Supplementary information

for the manuscript

Molecular and electronic structure of square-planar nickel(II), nickel(III) and nickel(III) π-cation radical complexes with a tetradentate *o*-phenylenedioxamidate redox-active ligand

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Table S1 Selected MO energy and composition data for $[NiL]^-$ (^2B)

			Nature[c]																		
MO[a]	Energy/au	n^b	$3d_{x^2-y^2}$ (Ni)	$3d_{z^2}$ (Ni)	$3d_{zx}$ (Ni)	$3d_{yz}$ (Ni)	$3d_{xy}$ (Ni)	$2p_x$ (N1)	$2p_y$ (N1)	$2p_z$ (N1)	$2p_x$ (N2)	$2p_y$ (N2)	$2p_z$ (N2)	$2p_z$ (O1)	$2p_z$ (O2)	$2p_z$ (C1)	$2p_z$ (C2)	$2p_z$ (C3)	$2p_z$ (C4)	$2p_z$ (C5)	Type
75a (α)	-0.21236	1	36.2	5.4	0.0	0.0	0.0	2.3	0.9	0.0	2.6	4.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{x^2-y^2}$
79a (α)	-0.16619	1	1.9	77.1	0.0	0.0	0.0	0.4	0.5	0.0	0.5	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{z^2}$
81a (α)	-0.14039	1	0.0	0.0	5.8	0.0	0.0	0.0	0.0	11.6	0.0	0.0	1.4	5.6	0.3	0.3	0.0	0.4	20.0	7.2	π_a
82b (α)	-0.13911	1	0.0	0.0	0.0	2.4	0.0	0.0	0.0	1.3	0.0	0.0	19.3	0.9	14.9	0.1	0.1	4.2	0.2	3.4	π_b
85a (α)	-0.11455	1	0.0	0.0	15.7	0.0	0.0	0.0	0.0	0.1	0.0	0.0	22.8	0.5	14.6	0.1	0.4	0.0	0.0	0.0	$3d_{zx}$
86b (α)	-0.10060	1	0.0	0.0	0.0	6.5	0.0	0.0	0.0	12.6	0.0	0.0	6.3	6.0	1.3	1.3	0.1	8.9	2.4	7.3	$3d_{yz}$
87b (α)	0.04471	0	0.0	0.0	0.0	0.0	54.9	4.3	3.8	0.0	1.2	15.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{xy}$
88a (α)	0.05319	0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.6	0.0	0.0	3.6	8.5	3.9	12.7	4.2	8.5	0.2	7.1	π_a*
89b (α)	0.05676	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.7	0.0	0.0	2.3	8.5	5.7	11.8	6.3	0.5	8.7	2.6	π_b*
75a (β)	-0.20675	1	49.5	5.7	0.0	0.0	0.0	1.7	0.5	0.0	1.8	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{x^2-y^2}$
79a (β)	-0.15582	1	5.0	27.3	0.0	0.0	0.0	0.2	1.1	0.0	1.0	4.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{z^2}$
83a (β)	-0.12901	1	0.0	0.0	7.9	0.0	0.0	0.0	0.0	14.1	0.0	0.0	1.6	6.9	0.4	0.2	0.0	0.0	16.1	6.5	π_a
84b (β)	-0.12134	1	0.0	0.0	0.0	16.2	0.0	0.0	0.0	4.5	0.0	0.0	6.6	3.1	6.3	0.2	0.1	10.0	0.8	7.7	π_b
85a (β)	-0.10384	1	0.0	0.0	16.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	22.4	0.6	14.4	0.1	0.8	0.0	0.0	0.0	$3d_{zx}$
86b (β)	-0.03572	0	0.0	0.0	0.0	36.7	0.0	0.0	0.0	9.0	0.0	0.0	6.0	4.4	1.3	1.7	0.3	2.8	2.3	3.0	$3d_{yz}$
87b (β)	0.05750	0	0.0	0.0	0.0	0.0	56.5	2.1	3.6	0.0	1.1	4.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{xy}$
88a (β)	0.05821	0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.5	0.0	0.0	4.3	9.1	3.5	12.0	4.1	8.6	0.2	7.0	π_a*
89b (β)	0.06094	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.6	0.0	0.0	2.5	8.8	5.5	10.9	6.4	0.4	8.7	2.8	π_b*

[a] The labels (*a*) and (*b*) refer to the orbital symmetry in the C_2 point group. [b] *n* is the orbital occupancy. [c] Percentage composition values of the relevant atomic orbitals.

Table S2 Selected MO energy and composition data for [NiL] (^{1}A)

			Nature[c]																		
MO[a]	Energy/au	n[b]	$3d_{x^2-y^2}$ (Ni)	$3d_{z^2}$ (Ni)	$3d_{zx}$ (Ni)	$3d_{yz}$ (Ni)	$3d_{xy}$ (Ni)	$2p_x$ (N1)	$2p_y$ (N1)	$2p_z$ (N1)	$2p_x$ (N2)	$2p_y$ (N2)	$2p_z$ (N2)	$2p_z$ (O1)	$2p_z$ (O2)	$2p_z$ (C1)	$2p_z$ (C2)	$2p_z$ (C3)	$2p_z$ (C4)	$2p_z$ (C5)	Type
75 (α)	-0.35787	1	36.2	5.0	0.0	0.0	0.2	3.1	0.9	0.0	1.5	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{x^2-y^2}$
79 (α)	-0.31209	1	1.0	77.4	0.0	0.0	0.0	0.4	0.6	0.0	0.5	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{z^2}$
81 (α)	-0.28546	1	0.0	0.0	1.0	7.5	0.0	0.0	0.0	0.3	0.0	0.0	36.5	0.0	21.1	0.0	0.1	4.2	3.0	0.4	$3d_{yz}$
82 (α)	-0.27952	1	0.0	0.0	5.9	0.1	0.0	0.0	0.0	10.6	0.0	0.0	2.6	5.3	2.4	0.1	0.0	0.0	18.0	8.2	π_a
85 (α)	-0.24856	1	0.0	0.0	8.1	0.0	0.0	0.0	0.0	3.7	0.0	0.0	7.1	1.1	2.5	0.1	0.2	4.9	0.3	3.9	$3d_{zx}$
86 (α)	-0.19578	0	0.0	0.0	1.8	7.6	0.0	0.0	0.0	10.3	0.0	0.0	0.9	6.0	0.0	1.7	0.0	6.0	1.8	3.9	π_b
87 (α)	-0.09963	0	0.0	0.0	0.0	0.0	56.2	4.1	3.5	0.0	1.3	4.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{xy}$
88 (α)	-0.09264	0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.7	0.0	0.0	4.0	12.6	6.2	15.0	7.1	7.6	0.1	6.6	π_a*
89 (α)	-0.08633	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.8	0.0	0.0	1.5	7.0	5.4	8.1	6.5	0.5	6.6	1.4	π_b*
75 (β)	-0.35764	1	40.3	4.9	0.0	0.0	0.0	1.6	0.4	0.0	2.4	4.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{x^2-y^2}$
79 (β)	-0.31106	1	1.0	76.3	0.0	0.0	0.0	0.3	0.3	0.0	0.6	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{z^2}$
81 (β)	-0.28301	1	0.0	0.0	0.0	7.3	0.0	0.0	0.0	5.5	0.0	0.0	0.3	2.4	0.9	0.2	0.0	1.9	3.0	5.7	$3d_{yz}$
82 (β)	-0.27940	1	0.0	0.0	6.3	0.7	0.0	0.0	0.0	6.7	0.0	0.0	4.1	2.7	1.5	0.2	0.0	1.4	14.9	3.1	π_a
85 (β)	-0.24889	1	0.0	0.0	9.0	0.0	0.0	0.0	0.0	3.6	0.0	0.0	21.6	3.7	16.5	1.0	0.6	5.2	0.6	3.6	$3d_{zx}$
86 (β)	-0.19481	0	0.0	0.0	1.6	7.1	0.0	0.0	0.0	8.2	0.0	0.0	19.4	2.1	7.1	0.8	1.0	4.7	1.9	3.9	π_b
87 (β)	-0.09820	0	0.0	0.0	0.0	0.0	56.4	4.1	3.6	0.0	1.3	5.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{xy}$
88 (β)	-0.09300	0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.4	0.0	0.0	5.1	10.3	4.0	14.7	3.9	7.8	0.3	6.1	π_a*
89 (β)	-0.08661	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	2.5	8.0	5.9	11.2	5.8	0.1	6.5	2.2	π_b*

[a] The labels (*a*) and (*b*) refer to the orbital symmetry in the C_2 point group. [b] n is the orbital occupancy. [c] Percentage composition values of the relevant atomic orbitals.

Table S3 Selected MO energy and composition data for [NiL] (^{3}B)

			Nature[c]																		
MO[a]	Energy/au	n^b	$3d_{x^2-y^2}$ (Ni)	$3d_{z^2}$ (Ni)	$3d_{zx}$ (Ni)	$3d_{yz}$ (Ni)	$3d_{xy}$ (Ni)	$2p_x$ (N1)	$2p_y$ (N1)	$2p_z$ (N1)	$2p_x$ (N2)	$2p_y$ (N2)	$2p_z$ (N2)	$2p_z$ (O1)	$2p_z$ (O2)	$2p_z$ (C1)	$2p_z$ (C2)	$2p_z$ (C3)	$2p_z$ (C4)	$2p_z$ (C5)	Type
75a (α)	-0.36537	1	29.1	1.7	0.0	0.0	0.0	2.7	1.3	0.0	3.4	5.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{x^2-y^2}$
78a (α)	-0.33378	1	0.0	77.9	0.0	0.0	0.0	0.5	0.2	0.0	0.9	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{z^2}$
81b (α)	-0.30173	1	0.0	0.0	0.0	9.6	0.0	0.0	0.0	0.1	0.0	0.0	20.8	0.2	12.4	0.0	0.0	3.1	0.0	3.4	$3d_{yz}$
82a (α)	-0.28555	1	0.0	0.0	9.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	25.6	0.2	13.1	0.0	0.4	0.0	0.0	0.0	$3d_{zx}$
85a (α)	-0.28076	1	0.0	0.0	1.5	0.0	0.0	0.0	0.0	8.8	0.0	0.0	0.2	4.0	0.0	0.3	0.0	1.9	25.3	8.7	π_a
86b (α)	-0.24546	1	0.0	0.0	0.0	5.3	0.0	0.0	0.0	13.0	0.0	0.0	3.0	6.6	0.2	1.4	0.0	12.0	1.7	9.1	π_b
87b (α)	-0.11846	0	0.0	0.0	0.0	0.0	53.7	4.8	3.0	0.0	1.4	5.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{xy}$
88a (α)	-0.09699	0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.8	0.0	0.0	3.6	8.9	5.0	12.3	6.7	6.5	0.5	5.0	π_a*
89b (α)	-0.09125	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	2.4	8.3	7.3	11.1	10.0	0.0	4.6	1.8	π_b*
73a (β)	-0.35744	1	41.8	0.4	0.0	0.0	0.0	1.8	0.7	0.0	3.4	4.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{x^2-y^2}$
77a (β)	-0.32356	1	0.3	80.0	0.0	0.0	0.0	0.5	0.5	0.0	0.6	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{z^2}$
83a (β)	-0.26482	1	0.0	0.0	4.9	0.0	0.0	0.0	0.0	11.8	0.0	0.0	3.9	5.1	1.2	0.1	0.0	0.1	17.8	6.7	π_a
84b (β)	-0.26331	1	0.0	0.0	0.0	7.7	0.0	0.0	0.0	0.6	0.0	0.0	19.3	0.8	11.8	0.1	0.1	4.6	0.0	3.8	$3d_{yz}$
85a (β)	-0.19466	0	0.0	0.0	37.1	0.0	0.0	0.0	0.0	0.2	0.0	0.0	15.4	1.3	10.2	0.3	1.7	0.0	0.1	0.1	$3d_{zx}$
86b (β)	-0.18536	0	0.0	0.0	0.0	5.4	0.0	0.0	0.0	12.3	0.0	0.0	5.1	6.5	0.5	1.8	0.1	8.9	2.4	7.4	π_b
87b (β)	-0.10158	0	0.0	0.0	0.0	0.0	55.5	4.4	0.0	0.0	1.3	5.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$3d_{xy}$
88a (β)	-0.08131	0	0.0	0.0	1.2	0.0	0.0	0.0	3.7	0.6	0.0	0.0	5.3	9.8	4.1	11.6	4.7	7.1	0.4	5.1	π_a*
89b (β)	-0.07984	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.2	0.0	0.0	2.5	9.0	7.7	10.0	8.3	0.0	5.3	2.4	π_b*

[a] The labels (*a*) and (*b*) refer to the orbital symmetry in the C_2 point group. [b] *n* is the orbital occupancy. [c] Percentage composition values of the relevant atomic orbitals.

Table S4 Selected electronic spectroscopic data for $[NiL]^-$ (^2B)

Transition	Energy[a]/nm	f[b]	Nature[c]	Type
1	3738	5.5×10^{-4}	85a (β) → 86b (β) (70.5)	d–d
2	1679	8.4×10^{-6}	78a (β) → 86b (β) (61.4)	
			79a (β) → 86b (β) (35.4)	d–d
3	829	7.7×10^{-2}	84b (β) → 86b (β) (87.6)	LMCT
4	794	3.4×10^{-2}	83a (β) → 86b (β) (77.2)	LMCT
5	613	1.2×10^{-2}	80b (β) → 86b (β) (91.3)	
6	595	5.1×10^{-10}	86b (α) → 87b (α) (38.7)	d–d
7	456	3.2×10^{-6}	75a (β) → 86b (β) (43.9)	d–d
8	411	8.7×10^{-3}	86b (α) → 88a (α) (57.6)	MLCT
9	403	1.4×10^{-3}	85a (α) → 88a (α) (29.5)	MLCT
			85a (β) → 88a (β) (37.1)	MLCT
10	400	9.0×10^{-3}	85a (α) → 89b (α) (27.9)	MLCT
			85a (β) → 89b (β) (34.4)	MLCT
11	379	1.2×10^{-2}	86b (α) → 89 (α) (68.8)	MLCT

[a] The transition energy is lower than 30000 cm^{-1} (330 nm). [b] f is the oscillator strength. [c] The transition contribution (%) values are given in parentheses.

Table S5 Selected electronic spectroscopic data for [NiL] (^{1}A)

Transition	Energy[a]/nm	f[b]	Nature[c]	Type
1	4277	1.2×10^{-2}	85 (α) → 86 (α) (27.4)	MLCT
			85 (β) → 86 (β) (28.0)	MLCT
2	1839	1.5×10^{-2}	85 (α) → 86 (α) (31.9)	MLCT
			85 (β) → 86 (β) (29.5)	MLCT
3	1204	1.6×10^{-2}	83 (α) → 86 (α) (45.4)	
			82 (β) → 86 (β) (23.2)	IL
4	792	0.6×10^{-1}	82 (α) → 86 (α) (25.2)	IL
			82 (β) → 86 (β) (26.1)	IL
5	664	1.0×10^{-1}	81 (α) → 86 (α) (36.3)	MLCT
			81 (β) → 86 (β) (41.4)	MLCT
6	645	3.3×10^{-3}	77 (α) → 86 (α) (24.3)	
			81 (α) → 86 (α) (21.3)	MLCT
			78 (β) → 86 (β) (20.9)	
			81 (β) → 86 (β) (13.9)	MLCT
7	473	9.0×10^{-4}	75 (α) → 87 (α) (18.8)	d–d
			75 (β) → 87 (β) (23.7)	d–d
8	471	5.6×10^{-3}	76 (α) → 86 (α) (29.9)	
			76 (β) → 86 (β) (33.7)	
9	417	1.2×10^{-2}	76 (α) → 86 (α) (39.4)	
			76 (β) → 86 (β) (20.0)	
11	405	3.5×10^{-3}	85 (α) → 89 (α) (20.9)	MLCT
			85 (β) → 89 (β) (33.7)	MLCT
12	401	2.2×10^{-2}	85 (α) → 88 (α) (17.9)	MLCT
			85 (β) → 88 (β) (29.0)	MLCT
13	399	1.1×10^{-3}	79 (α) → 87 (α) (36.9)	d–d
			79 (β) → 87 (β) (35.9)	d–d
14	367	3.6×10^{-3}	75 (α) → 87 (α) (14.4)	d–d
			75 (β) → 87 (β) (15.7)	d–d
15	363	1.3×10^{-2}	85 (α) → 88 (α) (33.7)	MLCT
			85 (β) → 88 (β) (23.1)	MLCT
16	341	9.1×10^{-3}	85 (α) → 89 (α) (32.4)	MLCT
			85 (β) → 89 (β) (36.7)	MLCT

[a] The transition energy is lower than 30000 cm^{-1} (330 nm). [b] f is the oscillator strength. [c] The transition contribution (%) values are given in parentheses.

Table S6 Selected electronic spectroscopic data for [NiL] (^{3}B)

Transition	Energy[a]/nm	f[b]	Nature[c]	Type
1	1951	6.1×10^{-3}	84b (β) → 85a (β) (57.2)	d–d
2	1509	2.0×10^{-10}	77a (β) → 85a (β) (29.5)	d–d
3	1147	2.0×10^{-2}	83a (β) → 85a (β) (93.3)	LMCT
4	990	1.4×10^{-2}	83a (β) → 86b (β) (97.1)	IL
5	844	0.9×10^{-1}	84b (β) → 86b (β) (95.5)	MLCT
6	697	0.7×10^{-1}	76b (β) → 85a (β) (50.4)	
			84b (β) → 85a (β) (22.0)	d–d
7	641	6.7×10^{-3}	78a (α) → 87b (α) (46.8)	d–d
			77a (β) → 87b (β) (40.8)	
8	563	3.4×10^{-3}	79a (β) → 86b (β) (97.7)	
9	417	2.1×10^{-2}	86b (α) → 88a (α) (67.3)	IL
10	397	1.3×10^{-2}	86b (α) → 89b (α) (34.0)	IL
			75a (β) → 85a (β) (37.6)	
11	376	3.2×10^{-2}	75a (β) → 86b (β) (62.1)	
12	349	1.2×10^{-2}	82a (α) → 88a (α) (20.0)	MLCT
			74b (β) → 86b (β) (30.6)	
13	347	2.8×10^{-2}	78a (α) → 87b (α) (12.6)	d–d
			74b (β) → 85a (β) (16.0)	
			77a (β) → 87b (β) (14.8)	d–d
14	343	2.0×10^{-2}	83b (α) → 87b (α) (82.1)	
15	335	1.1×10^{-2}	74b (β) → 86b (β) (29.9)	
			84b (β) → 89b (β) (16.6)	MLCT

[a] The transition energy is lower than 30000 cm^{-1} (330 nm). [b] f is the oscillator strength. [c] The transition contribution (%) values are given in parentheses.

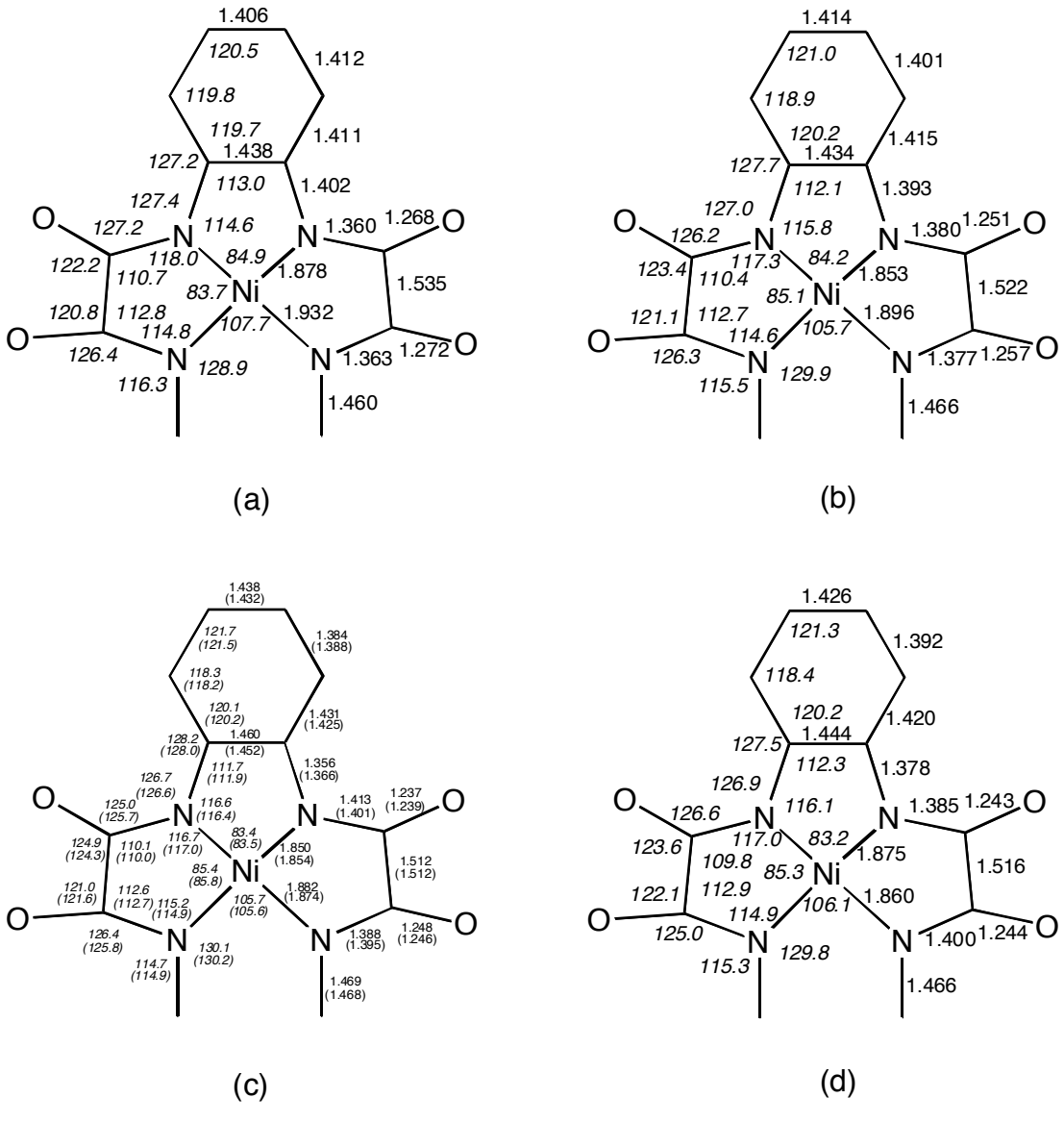

Fig. S1 Optimized bond lengths (Å) and bond angles (°) (italics) for $[NiL]^{2-}$ (^{1}A) (a), $[NiL]^{-}$ (^{2}B) (b), [NiL] (^{1}A) (c) and [NiL] (^{3}B) (d). The calculated structural data of the RB3LYP solution for [NiL] (^{1}A) (c) are given in parentheses.

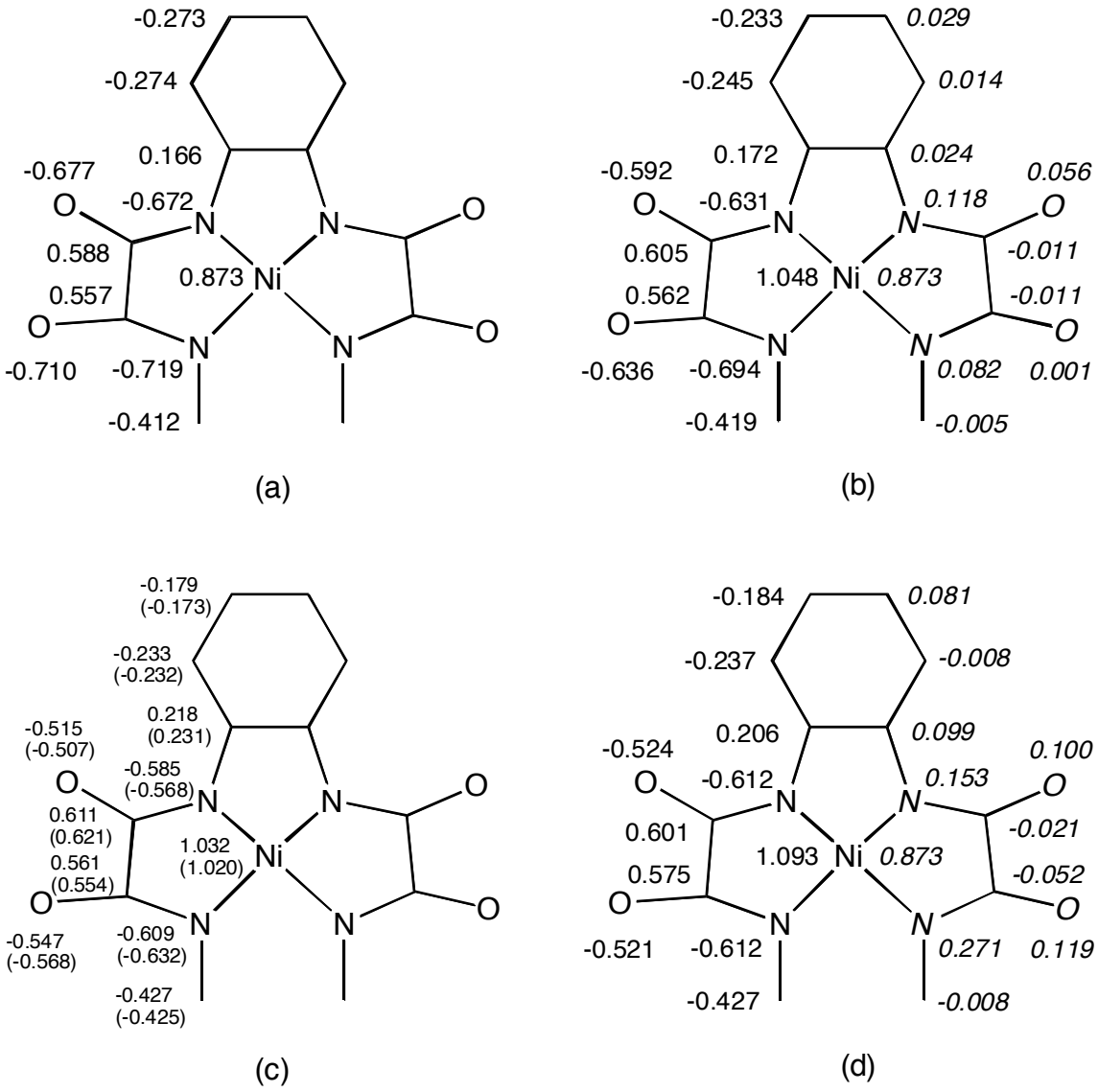

Fig. S2 Atomic charges and atomic spin densities (italics) for $[NiL]^{2-}$ (^{1}A) (a), $[NiL]^{-}$ (^{2}B) (b), [NiL] (^{1}A) (c) and [NiL] (^{3}B) (d). The calculated charge and spin density data of the RB3LYP solution for [NiL] (^{1}A) (c) are given in parentheses.