Ambiguous electrocatalytic CO_2 reduction behavior of a nickel bis(aldimino)pyridine pincer complex

Electronic Supplementary Information

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Materials and Methods.

The complexes Ni(NNN)Cl_2 and Ni(NNN)Br_2 were synthesized as previously described.[1] Cyclic voltammetry was carried out on a CH Instruments 620E potentiostat. A custom three electrode cell was used for both CV and bulk electrolysis experiments allowing airtight introduction of working, counter and reference electrodes as well as septa for gas purging.

Gas cylinders were ordered from Airgas containing known ratios of Ar:CO_2 (100:0, 80:20, 60:40, 50:50, 40:60, 20:80, 0:100). For cyclic voltammetry, glassy carbon (3 mm diameter) and Pt wire were used as working and counter electrodes, respectively, with 0.1 M Bu_4NPF_6 in spectrophotometric grade acetonitrile as the supporting electrolyte. A non-aqueous reference electrode was used to minimize ohmic potential drop at the solvent interface. This consisted of a Ag wire in 0.1 M Bu_4NPF_6 acetonitrile supporting electrolyte isolated by a vycor frit and was calibrated using the ferrocenium/ferrocene redox couple as a pseudo reference (+0.45 V vs. SCE).[2] Redox potentials (E) were determined from cyclic voltammetry as $(E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively. Where E could not be calculated due to irreversible behavior, E_{pc} or E_{pa} are reported accordingly. For controlled potential electrolysis experiments a vitreous carbon working electrode was used (soldered to a copper wire), a Pt gauze counter electrode was used isolated via a fine porosity vycor tube+frit to minimize mass transfer resistance. Gas chromatography data were recorded on a custom Shimadzu GC-2014 instrument where a Ni "methanizer" catalyst was used to convert CO to CH_4 prior to quantification by the thermally conductivity detector. H_2 was simultaneously monitored by a flame ionization detector during the same injection. The GC was precalibrated for CO and H_2 sensitivity by mimicking bulk electrolysis conditions (i.e. 5 mL supporting electrolyte in the same cell, with electrodes, under 1 atm CO_2). Standard curves for H_2 and CO were generated using this cell where known volumes of the analyte gas (H_2 or CO) were injected and the solution stirred for 15 min to allow equilibration of the analyte between the electrolyte and headspace prior to GC injection.

Electrochemical data

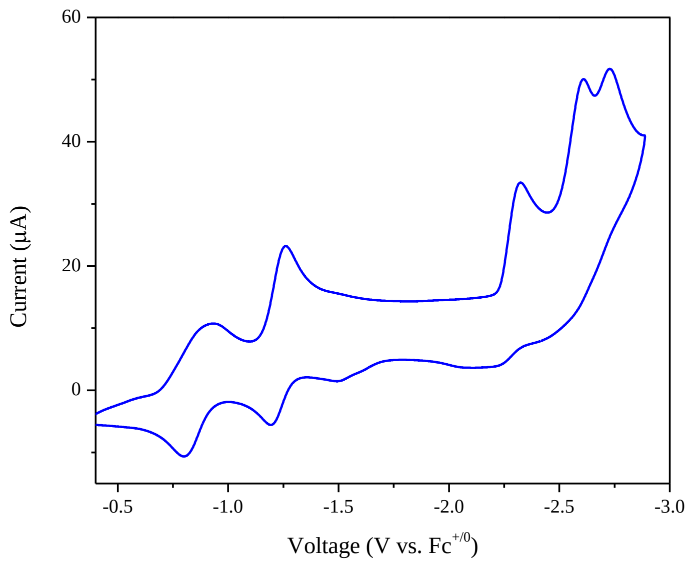


Figure ESI-1. Cyclic voltammetry of Ni(NNN)Cl_2 recorded under 1 atm Ar at 100 mV s^{-1} at glassy carbon in a 0.1 M Bu_4NPF_6 acetonitrile supporting electrolyte.

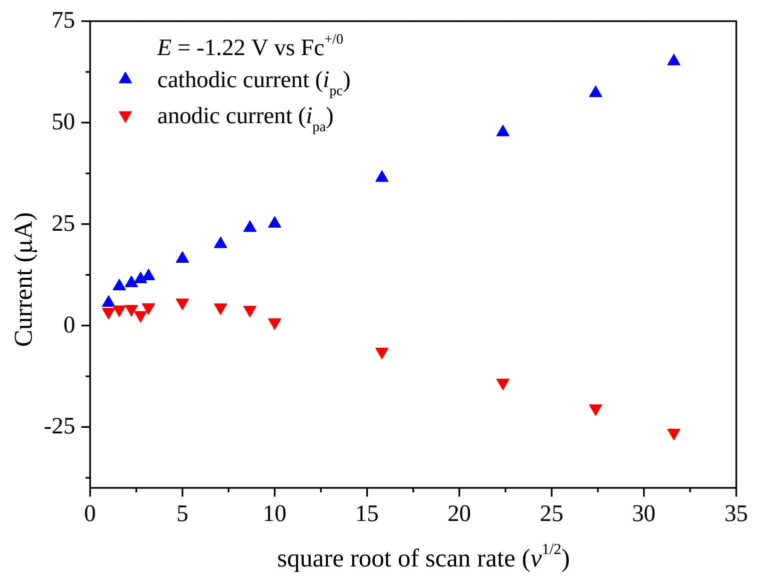


Figure ESI-2. Plot of cathodic and anodic currents versus the square root of the scan rate illustrating the irreversible nature of the anodic wave for the second redox wave of $Ni(NNN)Br_2$, i.e. Ni(NNN)Br + e^- → $[Ni(NNN)Br]^-$ → Ni(NNN) + Br^-.

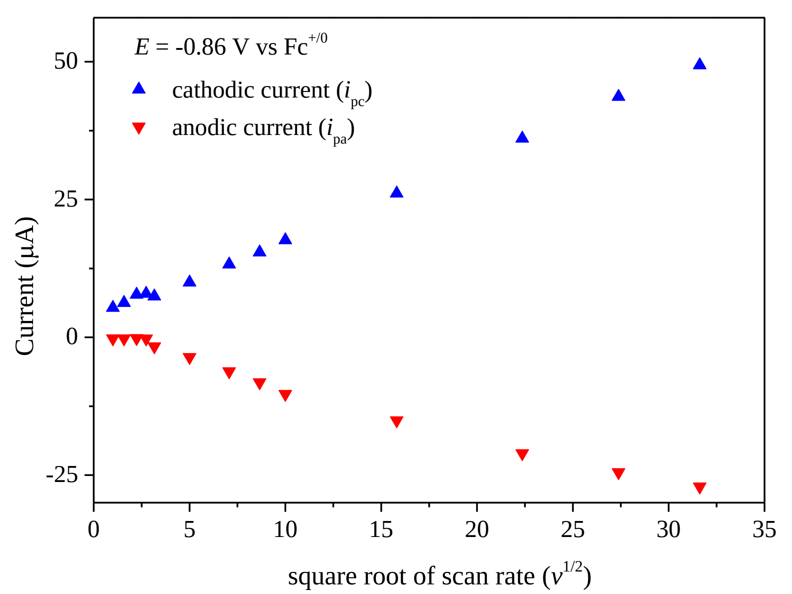


Figure ESI-3. Plot of cathodic and anodic currents versus the square root of the scan rate illustrating the irreversible nature of the anodic wave for the second redox wave of $Ni(NNN)Br_2$, i.e. Ni(NNN)Br + e^- → $[Ni(NNN)Br]^-$ → Ni(NNN) + Br^-.

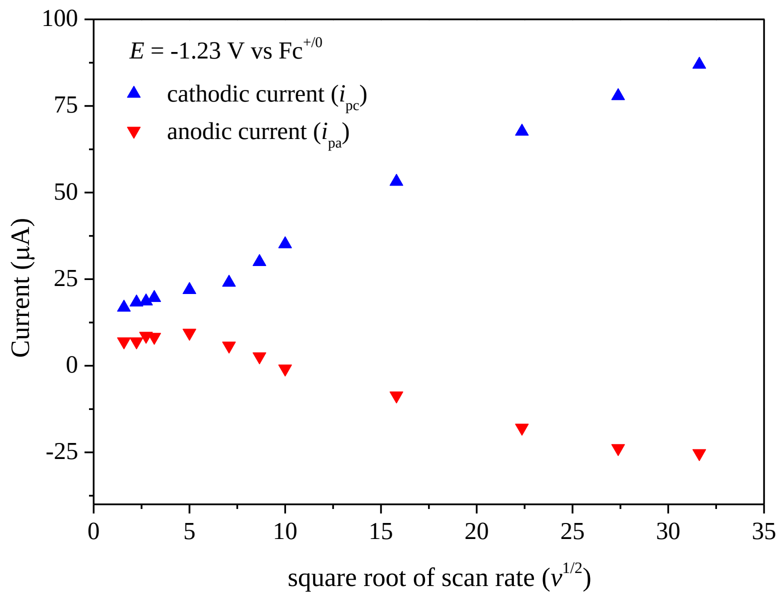


Figure ESI-4. Plot of cathodic and anodic currents versus the square root of the scan rate illustrating the irreversible nature of the anodic wave for the second redox wave of Ni(NNN)Cl_2, i.e. Ni(NNN)Cl + e^- → $[Ni(NNN)Cl]^-$ → Ni(NNN) + Cl^-.

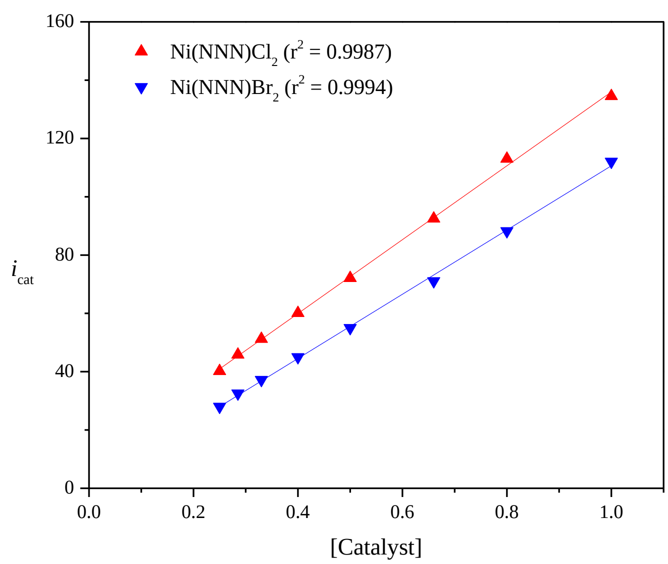


Figure ESI-5. Linear plot of catalytic current versus catalyst concentration.

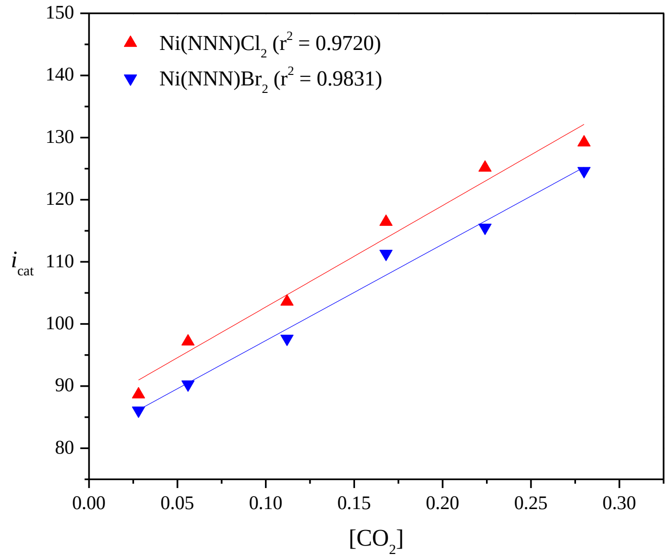


Figure ESI-6. Linear plot of catalytic current versus CO_2 concentration.

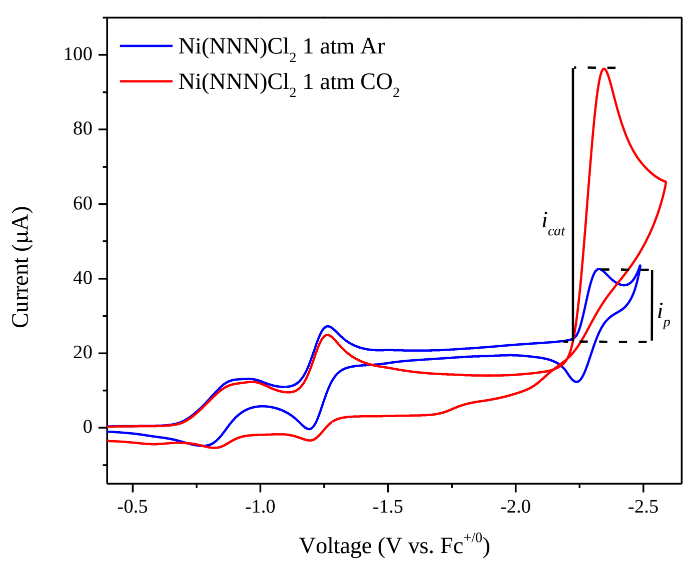


Figure ESI-7. Cyclic voltammetry of Ni(NNN)Cl_2 recorded under 1 atm Ar and 1 atm CO_2 at 100 mV s^{-1} at glassy carbon in a 0.1 M Bu_4NPF_6 acetonitrile supporting electrolyte.

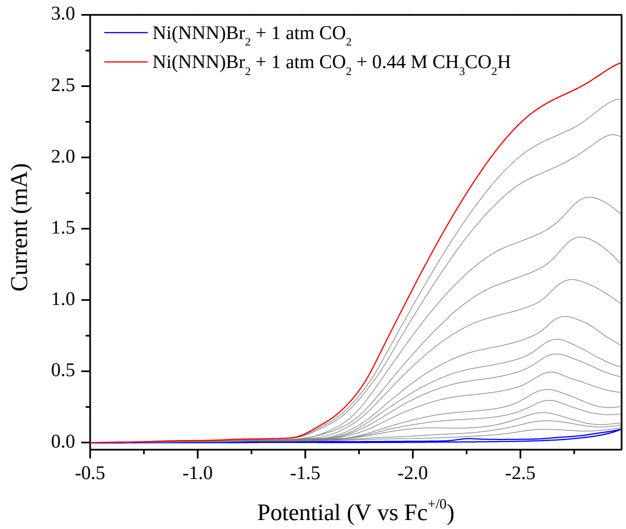
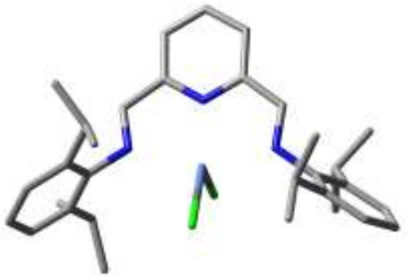


Figure ESI-8. Cyclic voltammetry of Ni(NNN)Br_2 recorded under 1 atm Ar and 1 atm CO_2 with incremental acetic acid concentrations (100 mV/s; 3 mm glassy carbon disc working electrode in a 0.1 M Bu_4NPF_6 acetonitrile supporting electrolyte).

Computational analysis

All theoretical calculations were carried out using density functional theory (DFT) with the B3LYP functional and acetonitrile polarizable continuum model (PCM)[3] as implemented in the Gaussian 09 B.01 program package.[4] The LANL08 relativistic effective core potential (RECP) basis set[5] was used for Ni and 6-311G(d,p)[6, 7] for C, H, N, Cl. A vibrational frequency analysis was carried out following geometry optimization to confirm the minimum-energy geometry and determine the zero-point energy for each species.[8]

Table ESI-1. Cartesian coordinates for $Ni(NNN)Cl_2$ (Energy = -2458.86597001 a.u.)



Tag	Symbol	X	Y	Z
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4	N	7.4374490	9.9084200	14.2649500
5	N	6.6690200	11.5464830	16.1370990
6	C	7.7470810	9.0957380	13.2496330
7	C	8.7071740	8.1031410	13.3737070
8	H	8.8925720	7.5118910	12.6535770
9	C	9.3907360	7.9949920	14.5765540
10	H	10.0654440	7.3335460	14.6804220
11	C	9.0928190	8.8493360	15.6275460
12	H	9.5614220	8.7959750	16.4515440
13	C	8.0760570	9.7945650	15.4310180
14	C	7.6126300	10.7403640	16.4442830
15	H	8.0030430	10.7563440	17.3102700
16	C	6.1139160	12.3090870	17.2248710
17	C	5.3858090	11.6345140	18.2264540
18	C	4.8999050	12.3895560	19.2848650
19	H	4.4231280	11.9562490	19.9827380
20	C	5.0940220	13.7628120	19.3483230
21	H	4.7623210	14.2590390	20.0885000
22	C	5.7748590	14.4065660	18.3255870
23	H	5.8752550	15.3505110	18.3521060
24	C	6.3132090	13.6901900	17.2594410
25	C	7.1929300	14.3831680	16.2273910
26	H	7.2047820	13.8167440	15.4033930
27	C	6.6770580	15.7618460	15.8395440
28	H	5.7649150	15.6829460	15.4886340
29	H	7.2592700	16.1466430	15.1524050
30	H	6.6748780	16.3435360	16.6283400
31	C	8.6263940	14.4616390	16.7675680
32	H	8.6296640	14.9581520	17.6133490
33	H	9.1963470	14.9210560	16.1168930

34	H	8.9688560	13.5556470	16.9187920
35	C	5.1005600	10.1386990	18.1784670
36	H	5.4175490	9.7947070	17.2944840
37	C	5.8587720	9.3943590	19.2695530
38	H	6.8206360	9.5407440	19.1571610
39	H	5.6654730	8.4364320	19.2060960
40	H	5.5782910	9.7276500	20.1469060
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42	H	3.2625170	10.1856400	19.1413760
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45	C	7.0518040	9.4488610	11.9975350
46	H	7.1952460	8.9543460	11.1997410
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48	C	5.7512930	10.9373990	10.7634330
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52	C	3.3633210	8.3465460	10.4774010
53	H	2.9410330	8.4892220	9.6038370
54	H	2.7884640	7.7758420	11.0276800
55	H	4.2324180	7.9113840	10.3520650
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58	H	1.6905150	9.7519050	12.0442600
59	H	1.7504530	10.5309160	10.6472520
60	C	4.0220910	11.1141750	9.1346950
61	H	3.1426420	10.9132870	8.8350880
62	C	4.8365620	11.9040290	8.3457410
63	H	4.5239330	12.2216260	7.5059580
64	C	6.1091480	12.2314710	8.7815760
65	H	6.6626180	12.7809160	8.2384000
66	C	6.5932810	11.7664900	10.0065230
67	C	7.9951420	12.1270320	10.4608270
68	H	8.0929490	11.8221330	11.4081090
69	C	8.2590040	13.6276980	10.4319390
70	H	8.2346200	13.9465790	9.5059680
71	H	9.1404960	13.8124640	10.8177350
72	H	7.5712190	14.0906820	10.9550680
73	C	9.0405090	11.3882560	9.6275150
74	H	8.9293520	10.4224820	9.7474850
75	H	9.9373950	11.6523490	9.9195450

76	H	8.9252650	11.6152530	8.6819700

Table ESI-2. Cartesian coordinates for Ni(NNN)Cl (Energy = -1999.07797253 a.u.)

Tag	Symbol	X	Y	Z
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3	C	0.8526760	2.0634860	0.1767130
4	C	-0.5428290	2.0818580	0.1654800
5	C	-1.2335920	0.8723650	0.1895250
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7	H	1.4121990	2.9897330	0.1585200
8	H	-1.0888970	3.0168250	0.1376500
9	C	-2.6852020	0.7345070	0.1719000
10	H	-3.3064470	1.6295500	0.1624030
11	C	1.3236280	-1.6853670	0.2559200
12	H	2.4048050	-1.8181660	0.2801130
13	C	-4.5993070	-0.6248040	0.1661740
14	C	-5.3275670	-0.4736510	1.3639140
15	C	-5.2268310	-1.0008800	-1.0405510
16	C	-6.7144900	-0.6552420	1.3113670
17	C	-6.6137490	-1.1636750	-1.0377580
18	C	-7.3571690	-0.9859990	0.1251760
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21	H	-8.4336470	-1.1146180	0.1072910
22	C	1.0147500	-4.0117990	0.2777880
23	C	1.4105170	-4.5817380	1.5047470
24	C	1.0537850	-4.7429060	-0.9284220
25	C	1.8994390	-5.8929380	1.4863690
26	C	1.5531050	-6.0465620	-0.8899410
27	C	1.9806240	-6.6185750	0.3044710
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29	H	1.6090470	-6.6240280	-1.8051250
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31	C	-4.4181700	-1.1821670	-2.3204800

32	H	-3.3765330	-1.3321640	-2.0239970
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41	H	-5.8488230	-2.3198490	-3.5372920
42	H	-4.1586260	-2.5639590	-3.9707180
43	C	-5.0607290	1.2373070	3.2209740
44	H	-4.8057560	2.0218580	2.5035070
45	H	-6.1368100	1.2941060	3.4095350
46	H	-4.5442230	1.4559750	4.1601850
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68	H	-0.5295520	-4.8159840	3.4812390
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70	H	0.3599300	-4.0006730	4.7758360
71	Ni	-1.5799600	-1.9625010	0.2806630
72	N	0.5032120	-2.6763240	0.2422790
73	N	-0.5826070	-0.3124590	0.2270200

74	N	-3.1795460	-0.4534500	0.1632280
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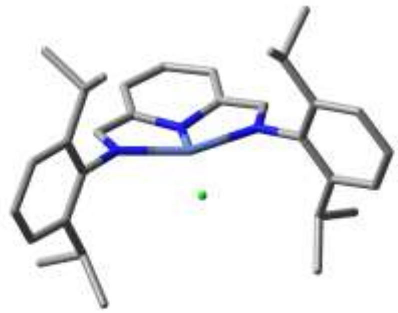
Table ESI-3. Cartesian coordinates for [Ni(NNN)Cl]$^-$ (Energy = -1999.18106236 a.u.)



Tag	Symbol	X	Y	Z
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4	C	-0.5147550	2.1804040	0.0273170
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8	H	-1.0624230	3.0956760	-0.1697020
9	C	-2.5942190	0.7612380	0.1558960
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25	C	1.5821000	-5.7877520	1.5074000
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27	C	1.6474440	-6.5086970	0.3207970
28	H	1.8804160	-6.2645450	2.4350110
29	H	1.3129550	-6.4742530	-1.7944670
30	H	1.9964170	-7.5357930	0.3252040

31	C	-4.1963040	-1.2201970	-2.3438010
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37	H	-4.1457230	0.9450860	-2.6583150
38	H	-3.8157160	-0.0043500	-4.1153350
39	C	-4.4986690	-2.4944960	-3.1501900
40	H	-4.3465790	-3.3911350	-2.5438770
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42	H	-3.8352460	-2.5560950	-4.0179880
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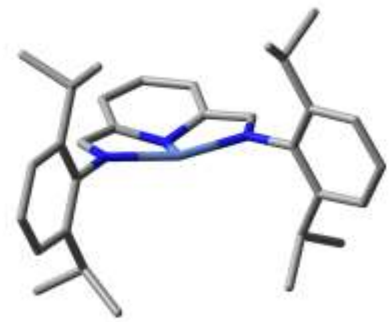
44	H	-4.5604800	1.7628200	2.4681220
45	H	-5.9094790	1.0702440	3.3779680
46	H	-4.3215250	1.2349310	4.1403650
47	C	-4.7493300	-1.4626620	3.7941560
48	H	-4.4739390	-2.4650100	3.4574080
49	H	-4.1850450	-1.2434060	4.7056420
50	H	-5.8105460	-1.4750560	4.0594570
51	C	0.4231490	-3.9355400	-2.2271540
52	H	-0.1045800	-3.0113160	-1.9830740
53	C	1.6741040	-3.5563600	-3.0440610
54	H	1.3896810	-3.0429350	-3.9679620
55	H	2.3318400	-2.8927020	-2.4769190
56	H	2.2487940	-4.4472550	-3.3175860
57	C	-0.5294510	-4.8062920	-3.0639610
58	H	-0.0499600	-5.7295000	-3.4025010
59	H	-1.4215150	-5.0782500	-2.4940440
60	H	-0.8515640	-4.2593940	-3.9550960
61	C	1.0776990	-3.7075600	2.8539780
62	H	0.5809010	-2.7553780	2.6621480
63	C	2.4855520	-3.3975920	3.3979810
64	H	3.0397360	-4.3173240	3.6104930
65	H	3.0681920	-2.8124940	2.6817200
66	H	2.4189420	-2.8245080	4.3280090
67	C	0.2393690	-4.4552170	3.9070090
68	H	-0.7658640	-4.6639020	3.5329350
69	H	0.6990160	-5.4062080	4.1918160
70	H	0.1457810	-3.8497020	4.8136020
71	Ni	-1.4511400	-1.7423020	0.4539570
72	N	0.3394820	-2.4910270	0.2791250

73	N	-0.5178470	-0.1656550	0.5916060
74	N	-2.9537720	-0.5327660	0.1819100
75	Cl	-2.6227870	-3.7106750	0.7372960

Table ESI-4. Cartesian coordinates for Ni(NNN) (Energy = -1538.75041850 a.u.)



Tag	Symbol	X	Y	Z
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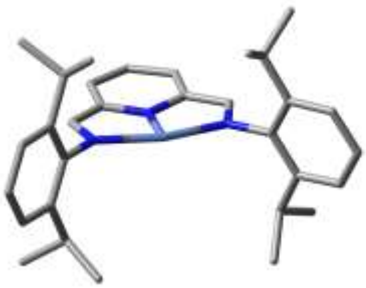
3	C	0.9624660	2.2457400	-0.2319320
4	C	-0.4366710	2.2707410	-0.1527720
5	C	-1.1307370	1.1115350	0.1792290
6	H	2.7023870	0.9587750	-0.3092160
7	H	1.5064790	3.1421470	-0.5017180
8	H	-0.9876900	3.1722120	-0.3961830
9	C	-2.5175630	0.8520730	0.0924630
10	H	-3.2690160	1.6320660	0.0228560
11	C	1.3577700	-1.4733040	0.1794490
12	H	2.4010340	-1.7708730	0.1478140
13	C	-4.2295020	-0.8180530	0.1987160
14	C	-4.8751570	-0.8637410	1.4553960
15	C	-4.9120780	-1.1764450	-0.9859850
16	C	-6.2181430	-1.2537860	1.4955720
17	C	-6.2556890	-1.5501090	-0.8910840
18	C	-6.9080820	-1.5890530	0.3366150
19	H	-6.7328960	-1.2925790	2.4492560
20	H	-6.8007890	-1.8149380	-1.7903070
21	H	-7.9506670	-1.8829270	0.3897160
22	C	0.6839550	-3.7680960	0.2811040
23	C	0.8555110	-4.3672760	1.5493320
24	C	0.7771420	-4.5304730	-0.9054620
25	C	1.1435500	-5.7353160	1.6013210
26	C	1.0756300	-5.8918170	-0.7980830
27	C	1.2595210	-6.4937640	0.4422680
28	H	1.2839030	-6.2132460	2.5646220
29	H	1.1654670	-6.4905440	-1.6976690

30	H	1.4901900	-7.5515940	0.5049070
31	C	-4.2255070	-1.1309750	-2.3463900
32	H	-3.1602940	-0.9781110	-2.1633020
33	C	-4.1560440	-0.5073740	2.7528860
34	H	-3.1125340	-0.3056770	2.5075080
35	C	-4.7293610	0.0580530	-3.1869150
36	H	-5.7966600	-0.0392550	-3.4087410
37	H	-4.5807200	1.0055940	-2.6625420
38	H	-4.1916350	0.1093170	-4.1384770
39	C	-4.3722380	-2.4529990	-3.1198520
40	H	-3.9980170	-3.2968230	-2.5339210
41	H	-5.4139110	-2.6598380	-3.3812030
42	H	-3.8015610	-2.4094550	-4.0520870
43	C	-4.7365970	0.7692010	3.3897770
44	H	-4.6849480	1.6144590	2.6984160
45	H	-5.7839890	0.6322090	3.6752180
46	H	-4.1763330	1.0339030	4.2915390
47	C	-4.1675490	-1.6778920	3.7532990
48	H	-3.7237960	-2.5753430	3.3140720
49	H	-3.5914970	-1.4183880	4.6463860
50	H	-5.1830210	-1.9272500	4.0740710
51	C	0.5864400	-3.8938780	-2.2775250
52	H	0.1978120	-2.8871510	-2.1122190
53	C	1.9279500	-3.7584870	-3.0234620
54	H	1.7827880	-3.2536440	-3.9833250
55	H	2.6487180	-3.1781680	-2.4416330
56	H	2.3699190	-4.7396310	-3.2232960
57	C	-0.4450330	-4.6479510	-3.1350310
58	H	-0.1112780	-5.6602840	-3.3798180
59	H	-1.4062940	-4.7256000	-2.6200590
60	H	-0.6089040	-4.1185640	-4.0781650
61	C	0.7387920	-3.5699860	2.8443580
62	H	0.4191950	-2.5604630	2.5814290
63	C	2.0978730	-3.4528860	3.5601600
64	H	2.4753080	-4.4347260	3.8617700
65	H	2.8472500	-2.9895820	2.9129360
66	H	2.0024890	-2.8395830	4.4611990
67	C	-0.3309560	-4.1535800	3.7855520
68	H	-1.3035040	-4.2111140	3.2894010
69	H	-0.0670650	-5.1587080	4.1268660
70	H	-0.4402850	-3.5210110	4.6712980
71	Ni	-1.3468990	-1.5817160	0.3503330

72	N	0.3722660	-2.3762630	0.1893380
73	N	-0.4190250	-0.0257330	0.5855070
74	N	-2.8526290	-0.4421630	0.1202570

Table ESI-5. Cartesian coordinates for [Ni(NNN)]$^{-}$ (Energy = -1538.85497864 a.u.)



Tag	Symbol	X	Y	Z
1	C	0.9024310	-0.2002010	-0.1389320
2	C	1.6373610	0.9843600	-0.2320140
3	C	0.9448200	2.2087300	-0.3086910
4	C	-0.4618920	2.2551730	-0.2531910
5	C	-1.1710150	1.0554700	-0.1589200
6	H	2.7230160	0.9669360	-0.2260560
7	H	1.5057840	3.1345930	-0.3776330
8	H	-0.9808530	3.2088960	-0.2633090
9	C	-2.5643990	0.8283110	-0.0178540
10	H	-3.3000930	1.6264260	-0.0378230
11	C	1.3448080	-1.5395180	0.0141370
12	H	2.3927050	-1.8227700	0.0060450
13	C	-4.3409810	-0.7269450	0.2518340
14	C	-4.9403110	-0.7673900	1.5366080
15	C	-5.1245340	-0.9724080	-0.9052070
16	C	-6.3082450	-1.0494800	1.6368870
17	C	-6.4876080	-1.2545160	-0.7528640
18	C	-7.0837510	-1.2917790	0.5053580
19	H	-6.7756610	-1.0789670	2.6160320
20	H	-7.0933930	-1.4470890	-1.6328530
21	H	-8.1423060	-1.5087220	0.6034360
22	C	0.7869800	-3.8415260	0.2601540
23	C	0.8847620	-4.4544520	1.5460350
24	C	1.0770260	-4.6011160	-0.9177960
25	C	1.2708240	-5.8074870	1.6310060
26	C	1.4613830	-5.9505160	-0.7821890
27	C	1.5624760	-6.5586920	0.4798610
28	H	1.3511080	-6.2783910	2.6066940
29	H	1.6830690	-6.5334130	-1.6717500

30	H	1.8622670	-7.5988970	0.5647430
31	C	-4.5102550	-0.9537420	-2.3011300
32	H	-3.4578810	-0.6938940	-2.1815510
33	C	-4.1259290	-0.5078790	2.7996660
34	H	-3.0804740	-0.4463160	2.4922920
35	C	-5.1560670	0.1123410	-3.2046840
36	H	-6.2141550	-0.0993340	-3.3880990
37	H	-5.0865020	1.1055660	-2.7525940
38	H	-4.6515690	0.1468440	-4.1754110
39	C	-4.5660790	-2.3440740	-2.9607840
40	H	-4.0521140	-3.0878900	-2.3455070
41	H	-5.5976130	-2.6798420	-3.1056040
42	H	-4.0804300	-2.3237430	-3.9415380
43	C	-4.5040290	0.8353330	3.4521850
44	H	-4.3686140	1.6641780	2.7523710
45	H	-5.5487010	0.8387450	3.7800050
46	H	-3.8776770	1.0271950	4.3292950
47	C	-4.2393620	-1.6606490	3.8132830
48	H	-3.9407110	-2.6110110	3.3625150
49	H	-3.5877590	-1.4764420	4.6730810
50	H	-5.2601060	-1.7734040	4.1910120
51	C	0.9659470	-3.9886720	-2.3121970
52	H	0.5588900	-2.9851290	-2.1876680
53	C	2.3429090	-3.8527230	-2.9890670
54	H	2.2447350	-3.3678730	-3.9656940
55	H	3.0219920	-3.2502100	-2.3801080
56	H	2.8095500	-4.8305940	-3.1473510
57	C	-0.0116850	-4.7691520	-3.2098100
58	H	0.3368750	-5.7881990	-3.4036390
59	H	-1.0008940	-4.8336590	-2.7480280
60	H	-0.1229310	-4.2682990	-4.1766090
61	C	0.5922330	-3.6730000	2.8237160
62	H	0.2525300	-2.6828730	2.5157510
63	C	1.8573150	-3.4915390	3.6830270
64	H	2.2483210	-4.4540330	4.0284650
65	H	2.6486190	-2.9920160	3.1175030
66	H	1.6381580	-2.8837890	4.5667910
67	C	-0.5429480	-4.3120870	3.6436270
68	H	-1.4551500	-4.3988810	3.0466020
69	H	-0.2755160	-5.3126320	3.9974960
70	H	-0.7719500	-3.7003200	4.5218780
71	Ni	-1.4378570	-1.7218230	0.1298410

72	N	0.3684350	-2.4813180	0.1520120
73	N	-0.4691360	-0.1257470	-0.1698530
74	N	-2.9466290	-0.4726370	0.1236010

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