	-1.819099	1.272042
55	1	0	6.592227	-2.436049	1.307722
56	1	0	7.003828	-0.934694	2.183976

57	6	0	7.802637	0.563060	0.000333
58	1	0	8.863891	0.241580	0.000352
59	1	0	7.639558	1.192425	0.897190
60	1	0	7.639686	1.192673	-0.896375
61	6	0	6.880538	-0.676659	0.000094
62	6	0	4.325146	3.863497	0.000529
63	1	0	4.962099	3.735543	0.898838
64	1	0	3.948307	4.906107	0.000674
65	1	0	4.962200	3.735826	-0.897750
66	6	0	2.275148	3.176845	1.266997
67	1	0	1.396032	2.509647	1.297964
68	1	0	1.924030	4.230028	1.263086
69	1	0	2.874669	3.017097	2.185766
70	6	0	-7.540840	-0.066256	1.265070
71	1	0	-7.385502	1.028668	1.311733
72	1	0	-7.106609	-0.505894	2.184219
73	1	0	-8.634726	-0.256646	1.271360

Table S5. Mulliken charges on complex **1** with hydrogens summed into heavy atoms.

Centre no.	atom	Mulliken charge
1	Se	-0.398479
2	Se	-0.401613
3	Ni	0.931407
4	C	-0.148910
5	H	0.000000

6	C	0.132993
7	C	0.202869
8	C	-0.201907
9	H	0.000000
10	C	-0.033383
11	C	0.280842
12	O	-0.615376
13	O	-0.614666
14	C	-0.037662
15	C	0.133188
16	C	-0.146675
17	H	0.000000
18	C	0.095107
19	C	0.282596
20	C	0.203710
21	C	0.077221
22	C	-0.091897
23	H	0.000000
24	H	0.000000
25	H	0.000000
26	C	-0.199988
27	H	0.000000
28	C	-0.040538
29	H	0.000000
30	H	0.000000

31	H	0.000000
32	C	-0.040533
33	H	0.000000
34	H	0.000000
35	H	0.000000
36	C	-0.069273
37	H	0.000000
38	H	0.000000
39	H	0.000000
40	C	-0.056852
41	H	0.000000
42	H	0.000000
43	H	0.000000
44	C	0.095813
45	C	-0.041872
46	H	0.000000
47	H	0.000000
48	H	0.000000
49	C	-0.053511
50	H	0.000000
51	H	0.000000
52	H	0.000000
53	C	-0.053514
54	H	0.000000
55	H	0.000000

56	H	0.000000
57	C	-0.075558
58	H	0.000000
59	H	0.000000
60	H	0.000000
61	C	0.076801
62	C	-0.091617
63	H	0.000000
64	H	0.000000
65	H	0.000000
66	C	-0.041873
67	H	0.000000
68	H	0.000000
69	H	0.000000
70	C	-0.056851
71	H	0.000000
72	H	0.000000
73	H	0.000000

Sum of Mulliken charges= -1.00000

Table S6. Mulliken spin density for complex **1**.

Metal ion (Ni)	Ligand
0.374284 (37.43%)	0.625716 (62.57%)

Table S7. Cartesian coordinates for the optimized structure for complex **1**^{red}.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	34	Se	-1.651863	-2.360424	-0.000915
2	34	Se	1.688141	-2.338609	0.001232
3	28	Ni	0.007847	-0.799163	0.000160
4	6	C	4.451421	-1.282492	0.000403
5	1	H	4.768518	-2.338865	0.000729
6	6	C	3.563363	1.410232	-0.000347
7	6	C	5.418224	-0.246054	-0.000098
8	6	C	4.938159	1.080962	-0.000450
9	1	H	5.663606	1.904473	-0.000867
10	6	C	3.081867	-1.002386	0.000490
11	6	C	2.593982	0.345592	0.000115
12	8	O	1.291544	0.584852	0.000193
13	8	O	-1.292548	0.568548	0.000061
14	6	C	-3.062453	-1.041371	-0.000512
15	6	C	-3.575462	1.364202	0.000286
16	6	C	-4.430509	-1.344979	-0.000764
17	1	H	-4.725788	-2.404525	-0.001147
18	6	C	-3.115816	2.838009	0.000937
19	6	C	-2.591612	0.309508	-0.000059
20	6	C	-5.406607	-0.322322	-0.000593
21	6	C	-6.923594	-0.604883	-0.000389

22	6	C	-4.296142	3.834637	0.001236
23	1	H	-4.936808	3.714602	-0.896588
24	1	H	-3.903040	4.872970	0.001684
25	1	H	-4.936942	3.713882	0.898868
26	6	C	-4.941237	1.013736	0.000057
27	1	H	-5.686893	1.823666	0.000494
28	6	C	-2.255377	3.111687	-1.262533
29	1	H	-1.405572	2.405921	-1.285807
30	1	H	-1.864437	4.152582	-1.254922
31	1	H	-2.860403	2.974954	-2.182524
32	6	C	-2.255628	3.110645	1.264804
33	1	H	-2.860945	2.973554	2.184551
34	1	H	-1.864352	4.151418	1.257927
35	1	H	-1.406042	2.404609	1.287884
36	6	C	-7.241530	-2.117177	-0.003505
37	1	H	-6.821987	-2.619426	0.890147
38	1	H	-6.820784	-2.615896	-0.898568
39	1	H	-8.340763	-2.277395	-0.004516
40	6	C	-7.581008	0.020099	-1.261515
41	1	H	-8.681587	-0.146184	-1.271186
42	1	H	-7.152741	-0.427328	-2.180067
43	1	H	-7.397417	1.110812	-1.306781
44	6	C	3.084230	2.878217	-0.000820
45	6	C	2.220424	3.140635	-1.264476
46	1	H	2.827316	3.011330	-2.184332

47	1	H	1.815951	4.176435	-1.257551
48	1	H	1.379727	2.424083	-1.287940
49	6	C	7.264404	-1.438900	-1.261941
50	1	H	7.058963	-0.854263	-2.180475
51	1	H	6.647282	-2.356044	-1.308666
52	1	H	8.335978	-1.740051	-1.270268
53	6	C	7.264868	-1.436765	1.263004
54	1	H	8.336225	-1.738705	1.271036
55	1	H	6.647050	-2.353330	1.311908
56	1	H	7.060616	-0.850238	2.180599
57	6	C	7.827768	0.649522	-0.001414
58	1	H	8.896392	0.346508	-0.001513
59	1	H	7.649460	1.277808	0.893582
60	1	H	7.648846	1.276338	-0.897317
61	6	C	6.919817	-0.600838	-0.000111
62	6	C	4.250466	3.891569	-0.001215
63	1	H	4.893105	3.781361	0.896478
64	1	H	3.842290	4.924174	-0.001637
65	1	H	4.893112	3.780632	-0.898813
66	6	C	2.220513	3.141506	1.262715
67	1	H	1.379873	2.424909	1.286767
68	1	H	1.815982	4.177277	1.255068
69	1	H	2.827491	3.012902	2.182613
70	6	C	-7.579377	0.014780	1.264217
71	1	H	-7.395412	1.105251	1.313785

72	1	H	-7.149948	-0.436628	2.180273
73	1	H	-8.679987	-0.151321	1.274694

Table S8. Atomic charges on **1**^{red} with hydrogens summed into heavy atoms.

Centre no.	Atom	Mulliken charge
1	Se	-0.555543
2	Se	-0.555282
3	Ni	0.802619
4	C	-0.197772
5	H	0.000000
6	C	0.112109
7	C	0.196983
8	C	-0.248353
9	H	0.000000
10	C	-0.019311
11	C	0.277541
12	O	-0.626792
13	O	-0.627577
14	C	-0.024509
15	C	0.113660
16	C	-0.192819
17	H	0.000000
18	C	0.108132
19	C	0.278967
20	C	0.195336

21	C	0.089867
22	C	-0.132493
23	H	0.000000
24	H	0.000000
25	H	0.000000
26	C	-0.247697
27	H	0.000000
28	C	-0.063206
29	H	0.000000
30	H	0.000000
31	H	0.000000
32	C	-0.063209
33	H	0.000000
34	H	0.000000
35	H	0.000000
36	C	-0.095761
37	H	0.000000
38	H	0.000000
39	H	0.000000
40	C	-0.091697
41	H	0.000000
42	H	0.000000
43	H	0.000000
44	C	0.108893
45	C	-0.064471

46	H	0.000000
47	H	0.000000
48	H	0.000000
49	C	-0.084961
50	H	0.000000
51	H	0.000000
52	H	0.000000
53	C	-0.084955
54	H	0.000000
55	H	0.000000
56	H	0.000000
57	C	-0.107296
58	H	0.000000
59	H	0.000000
60	H	0.000000
61	C	0.088059
62	C	-0.132367
63	H	0.000000
64	H	0.000000
65	H	0.000000
66	C	-0.064484
67	H	0.000000
68	H	0.000000
69	H	0.000000
70	C	-0.091607

71	H	0.000000
72	H	0.000000
73	H	0.000000

Sum of Mulliken charges= -2.00000

Table S9. Cartesian coordinates for the optimized structure for complex **1**^{ox}.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	34	0	-1.686917	-2.331618	-0.107211
2	34	0	1.718210	-2.312998	-0.140884
3	28	0	0.007350	-0.741640	-0.106581
4	6	0	4.419806	-1.321789	0.042583
5	1	0	4.712739	-2.366470	0.055880
6	6	0	3.606944	1.430553	-0.009053
7	6	0	5.381099	-0.313003	0.095907
8	6	0	4.932775	1.044345	0.062036
9	1	0	5.685669	1.817691	0.096432
10	6	0	3.061791	-1.008299	-0.033006
11	6	0	2.616602	0.369896	-0.040447
12	8	0	1.353147	0.626338	-0.069233
13	8	0	-1.353063	0.610512	-0.049659
14	6	0	-3.042261	-1.043024	-0.012349
15	6	0	-3.618157	1.387335	0.003738
16	6	0	-4.401514	-1.380244	0.055889

17	1	0	-4.675270	-2.428293	0.068955
18	6	0	-3.210677	2.871252	-0.035383
19	6	0	-2.613852	0.338005	-0.022326
20	6	0	-5.369551	-0.386106	0.099542
21	6	0	-6.871957	-0.686950	0.174620
22	6	0	-4.437798	3.805364	-0.014587
23	1	0	-5.092577	3.644169	-0.877875
24	1	0	-4.094196	4.844216	-0.050711
25	1	0	-5.031192	3.685889	0.898357
26	6	0	-4.934767	0.981326	0.066711
27	1	0	-5.704159	1.741626	0.094739
28	6	0	-2.419540	3.163620	-1.336582
29	1	0	-1.511961	2.560936	-1.398427
30	1	0	-2.134983	4.221798	-1.364876
31	1	0	-3.036489	2.957167	-2.218749
32	6	0	-2.338825	3.212671	1.200551
33	1	0	-2.894769	3.032252	2.127824
34	1	0	-2.062640	4.273172	1.174517
35	1	0	-1.423751	2.618690	1.222961
36	6	0	-7.166744	-2.199154	0.210891
37	1	0	-6.714156	-2.682715	1.083244
38	1	0	-6.808266	-2.707259	-0.690712
39	1	0	-8.248575	-2.355688	0.270521
40	6	0	-7.577967	-0.084035	-1.067212
41	1	0	-8.653177	-0.289341	-1.017993

42	1	0	-7.188465	-0.526093	-1.990678
43	1	0	-7.448358	1.000637	-1.128997
44	6	0	3.180720	2.908757	-0.049543
45	6	0	2.390555	3.190904	-1.353938
46	1	0	3.013040	2.991473	-2.233801
47	1	0	2.093780	4.245655	-1.383612
48	1	0	1.490260	2.577723	-1.418944
49	6	0	7.265942	-1.549967	-1.029906
50	1	0	7.103575	-1.006666	-1.967179
51	1	0	6.691453	-2.480024	-1.072357
52	1	0	8.327482	-1.814738	-0.969103
53	6	0	7.111469	-1.487124	1.492894
54	1	0	8.169897	-1.759832	1.571873
55	1	0	6.524674	-2.410222	1.514075
56	1	0	6.845569	-0.895116	2.375454
57	6	0	7.791705	0.557721	0.216442
58	1	0	8.833733	0.229129	0.284512
59	1	0	7.591925	1.199494	1.081012
60	1	0	7.694308	1.160170	-0.692972
61	6	0	6.871953	-0.679416	0.190915
62	6	0	4.395113	3.859333	-0.024383
63	1	0	4.986124	3.748863	0.891205
64	1	0	4.037364	4.893306	-0.062896
65	1	0	5.055644	3.706258	-0.884729
66	6	0	2.299647	3.239441	1.183137

67	1	0	1.391219	2.635276	1.201863
68	1	0	2.011666	4.296759	1.156013
69	1	0	2.853889	3.065309	2.112604
70	6	0	-7.458796	-0.047761	1.459902
71	1	0	-7.328701	1.038411	1.477491
72	1	0	-6.982139	-0.461789	2.355067
73	1	0	-8.532916	-0.255662	1.518388

Table S10. Mulliken charges on **1^{ox}** with hydrogens summed into heavy atoms.

Centre no.	Atom	Mulliken charge
1	Se	-0.339071
2	Se	-0.277421
3	Ni	0.250673
4	C	0.319486
6	C	-0.072418
7	C	-0.196631
8	C	-0.111960
10	C	0.526901
11	C	-0.426868
12	O	-0.374689
13	O	-0.388501
14	C	0.087181
15	C	0.310607
16	C	-0.054364
18	C	0.458615

19	C	-0.245022
20	C	-0.015623
21	C	0.380094
22	C	-0.001885
26	C	-0.158976
28	C	-0.080769
32	C	-0.085055
36	C	0.049361
40	C	-0.023702
44	C	0.205565
45	C	-0.094572
49	C	-0.036988
53	C	-0.041651
57	C	0.069143
61	C	0.430193
62	C	0.058115
66	C	-0.093779
70	C	-0.025988

Sum of Mulliken charges with hydrogens summed into heavy atoms = 0.00000

Table S11. Cartesian coordinates for the optimized structure for complex **2** ($[(L^{SO})_2Ni]^-$).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	-0.009076	-0.883279	-0.000169

2	6	0	-4.278124	-1.648389	0.000026
3	1	0	-4.501642	-2.726044	0.000099
4	6	0	-3.610282	1.128699	-0.000152
5	6	0	-5.311355	-0.693234	0.000114
6	6	0	-4.942223	0.675598	0.000023
7	1	0	-5.739631	1.427278	0.000104
8	6	0	-2.935021	-1.244246	-0.000113
9	6	0	-2.574155	0.136727	-0.000220
10	8	0	-1.282099	0.455226	-0.000421
11	8	0	1.279336	0.441252	0.000158
12	6	0	2.912283	-1.276191	-0.000138
13	6	0	3.615682	1.088983	0.000124
14	6	0	4.253235	-1.700869	-0.000195
15	1	0	4.458188	-2.779635	-0.000374
16	6	0	3.275430	2.593398	0.000238
17	6	0	2.566629	0.106333	0.000039
18	6	0	5.293035	-0.758798	-0.000085
19	6	0	6.783847	-1.158987	0.000055
20	6	0	4.537686	3.484144	0.000193
21	1	0	5.164623	3.313580	0.898476
22	1	0	4.233105	4.550117	0.000311
23	1	0	5.164458	3.313720	-0.898233
24	6	0	4.936925	0.617677	0.000071
25	1	0	5.749116	1.356680	0.000145
26	6	0	2.443659	2.935663	1.266451

27	1	0	1.519922	2.331375	1.291652
28	1	0	2.167966	4.011012	1.266343
29	1	0	3.027634	2.729448	2.185842
30	6	0	2.443460	2.935781	-1.265809
31	1	0	3.027270	2.729598	-2.185313
32	1	0	2.167813	4.011142	-1.265587
33	1	0	1.519696	2.331532	-1.290889
34	6	0	6.977091	-2.691364	-0.000170
35	1	0	6.524363	-3.158618	-0.896536
36	1	0	6.524257	-3.158907	0.895999
37	1	0	8.058658	-2.936158	-0.000115
38	6	0	7.479534	-0.587625	1.264910
39	1	0	8.559367	-0.846309	1.270868
40	1	0	7.018634	-0.999988	2.183723
41	1	0	7.393381	0.514921	1.312487
42	6	0	-3.252744	2.629421	-0.000267
43	6	0	-2.416733	2.962920	1.265603
44	1	0	-3.003498	2.765428	2.185160
45	1	0	-2.127109	4.034688	1.264403
46	1	0	-1.500787	2.346878	1.291989
47	6	0	-7.059273	-2.017328	1.264453
48	1	0	-6.894233	-1.422496	2.184190
49	1	0	-6.389119	-2.896605	1.310608
50	1	0	-8.107204	-2.384902	1.271322
51	6	0	-7.059653	-2.017358	-1.263696

52	1	0	-8.107564	-2.384992	-1.270192
53	1	0	-6.389462	-2.896592	-1.310089
54	1	0	-6.894979	-1.422527	-2.183494
55	6	0	-7.779817	0.021541	0.000438
56	1	0	-8.819496	-0.363983	0.000593
57	1	0	-7.655381	0.659730	-0.896423
58	1	0	-7.655137	0.659815	0.897206
59	6	0	-6.784103	-1.159472	0.000326
60	6	0	-4.504207	3.535211	-0.000045
61	1	0	-5.133297	3.372029	-0.898136
62	1	0	-4.186797	4.597484	-0.000109
63	1	0	-5.132941	3.372024	0.898293
64	6	0	-2.417222	2.962763	-1.266498
65	1	0	-1.501333	2.346651	-1.293179
66	1	0	-2.127515	4.034507	-1.265535
67	1	0	-3.004365	2.765210	-2.185804
68	6	0	7.480036	-0.587208	-1.264320
69	1	0	7.393965	0.515351	-1.311579
70	1	0	7.019513	-0.999223	-2.183481
71	1	0	8.559859	-0.845913	-1.269926
72	16	0	-1.564714	-2.365323	-0.000139
73	16	0	1.530603	-2.381556	-0.000245

Table S12. Mulliken spin density for complex **2** ($[(L^{SO})_2Ni]^-$).

Metal ion (Ni)	Ligand
0.363479 (36.3%)	0.636521 (63.7%)

Table S13. Mulliken charges on complex **2** with hydrogens summed into heavy atoms.

Centre no.	Atom	Mulliken charge
1	Ni	0.892497
2	C	-0.116279
4	C	0.133589
5	C	0.199382
6	C	-0.203817
8	C	-0.162820
9	C	0.310543
10	O	-0.618743
11	O	-0.618314
12	C	-0.169810
13	C	0.133722
14	C	-0.111775
16	C	0.094206
17	C	0.314085
18	C	0.199577
19	C	0.078073
20	C	-0.091230
24	C	-0.202128

26	C	-0.041163
30	C	-0.041159
34	C	-0.068818
38	C	-0.057025
42	C	0.094921
43	C	-0.042532
47	C	-0.053096
51	C	-0.053098
55	C	-0.075943
59	C	0.076596
60	C	-0.090937
64	C	-0.042538
68	C	-0.057038
72	S	-0.305882
73	S	-0.303043

Sum of Mulliken charges with hydrogens summed into heavy atoms = -1.00000

Table S14. Cartesian coordinates for the optimized structure of **2^{red}** ([$(L^{SO})_2$Ni]$^{2-}$).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	-0.009280	-0.948966	-0.000427
2	6	0	-4.327160	-1.622557	0.000109
3	1	0	-4.575287	-2.697278	0.000164
4	6	0	-3.607622	1.120997	0.000119

5	6	0	-5.354262	-0.646149	0.000095
6	6	0	-4.960983	0.709202	0.000143
7	1	0	-5.737486	1.485103	0.000167
8	6	0	-2.974236	-1.262933	0.000110
9	6	0	-2.581569	0.116854	0.000039
10	8	0	-1.290123	0.420902	-0.000023
11	8	0	1.285924	0.406608	-0.000667
12	6	0	2.950813	-1.295996	-0.000512
13	6	0	3.612371	1.079309	-0.000163
14	6	0	4.301184	-1.677217	-0.000188
15	1	0	4.528598	-2.753336	-0.000287
16	6	0	3.235304	2.575988	-0.000245
17	6	0	2.573557	0.084996	-0.000436
18	6	0	5.336117	-0.714387	0.000207
19	6	0	6.833136	-1.090942	0.000666
20	6	0	4.468573	3.506194	0.000088
21	1	0	5.101402	3.350291	0.897863
22	1	0	4.133584	4.564776	0.000050
23	1	0	5.101852	3.350360	-0.897382
24	6	0	4.955964	0.648314	0.000176
25	1	0	5.749253	1.411124	0.000397
26	6	0	2.389157	2.894379	1.262629
27	1	0	1.501914	2.235830	1.282205
28	1	0	2.056493	3.955558	1.257593
29	1	0	2.983919	2.721480	2.183133

30	6	0	2.389819	2.894370	-1.263563
31	1	0	2.985073	2.721482	-2.183753
32	1	0	2.057129	3.955541	-1.258695
33	1	0	1.502609	2.235793	-1.283601
34	6	0	7.054302	-2.619941	0.000640
35	1	0	6.602833	-3.091704	-0.893924
36	1	0	6.602172	-3.091821	0.894810
37	1	0	8.140856	-2.851366	0.001031
38	6	0	7.526844	-0.511092	1.263812
39	1	0	8.615453	-0.743599	1.273368
40	1	0	7.071797	-0.934758	2.180789
41	1	0	7.409329	0.588605	1.312554
42	6	0	-3.212684	2.613385	0.000164
43	6	0	-2.363303	2.922992	1.263167
44	1	0	-2.960608	2.758186	2.183539
45	1	0	-2.017663	3.980113	1.257574
46	1	0	-1.483910	2.254052	1.284223
47	6	0	-7.125485	-1.947891	1.262682
48	1	0	-6.960090	-1.349605	2.180591
49	1	0	-6.451736	-2.824013	1.312992
50	1	0	-8.175908	-2.316351	1.269120
51	6	0	-7.125876	-1.947694	-1.262242
52	1	0	-8.176274	-2.316216	-1.268336
53	1	0	-6.452097	-2.823766	-1.313028
54	1	0	-6.960909	-1.349242	-2.180122

55	6	0	-7.812746	0.101195	0.000399
56	1	0	-8.861384	-0.264943	0.000307
57	1	0	-7.670833	0.738147	-0.894981
58	1	0	-7.670936	0.737953	0.895938
59	6	0	-6.831510	-1.091981	0.000236
60	6	0	-4.434597	3.558518	0.000242
61	1	0	-5.069665	3.410380	-0.897242
62	1	0	-4.086760	4.613014	0.000258
63	1	0	-5.069520	3.410300	0.897813
64	6	0	-2.363337	2.922978	-1.262860
65	1	0	-1.483962	2.254018	-1.283901
66	1	0	-2.017683	3.980089	-1.257352
67	1	0	-2.960668	2.758103	-2.183208
68	6	0	7.527682	-0.510948	-1.261958
69	1	0	7.410560	0.588800	-1.310450
70	1	0	7.072968	-0.934194	-2.179285
71	1	0	8.616226	-0.743786	-1.271005
72	16	0	-1.623813	-2.424458	0.000407
73	16	0	1.587318	-2.443155	-0.001268

Table S15. Mulliken charges on **2^{red}** with hydrogens summed into heavy atoms.

Centre no.	atom	Mulliken charge
1	Ni	0.781158
2	C	-0.167475
4	C	0.111314

5	C	0.193633
6	C	-0.251354
8	C	-0.147292
9	C	0.305549
10	O	-0.633316
11	O	-0.634485
12	C	-0.154946
13	C	0.112967
14	C	-0.160421
16	C	0.107849
17	C	0.308598
18	C	0.191411
19	C	0.091336
20	C	-0.132570
24	C	-0.251287
26	C	-0.065510
30	C	-0.065527
34	C	-0.096184
38	C	-0.092710
42	C	0.108697
43	C	-0.066809
47	C	-0.085479
51	C	-0.085491
55	C	-0.108174
59	C	0.088168

60	C	-0.132373
64	C	-0.066805
68	C	-0.092714
72	S	-0.454513
73	S	-0.455246

Sum of Mulliken charges with hydrogens summed into heavy atoms = -2.00000

Table S16. Cartesian coordinates for the optimized structure for complex **2^{ox}** ([$(L^{SO})_2$Ni]).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	0.009584	-0.822271	-0.000397
2	6	0	4.259776	-1.669866	-0.000208
3	1	0	4.460841	-2.736342	-0.000283
4	6	0	3.649406	1.138720	0.000011
5	6	0	5.292117	-0.740941	-0.000024
6	6	0	4.945900	0.645694	0.000080
7	1	0	5.756823	1.358984	0.000225
8	6	0	2.923317	-1.239308	-0.000284
9	6	0	2.590417	0.162650	-0.000171
10	8	0	1.331025	0.494450	-0.000220
11	8	0	-1.331815	0.480799	-0.000159
12	6	0	-2.899759	-1.273256	-0.000211
13	6	0	-3.656619	1.099665	0.000191

14	6	0	-4.235027	-1.724452	-0.000132
15	1	0	-4.419062	-2.792050	-0.000253
16	6	0	-3.363887	2.611261	0.000367
17	6	0	-2.583488	0.133541	-0.000063
18	6	0	-5.272275	-0.808132	0.000100
19	6	0	-6.751620	-1.221290	0.000198
20	6	0	-4.658823	3.449638	0.000565
21	1	0	-5.271421	3.263137	-0.888262
22	1	0	-4.394505	4.512186	0.000701
23	1	0	-5.271318	3.262881	0.889409
24	6	0	-4.940624	0.588296	0.000255
25	1	0	-5.765800	1.287836	0.000436
26	6	0	-2.557653	2.989725	-1.268313
27	1	0	-1.601578	2.464731	-1.307260
28	1	0	-2.360162	4.067898	-1.272188
29	1	0	-3.125136	2.747514	-2.174187
30	6	0	-2.557481	2.989405	1.269036
31	1	0	-3.124826	2.746932	2.174927
32	1	0	-2.360026	4.067585	1.273174
33	1	0	-1.601384	2.464433	1.307705
34	6	0	-6.929884	-2.751657	-0.000049
35	1	0	-6.486316	-3.214394	0.888118
36	1	0	-6.486547	-3.214080	-0.888495
37	1	0	-7.997664	-2.993340	0.000048
38	6	0	-7.444906	-0.651967	-1.264224

39	1	0	-8.502774	-0.937931	-1.267860
40	1	0	-6.981894	-1.046905	-2.175096
41	1	0	-7.395720	0.440393	-1.304942
42	6	0	3.338659	2.646951	0.000132
43	6	0	2.527339	3.015608	-1.268370
44	1	0	3.098672	2.782831	-2.174342
45	1	0	2.313826	4.090816	-1.271282
46	1	0	1.579357	2.476168	-1.308031
47	6	0	7.016339	-2.077219	-1.263386
48	1	0	6.844289	-1.494396	-2.174991
49	1	0	6.369085	-2.958848	-1.297716
50	1	0	8.055770	-2.424743	-1.272434
51	6	0	7.015942	-2.077645	1.263400
52	1	0	8.055349	-2.425235	1.272623
53	1	0	6.368619	-2.959244	1.297262
54	1	0	6.843674	-1.495109	2.175148
55	6	0	7.763763	-0.050436	0.000465
56	1	0	8.781941	-0.452922	0.000413
57	1	0	7.658818	0.581029	0.889162
58	1	0	7.658903	0.581488	-0.887917
59	6	0	6.756967	-1.217991	0.000111
60	6	0	4.622198	3.502689	0.000276
61	1	0	5.237189	3.324045	0.889052
62	1	0	4.343531	4.561625	0.000391
63	1	0	5.237249	3.324257	-0.888501

64	6	0	2.527209	3.015387	1.268616
65	1	0	1.579208	2.475965	1.308073
66	1	0	2.313728	4.090600	1.271709
67	1	0	3.098436	2.782422	2.174607
68	6	0	-7.444616	-0.652413	1.264980
69	1	0	-7.395440	0.439933	1.306064
70	1	0	-6.981384	-1.047661	2.175606
71	1	0	-8.502479	-0.938397	1.268766
72	16	0	1.578016	-2.331172	-0.000494
73	16	0	-1.546018	-2.346231	-0.000476

Table S17. Mulliken charges on **2^{ox}** with hydrogens summed into heavy atoms.

Centre no.	atom	Mulliken charge
1	Ni	-0.420987
2	C	0.403290
4	C	-0.013945
5	C	-0.137261
6	C	-0.225232
8	C	-0.044521
9	C	-0.119893
10	O	-0.383390
11	O	-0.390146
12	C	-0.344301
13	C	0.417507
14	C	-0.027836

16	C	0.556154
17	C	0.098892
18	C	0.117973
19	C	0.509321
20	C	-0.033516
24	C	-0.222462
26	C	-0.079773
30	C	-0.079791
34	C	0.019474
38	C	-0.026490
42	C	0.410554
43	C	-0.075025
47	C	-0.035630
51	C	-0.035627
55	C	0.058442
59	C	0.519051
60	C	0.011552
64	C	-0.075028
68	C	-0.026491
72	S	0.024413
73	S	-0.349277

Sum of Mulliken charges with hydrogens summed into heavy atoms = 0.00000

Table S18. Calculated energies for the optimized geometries of the complexes.

Complex	Stabilization energy (kcal mol^{-1})	Complex	Stabilization energy (kcal mol^{-1})
1	0	**2**	0
$\mathbf{1}^{red}$	31.49	$\mathbf{2}^{red}$	31.62
$\mathbf{1}^{ox}$	58.38	$\mathbf{2}^{ox}$	58.66

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