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Electrocatalytic CO_2 Reduction with Nickel Complexes Supported by Tunable Bipyridyl-*N*-Heterocyclic Carbene Donors: Understanding Redox-Active Macrocycles

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-Supporting Information-

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Materials and Methods. All synthetic manipulations were performed under N_2 atmosphere using standard Schlenk techniques, unless otherwise noted. Acetonitrile was distilled over CaH_2 and stored over molecular sieves before use. Water was purified with a Barnstead NANOpure Diamond water purification system. All other chemicals were reagent or ACS grade, purchased from commercial vendors, and used without further purification. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were acquired with a Waters SYNAPT HDMS Q-TOF mass spectrometer. ^1H and ^{13}C NMR spectra were obtained using a Bruker Advance DRX-500 spectrometer operating at 500 MHz (^1H) or 125 MHz (^{13}C). Spectra were referenced to residual protiated solvent peaks and chemical shifts are reported in ppm.

Electrochemical Measurements. Electrochemistry was performed with a Bioanalytical Systems, Inc. (BASi) Epsilon potentiostat. Cyclic voltammetry was carried out in a three-electrode cell equipped with a glassy carbon disc working electrode (3 mm dia.), a platinum wire counter electrode, and a silver wire quasi-reference electrode that was referenced at the end of experiments by addition of ferrocene as an internal standard. Electrochemistry was conducted in acetonitrile (CH_3CN) solutions containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. Solutions for cyclic voltammetry were degassed with N_2 or CO_2 thoroughly before collecting data.

Controlled potential electrolyses (CPE) were performed in a 3-neck pear-shaped glass cell with a glassy carbon rod (2 mm diameter, type 2, Alfa Aesar) working electrode, a silver wire quasi-reference electrode, and a platinum mesh (2.5 cm^2 area, 150 mesh) counter electrode that was housed in an isolation chamber, separated from the other electrodes with a fine glass frit. Solutions were degassed with CO_2 for 30 min before collecting data. Applied potentials in CPE experiments were determined by cyclic voltammetry. Constant stirring was maintained during electrolysis. Headspace gases in the airtight vessel employed for electrolyses were quantified by gas chromatographic analysis using an Agilent 7890B Gas Chromatograph and an Agilent PorapakQ (6' long, 1/8" O.D.) column. Integrated gas peaks were quantified with calibration curves generated from known standards purchased from BuyCalGas.com. CO was measured at an FID detector equipped with a methanizer, while H_2 was quantified at the TCD detector. Faradaic efficiencies were determined from the experimental amount of product

formed during electrolysis divided by the theoretical amount of product possible based on accumulated charge passed and the electron stoichiometry of the reaction × 100.

Kinetics by cyclic voltammetry. The peak catalytic current for an electrocatalytic reaction involving heterogeneous electron transfers at the electrode surface is described by equation 1:[1]

$$i_{cat} = n_{cat}FA[cat](Dk_{cat}[S]^{y})^{1/2} \quad (1)$$

where n_{cat} is the number of electrons transferred in the catalytic process, F is the Faraday constant, A is the electrode surface area, [cat] is the molar concentration of catalyst, D is its diffusion coefficient, k_{cat} is the catalytic rate constant, and [S] is the molar concentration of dissolved substrate. Reaction orders with respect to catalyst, carbon dioxide, and water (as an added proton source) were determined from cyclic voltammetry studies (Figures S5-S8) using equation 1.

A commonly employed electroanalytical equation (eq 2) was used to estimate the turnover frequency (TOF) of **2-Ni** and **3-Ni**. From eq 2, estimated TOFs were calculated from the ratio of $(i_{cat}/i_p)^2$, in which i_p and i_{cat} are designated as peak current with catalyst under N_2 and CO_2, respectively. As shown, the quantity $(i_{cat}/i_p)^2$ is proportional to k_{cat} as well as the TOF.[1b,2]

$$\text{TOF} = k_{cat}[CO_2] = \frac{Fvn_p^3}{RT}\left(\frac{0.4463}{n_{cat}}\right)^2\left(\frac{i_{cat}}{i_p}\right)^2 \quad (2)$$

In this equation, n_{cat} is the number of electrons transferred in the catalytic process, here n_{cat} = 2 for the conversion of CO_2 to CO (or H_2O to H_2), F is the Faraday constant, A is the electrode surface area (0.071 cm^2), [cat] is the molar concentration of catalyst, D is the diffusion coefficient (cm^2 s^{-1}), k_{cat} is the rate constant of the catalytic reaction, and $[CO_2]$ is the concentration of dissolved CO_2. The concentration of dissolved CO_2 in CH_3CN is 0.28 M under CO_2-saturation conditions at 1 atm.[3] Steady state conditions are required for the application of eq 2, which can often be achieved at fast scan rates.[1b] Linear sweep voltammetry of **2-Ni** and **3-Ni** was conducted in CH_3CN/2% H_2O under CO_2 at increasing scan rates (Figures S9, S10) in order to reach scan rate independent TOFs.

X-ray Crystallography. Single crystals were coated with Paratone-N hydrocarbon oil and mounted on a Kapton loop. The specified temperature (Table S1) was maintained with an Oxford Cryostream 700 during data collection at the University of Mississippi, Department of Chemistry and Biochemistry, X-ray Crystallography Facility. Samples were irradiated with Mo-Kα radiation (λ = 0.71073 Å) using a Bruker Smart APEX II diffractometer equipped with a Microfocus Sealed Source (Incoatec IμS) and APEX-II detector. The Bruker APEX2 v. 2009.1 software package was used to integrate raw data which were corrected for Lorentz and polarization effects.[4] A semi-empirical absorption correction (SADABS) was applied.[5] The structure was solved using direct methods and refined by least-squares refinement on F^2 and standard difference Fourier techniques using SHELXL.[6] Thermal parameters for all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at ideal positions.

Computational Details. Density functional theory (DFT) calculations were run with Gaussian 09 Rev. E 01.[7] Geometry optimizations were carried out at the unrestricted ωB97X-D[8] level of theory in solution (acetonitrile, dielectric constant, ε = 35.688) using the SMD approach.[9] The ωB97X-D functional is a range-separated hybrid (RSH) functional that separates the Coulomb electron-electron interaction into long-range and short-range components. This functional contains 22% of exact-exchange for the short range and 100% of Hartree-Fock (HF) exchange for long-range electron-electron interactions, and has been parametrized to take into account atom-atom dispersion interactions (i.e. non-covalent interactions). The Def2-TZVPP basis set was used for all atoms.[10,11] Exchange correlation integrals were evaluated with a quadrature grid of 99 radial shells and 590 angular points per shell. Minimum energy and transition state geometries were confirmed as such through analytical frequency calculations, having no imaginary frequencies and a single imaginary frequency, respectively. Transition states were further characterized through IRC calculations and subsequent geometry optimizations.[12,13] All computed structures were confirmed to have no internal instabilities by using the "stable=opt" and "scf=qc") keywords.

All reported redox potentials were calculated using the direct approach in which free energies of the reactants and products are calculated directly in solution (acetonitrile using the SMD approach), rather than by a thermodynamic cycle involving gas phase energies.[14-16] All

potential reported herein (in V) are versus the $Fc^{+/0}$ redox couple and were obtained using the following expressions:

$$A + Fc \leftrightharpoons A^- + Fc^+ \quad (3)$$

$$\Delta G^*_{red,soln} = G^*_{red,soln}(A^-) + G^*_{red,soln}(Fc^+) - G^*_{red,soln}(A) - G^*_{red,soln}(Fc) \quad (4)$$

$$E^0 = -\frac{\Delta G^*_{red,soln}}{nF} \quad (5)$$

where the "$*$" superscripts denote that the quantities were computed at a standard state of 1 M. In equation 4, $G^*_{red,soln}(A^-)$ is the free energy in solution of the one-electron reduced species, $G^*_{red,soln}(Fc^+)$ is the free energy in solution of ferrocenium, $G^*_{red,soln}(A)$ is the free energy in solution of the non-reduced species, and $G^*_{red,soln}(Fc)$ is the free energy in solution of ferrocene. Based on the free energy change, the reduction potentials were calculated according to equation 5 where n is the number of electrons involved in the process (in this case $n = 1$ for a one-electron process) and F is the Faraday constant. All computed free energies include the zero-point vibrational energy corrections as well as thermal corrections and entropies computed by standard statistical thermodynamic methods at 298.15 K.

Synthetic Procedures. The ligand precursors of **L1**[17] and di(1*H*-imidazol-1-yl)methane[18] and 1,2-di(1H-imidazol-1-yl)ethane[19] were prepared according to literature procedures.

L2: A mixture of 6,6'-bis(bromomethyl)-2,2'-bipyridyl (1.0 mmol, 340 mg) and 1-(2-(1*H*-imidazol-1-yl)ethyl)-1*H*-imidazole (1.0 mmol, 162 mg) was stirred at reflux in 50 mL of CH_3CN-H_2O solution (1/1, v/v) for 2 days. The solvent was removed and water containing NH_4PF_6 (8.0 mmol, 1.3 g) was added. The resulting solution was stirred at reflux for another 3 h before the solvent was removed under reduced pressure. The crude solid was washed with dichloromethane (3 × 10 mL) followed by water (3 × 15 mL), and dried to give pure product as a white solid. Yield: 348 mg, 55%. ^{1}H NMR (500 MHz, CD_3CN): δ = 4.77 (s, 4H), 5.57 (s, 4H), 7.50~7.58 (m, 6 H), 7.88 (d, 2 H, J = 8.0 Hz), 8.02 (d, 2 H, J = 8.0 Hz), 8.64 (t, 2 H, J = 8.0 Hz), 8.64 (s, 2 Hz). ^{13}C NMR (125 MHz, CD_3CN): δ = 48.54, 53.44, 122.28, 122.42, 122.71, 124.40, 137.14, 138.43, 152.73, 155.57. HR-ESI-MS: *m/z* calc. for

[**L2** – $2PF_6$]$^{2+}$, 172.0869, found, 172.0888; *m/z* calc. for [**L2** – PF_6]$^{+}$, 489.1386, found, 489.1380.

L3: A mixture of 6,6'-bis(bromomethyl)-2,2'-bipyridyl (1.0 mmol, 340 mg) and di(1*H*-imidazol-1-yl)methane (1.0 mmol, 148 mg) was stirred at reflux in 50 mL of CH_3CN-H_2O solution (3/1, v/v) for 7 days. The solvent was removed and water containing NH_4PF_6 (8.0 mmol, 1.3 g) was added. The resulting solution was stirred at reflux for another 3 h before the solvent was removed under reduced pressure. The crude solid was washed with dichloromethane (3 × 10 mL) followed by water (3 × 15 mL), and dried to give pure product as a white solid. Yield: 258 mg, 41.6%. ^{1}H NMR (500 MHz, CD_3CN): δ = 5.67 (s, 4 H), 6.63 (s, 2 H), 7.57 (m, 4 H), 7.76 (s, 2 H), 7.89 (d, 2 H, *J* = 8.0 Hz), 8.01 (t, 2 H, *J* = 8.0 Hz), 9.28 (s, 2 Hz). ^{13}C NMR (125 MHz, CD_3CN): δ = 53.51, 59.64 122.10, 122.35, 123.08, 124.39, 138.09, 138.60, 152.16, 155.94. HR-ESI-MS: *m/z* calc. for [**L3** – $2PF_6$]$^{2+}$, 165.0791, found, 165.0789; *m/z* calc. for [**L3** – PF_6]$^{+}$, 475.1224, found, 475.1202.

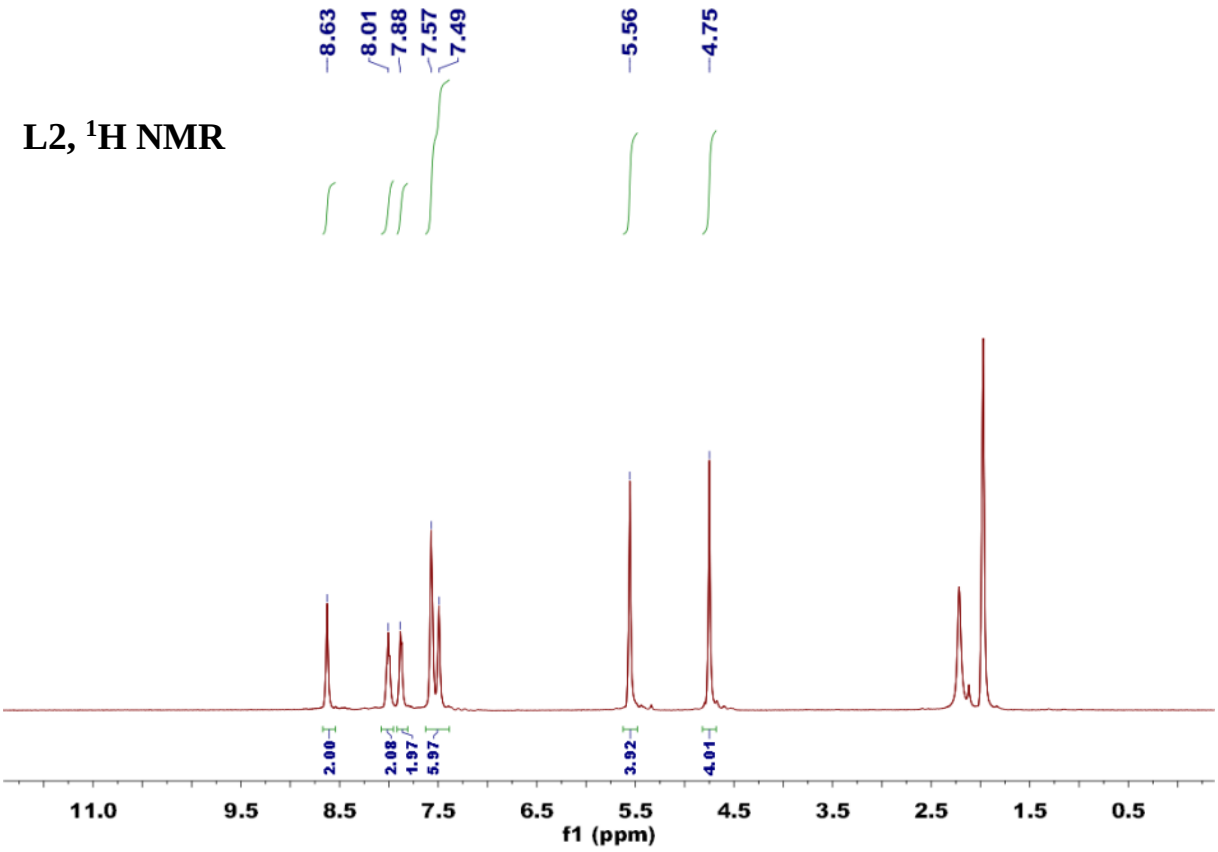
1-Ni: A solution of **L1** (191 mg, 0.3 mmol) and excess Ag_2O (556 mg, 2.4 mmol) in 20 mL of anhydrous CH_3CN was stirred at room temperature for 12 h, then the fine precipitate was removed by centrifugation. Ni(DME)Cl_2 (66 mg, 0.3 mmol) was added to the light yellow filtrate, and the mixture was stirred for 12 h. After which, the resulting solution was centrifuged, and $NaPF_6$ (50 mg, 0.3 mmol) was added to the filtrate. The resulting solution was stirred for 12 h and centrifuged before the filtrate was evaporated to obtain a yellow solid (156 mg, 75%). Single crystals were obtained by diffusing diethyl ether slowly into a concentrated solution of **1-Ni** in CH_3CN. ^{1}H NMR (500 MHz, CD_3CN): δ = 3.37 (s, 6 H), 5.68~5.81 (m, 4 H), 7.32 (s, 2 H), 7.51 (s, 2 H), 7.87 (s, 2 H), 8.34 (s, 4 H). ^{13}C NMR (125 MHz, CD_3CN): δ = 29.90, 37.28, 53.10, 122.40, 123.68, 125.15, 126.53, 142.14, 153.47, 153.86, 155.57. HR-ESI-MS: *m/z* calc. for [**1-Ni** – PF_6]$^{+}$, 547.0739, found, 547.0743; m/z calc. for [**1-Ni** – $2PF_6$]$^{2+}$, 201.0546, found, 201.0584.

2-Ni: The synthesis of **2-Ni** followed the procedure of **1-Ni**, starting with 248 mg (0.4 mmol) of **L2**, 742 mg (3.2 mmol) of Ag_2O, 88 mg (0.4 mmol) of Ni(DME)Cl_2, and 67 mg (0.4 mmol) of $NaPF_6$ to yield a yellow product (216 mg, 78%). Single crystals were obtained by diffusing diethyl ether slowly into a concentrated solution of **2-Ni** in CH_3CN. ^{1}H NMR (500 MHz, CD_3CN): δ = 4.54 (s, 4 H), 5.52 (s, 4 H), 7.24 (s, 2 H), 7.48 (s, 2 H), 7.75 (q, 2 H,

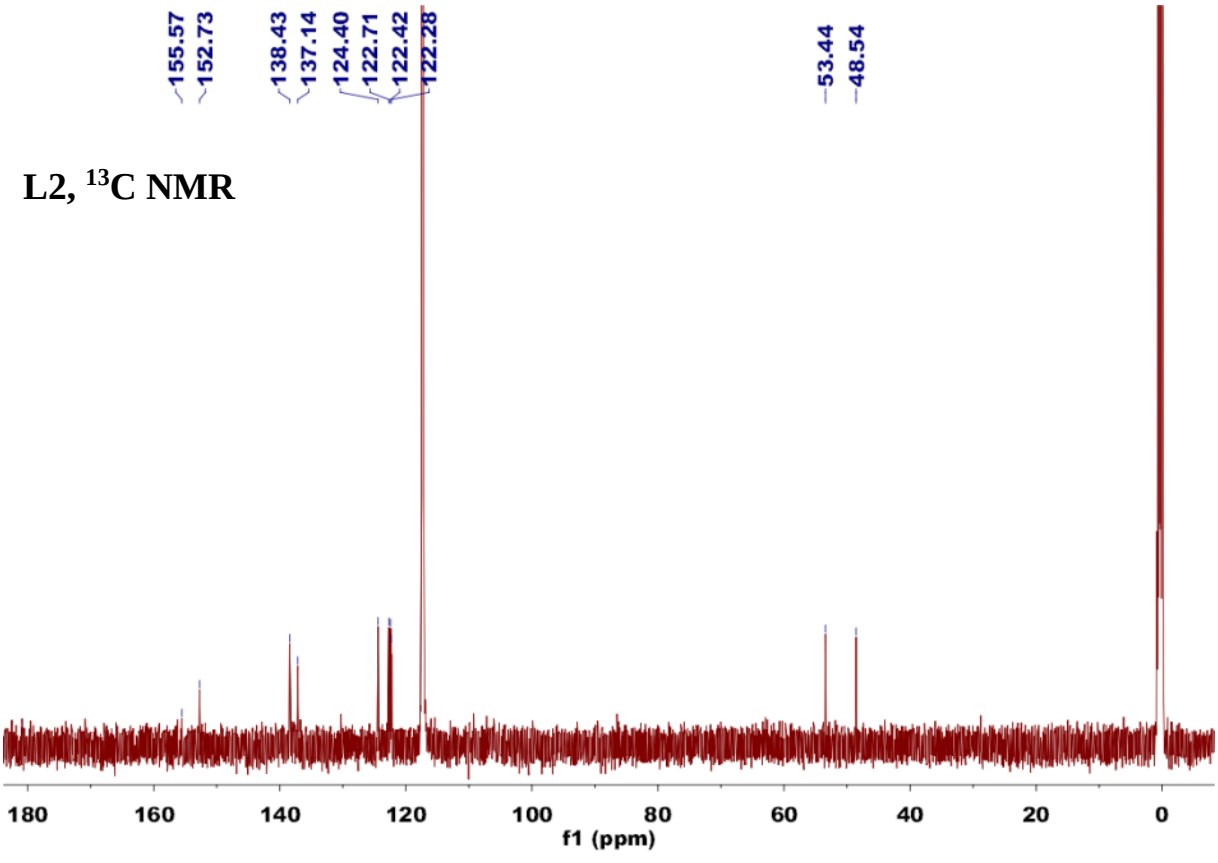
J = 6.5 Hz), 8.28 (s, 4 H). ^{13}C NMR (125 MHz, CD_3CN): δ = 29.90, 49.49, 52.86, 122.30, 123.78, 124.57, 125.47, 142.63, 149.19, 154.74, 155.97. HR-ESI-MS: *m/z* calc. for [**2-Ni** – PF_6]$^+$, 545.0577, found, 545.0583; m/z calc. for [**2-Ni** – $2PF_6$]$^{2+}$, 200.0468, found, 200.0497.

3-Ni: The synthesis of **3-Ni** followed the procedure of **1-Ni**, starting with 254 mg (0.4 mmol) of **L3**, 742 mg (3.2 mmol) of Ag_2O, 88 mg (0.4 mmol) of $Ni(DME)Cl_2$, and 67 mg (0.4 mmol) of $NaPF_6$ to yield a yellow product (190 mg, 70%). ^{1}H NMR (500 MHz, CD_3CN): δ = 5.64 (s, 4 H), 6.23 (s, 2 H), 7.58 (s, 2 H), 7.63 (s, 2 H), 7.87 (d, 2 H, J = 9.0 Hz), 8.41 (s, 4 H). ^{13}C NMR (125 MHz, CD_3CN): δ = 55.76, 62.27, 121.75, 122.70, 124.34, 126.90, 142.52, 153.76, 155.66. HR-ESI-MS: *m/z* calc. for [**3-Ni** – PF_6]$^+$, 531.0421, found, 531.0411; m/z calc. for [**3-Ni** – $2PF_6$]$^{2+}$, 193.0389, found, 193.0369. Synthesis of [**3-Ni**]$(ClO_4)_2$ was performed in the same manner, but from the perchlorate salt of **L3** and addition of 1 equivalent of $NaClO_4$ in the last step. Single crystals were obtained by diffusing diethyl ether slowly into a concentrated solution of [**3-Ni**]$(ClO_4)_2$ in CH_3CN.

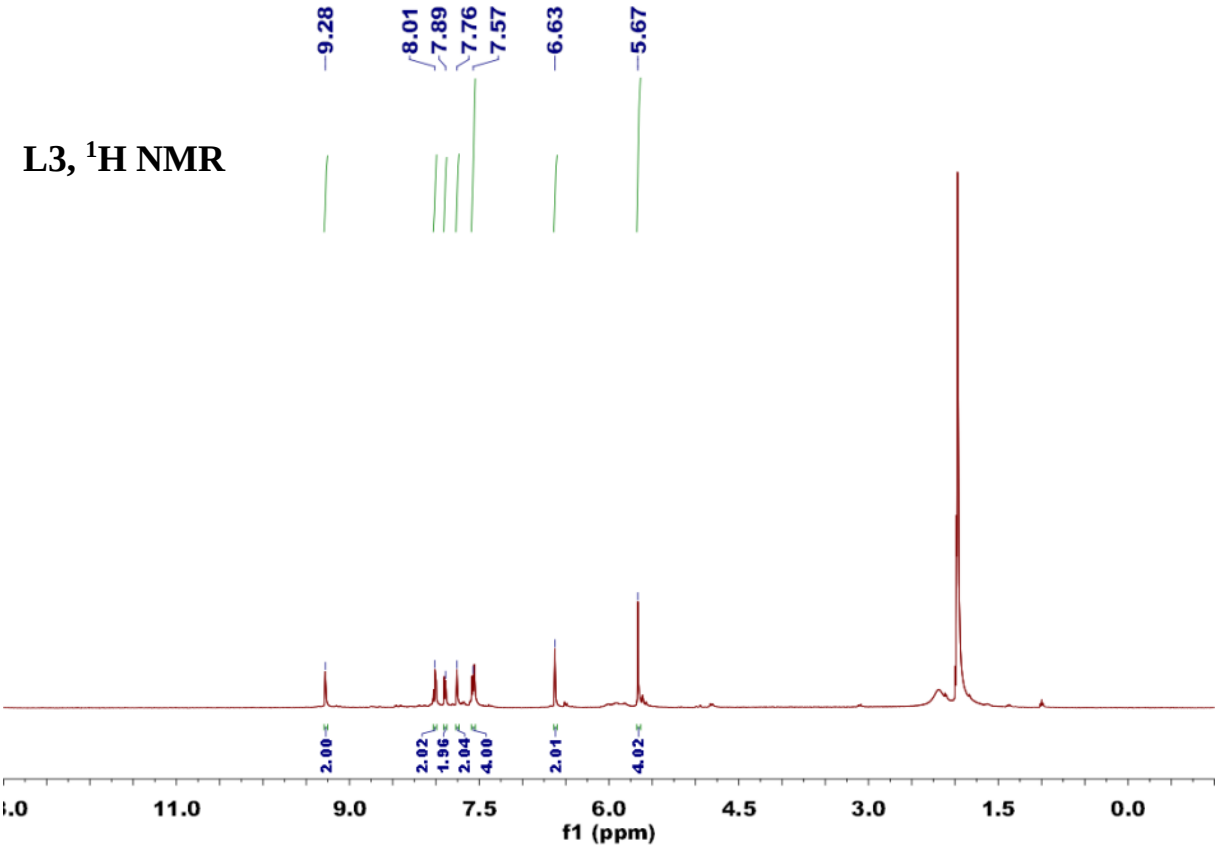
L2, ^{1}H NMR



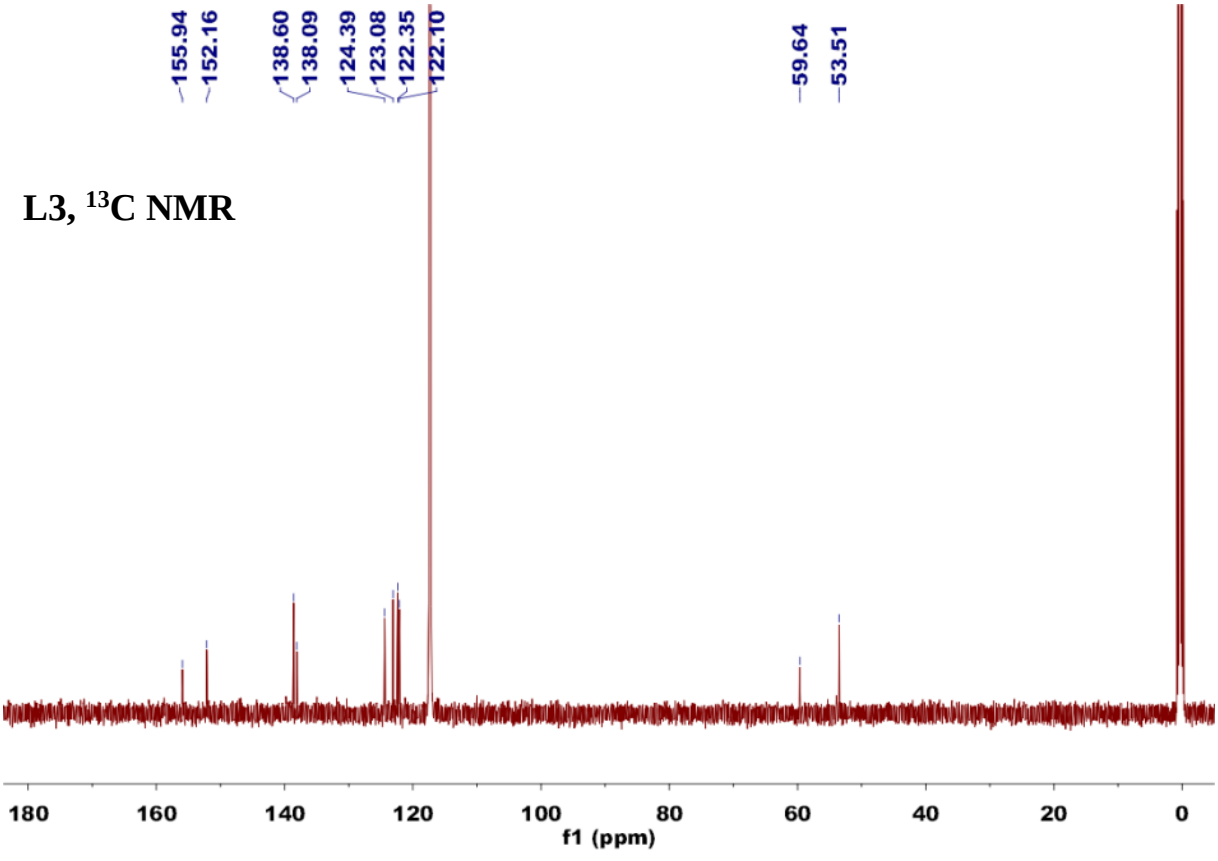
L2, ^{13}C NMR



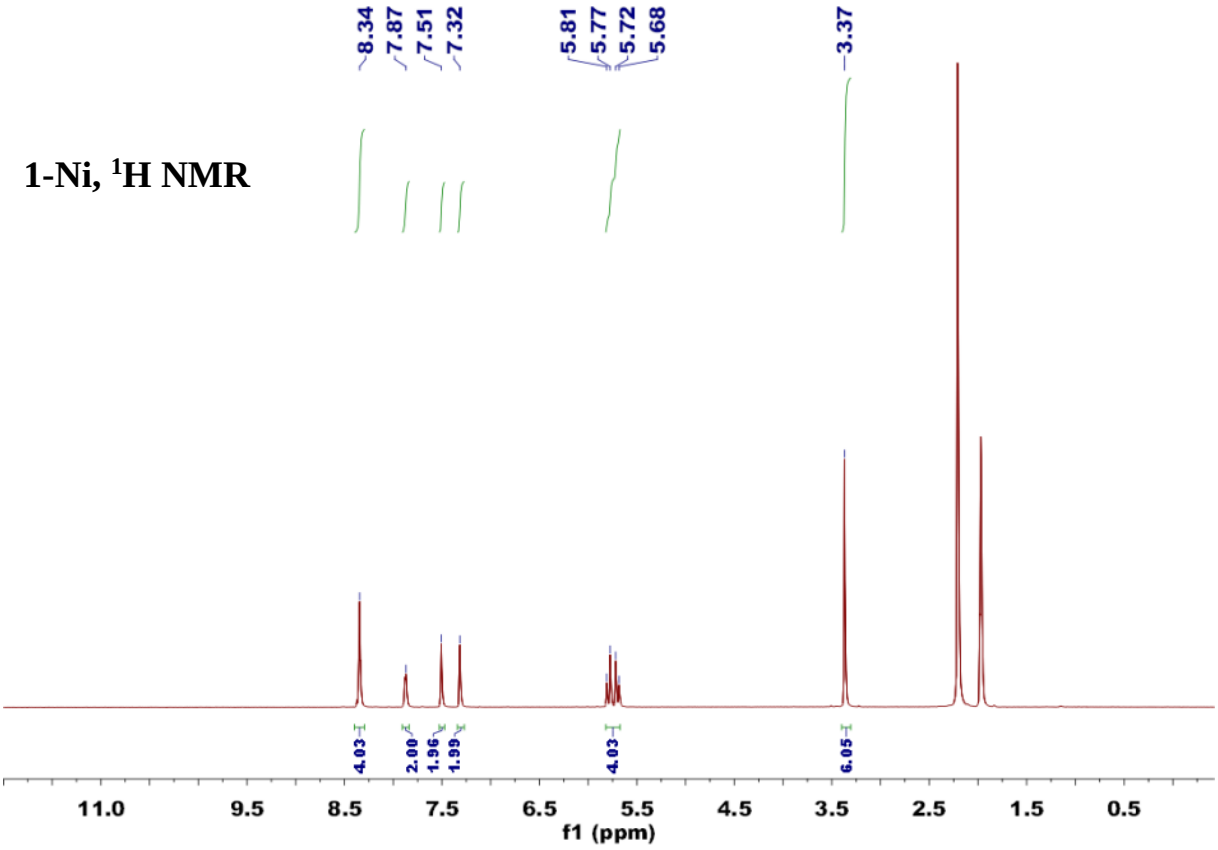
L3, ^{1}H NMR



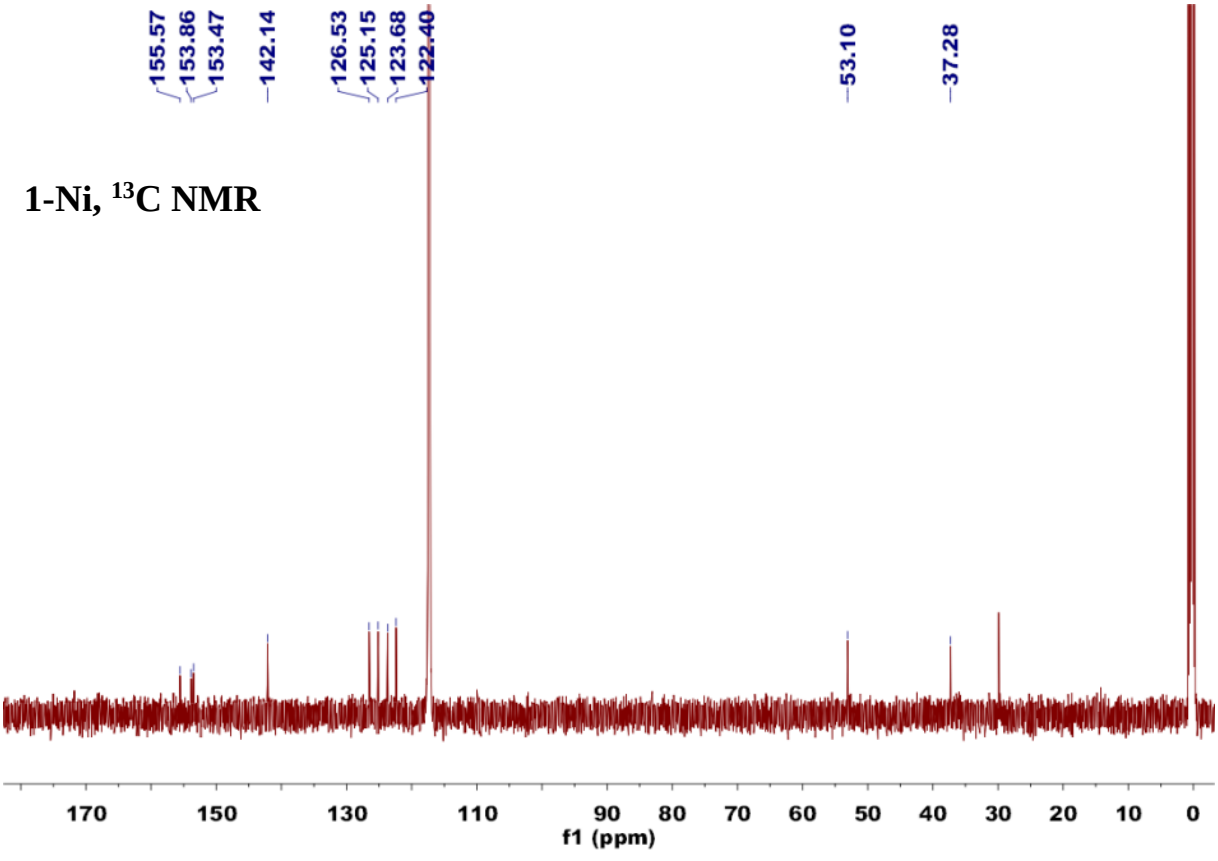
L3, ^{13}C NMR



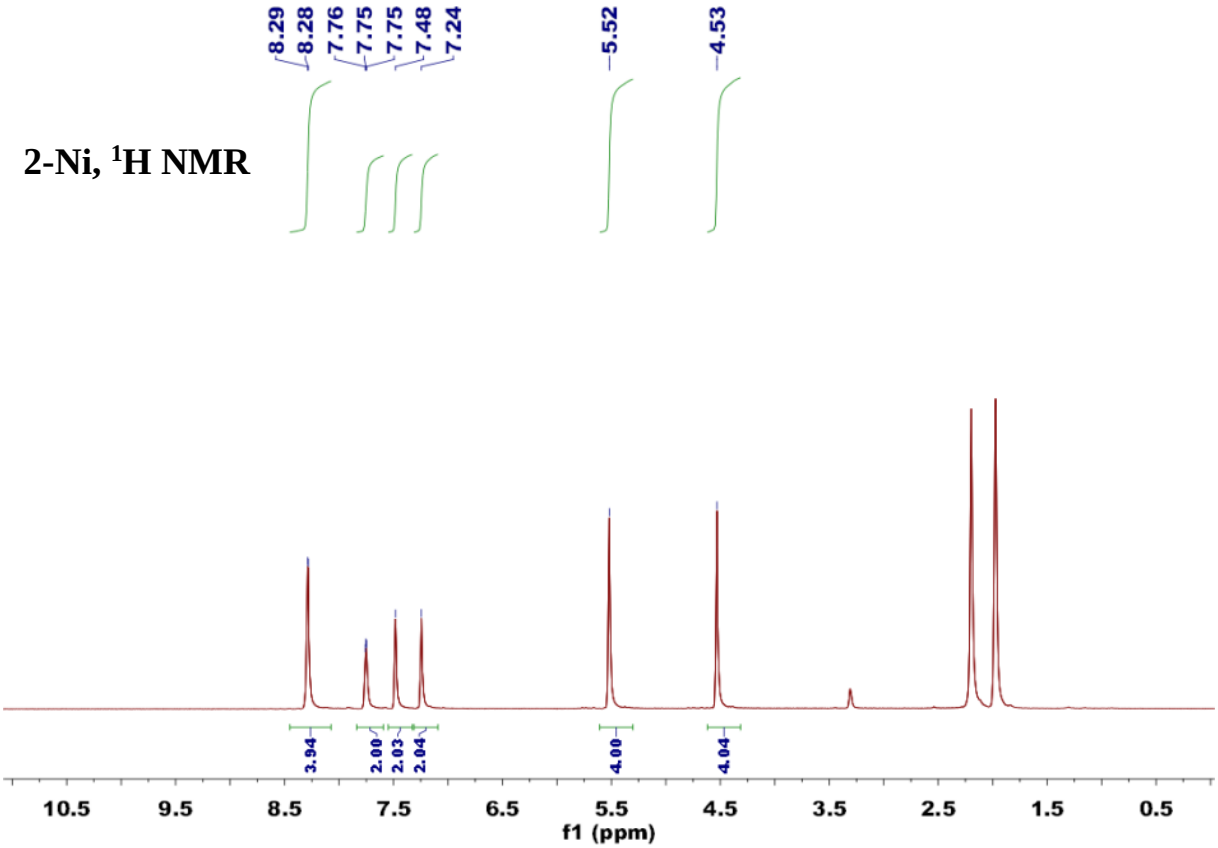
1-Ni, ^{1}H NMR



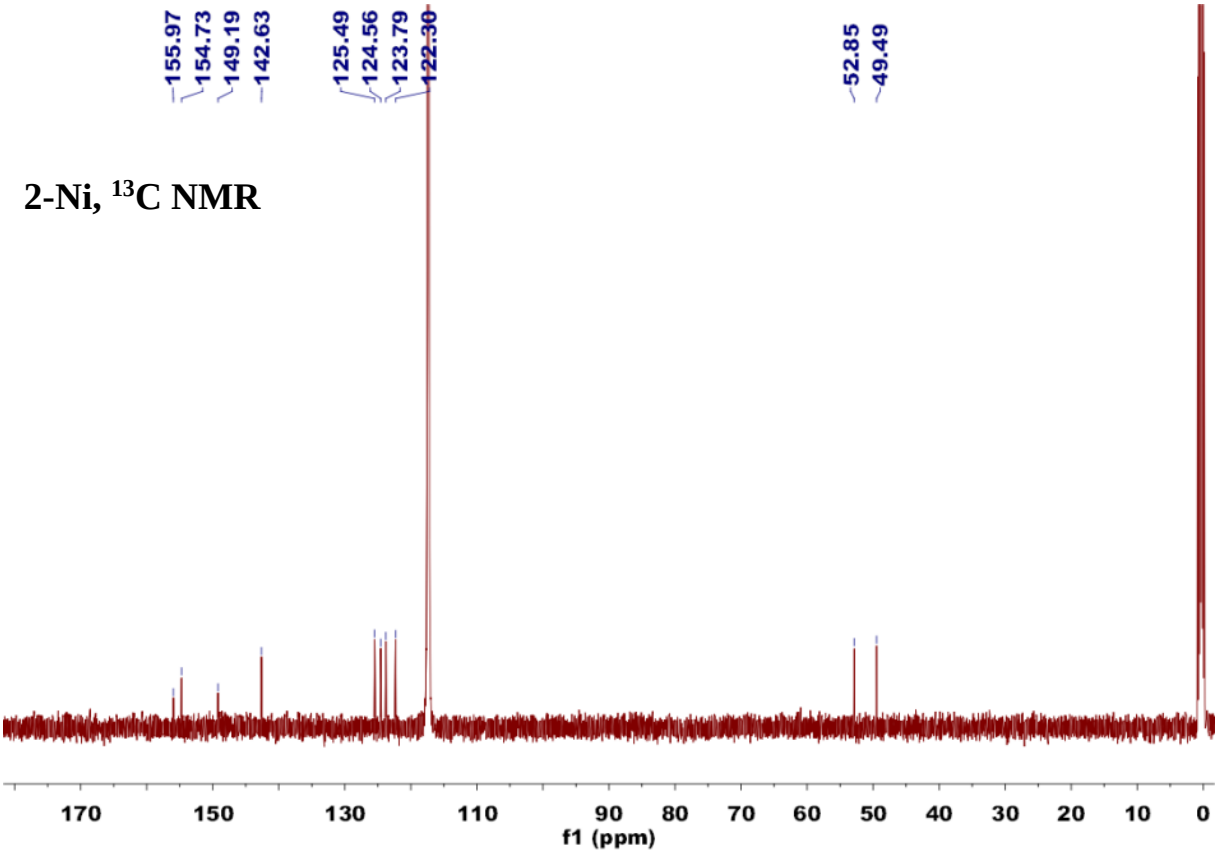
1-Ni, ^{13}C NMR



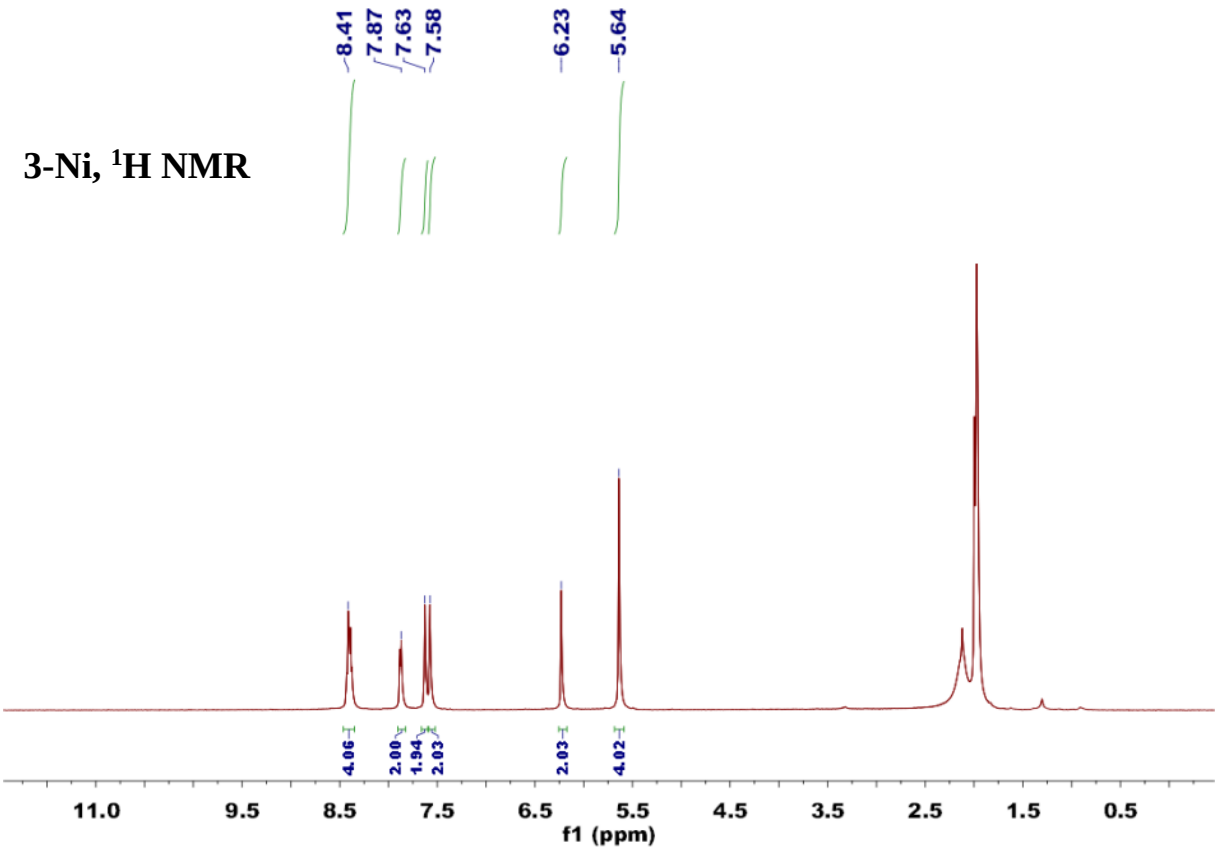
2-Ni, ^{1}H NMR



2-Ni, ^{13}C NMR



3-Ni, ^{1}H NMR



3-Ni, ^{13}C NMR

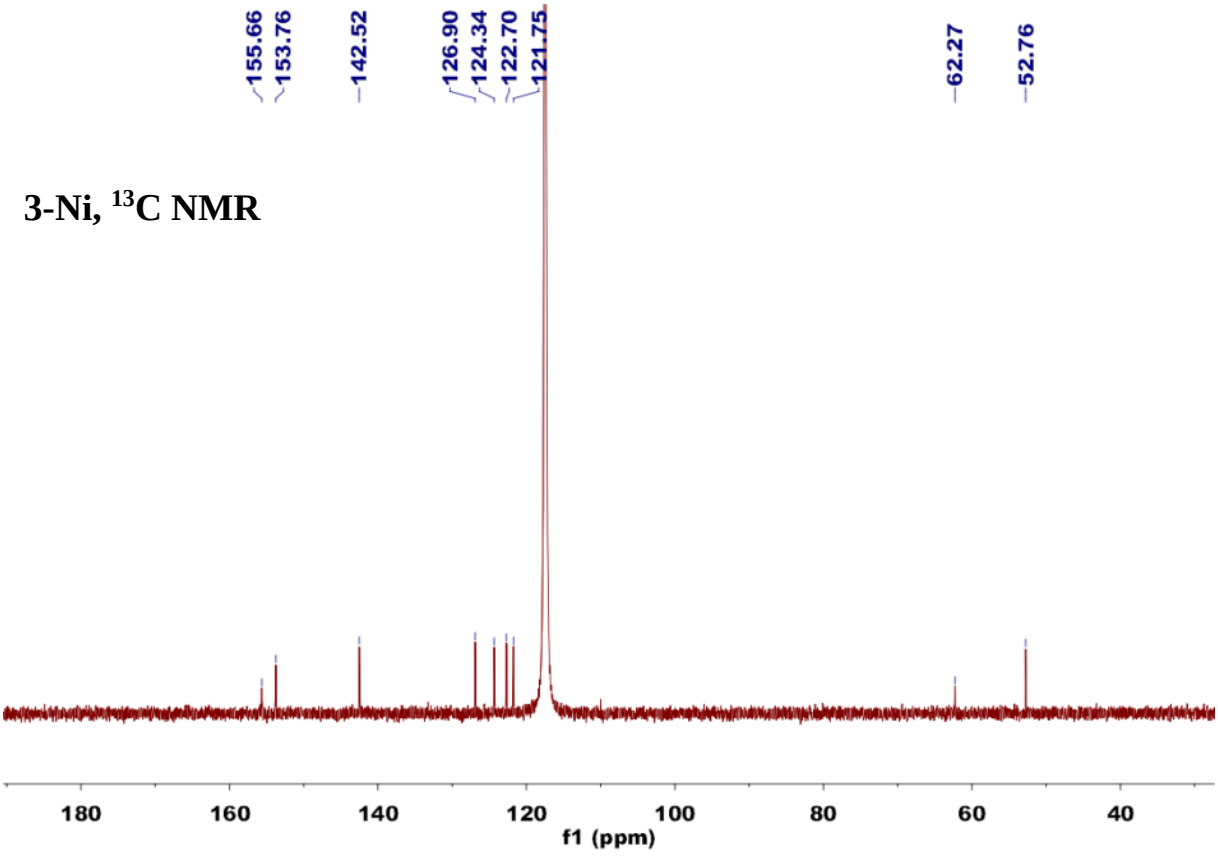


Table S1. Crystallographic Data for Complexes **1-Ni**, **2-Ni**, and **3-Ni**.

Complex	**1-Ni**	**2-Ni**	**3-Ni (ClO_4 salt)**
CCDC deposition #	1811793	1811794	1811795
Empirical Formula	$C_{22}H_{23}F_{12}N_7NiP_2$	$C_{22}H_{21}F_{12}N_7NiP_2$	$C_{19}H_{16}Cl_2N_6NiO_8$
Formula Weight	734.12 g/mol	732.11 g/mol	585.99 g/mol
T (K)	100(2)	100(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Triclinic	Monoclinic
Space Group	C2/c	P-1	C2/m
a (Å)	37.426(4)	9.9845(2)	13.978(9)
b (Å)	8.0756(8)	12.1671(3)	12.184(8)
c (Å)	23.616(3)	12.4094(3)	13.374(9)
α (°)	90	69.4740(10)	90
β (°)	128.460(5)	70.9980(10)	109.402(11)
γ (°)	90	83.8040(10)	90
V (Å^3)	5589.1(10)	1334.85(5)	2148(2)
Z	8	2	4
ρ_{calc} (g/cm^3)	1.745	1.821	1.812
μ (mm^{-1})	0.918	0.961	1.216
F(000)	2960	736	1192
θ range for data collectn	1.39 to 25.35°	1.79 to 25.44°	1.61 to 25.39°
Index ranges	-44 ≤ h ≤ 44 -9 ≤ k ≤ 9 -28 ≤ l ≤ 27	-11 ≤ h ≤ 12 -14 ≤ k ≤ 14 -14 ≤ l ≤ 15	-16 ≤ h ≤ 16 -14 ≤ k ≤ 14 -16 ≤ l ≤ 15
Reflections collected	43232	23990	7489
Independent reflections	5050 [R(int) = 0.0411]	4634 [R(int) = 0.0168]	2050 [R(int) = 0.0202]
Completeness to θ = 25.00	100.0 %	94.2 %	99.5%
Max. and min. transmission	0.8822 and 0.8377	0.9101 and 0.7615	0.8881 to 0.7117
data/restr/params	5050 / 0 / 402	4634 / 6 / 432	2050 / 0 / 175
GOF on F^2	1.045	1.079	1.059
Final R indices [I > 2σ(I)]	R1 = 0.0369, wR2 = 0.0861	R1 = 0.0234, wR2 = 0.0561	R1 = 0.0479, wR2 = 0.1298
R indices (all data)	R1 = 0.0440, wR2 = 0.0904	R1 = 0.0251, wR2 = 0.0570	R1 = 0.0571, wR2 = 0.1398
Largest diff. peak and hole (e Å^{-3})	0.961 and -0.798	0.272 and -0.323	0.701 and -0.516

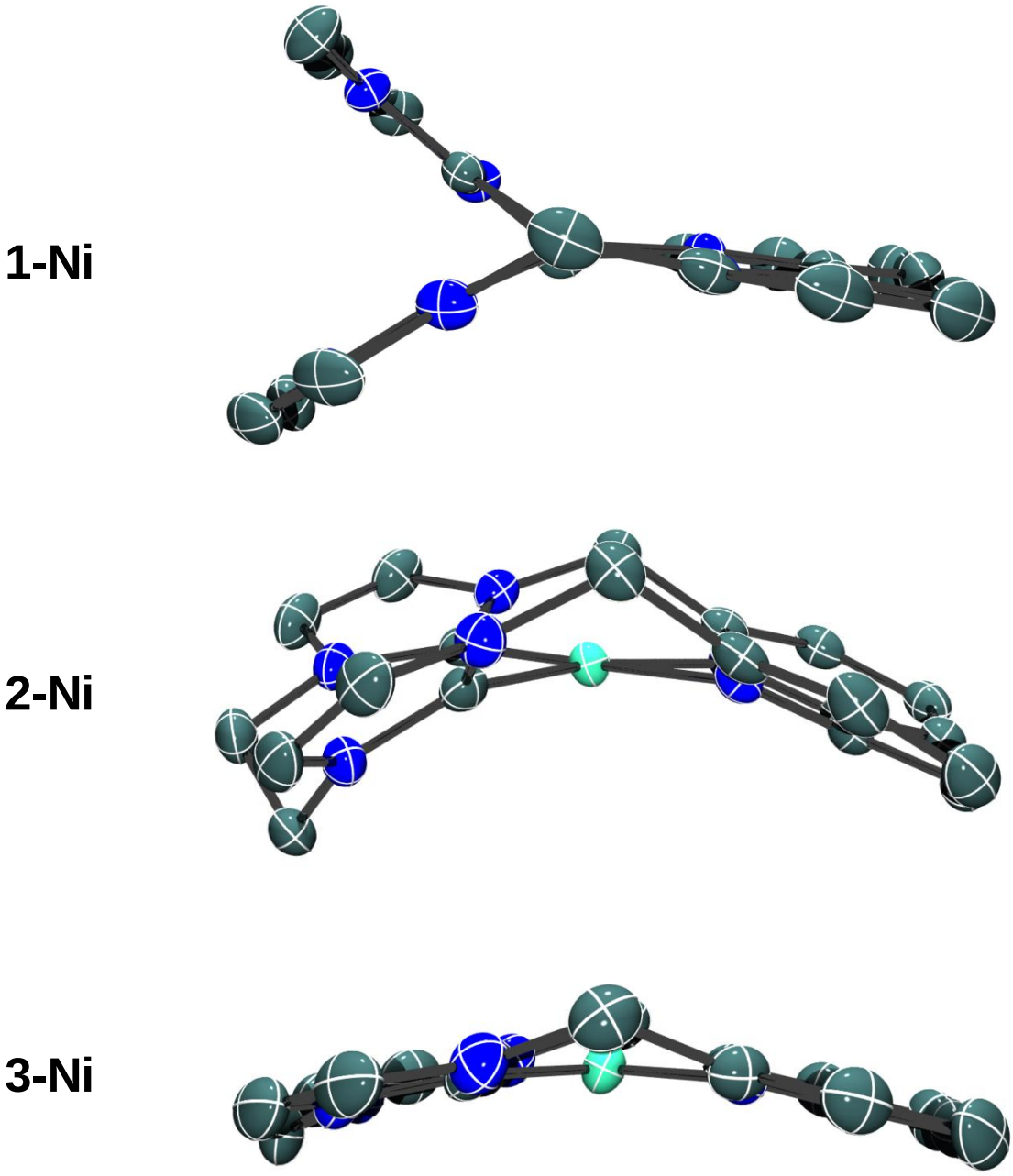


Figure S1. Side-on view of ORTEP diagrams of cations in **1-Ni**, **2-Ni**, and **3-Ni** (top to bottom) are shown with thermal ellipsoids at the 70%, 70%, and 35% probability levels, respectively. Hydrogen atoms are omitted for clarity.

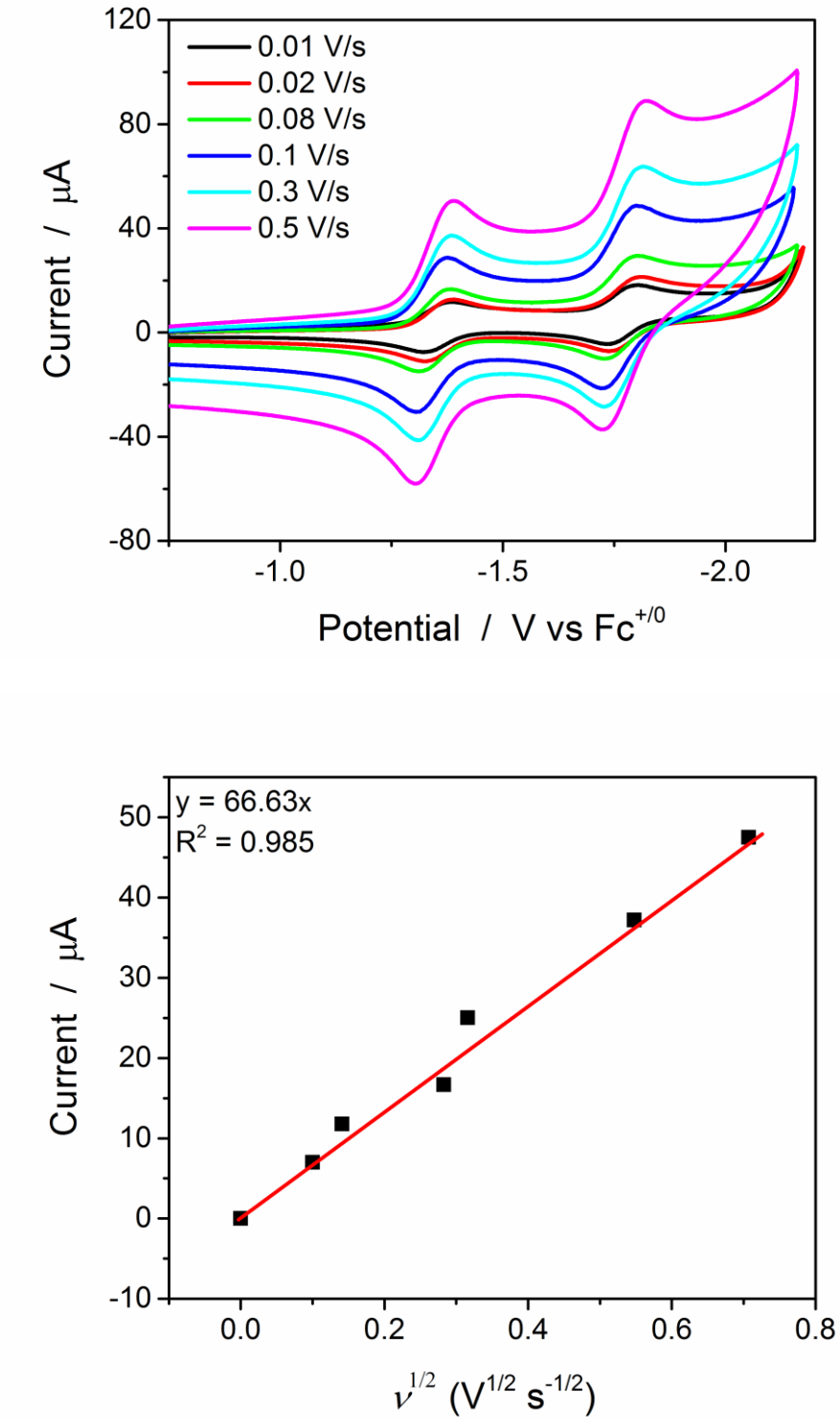


Figure S2. (Top) CVs of 1 mM **1-Ni** at different scan rates in CH_3CN containing 0.1 M Bu_4NPF_6 supporting electrolyte at a glass carbon working electrode under N_2. (Bottom) Dependence of the first reduction peak current versus $\nu^{1/2}$.

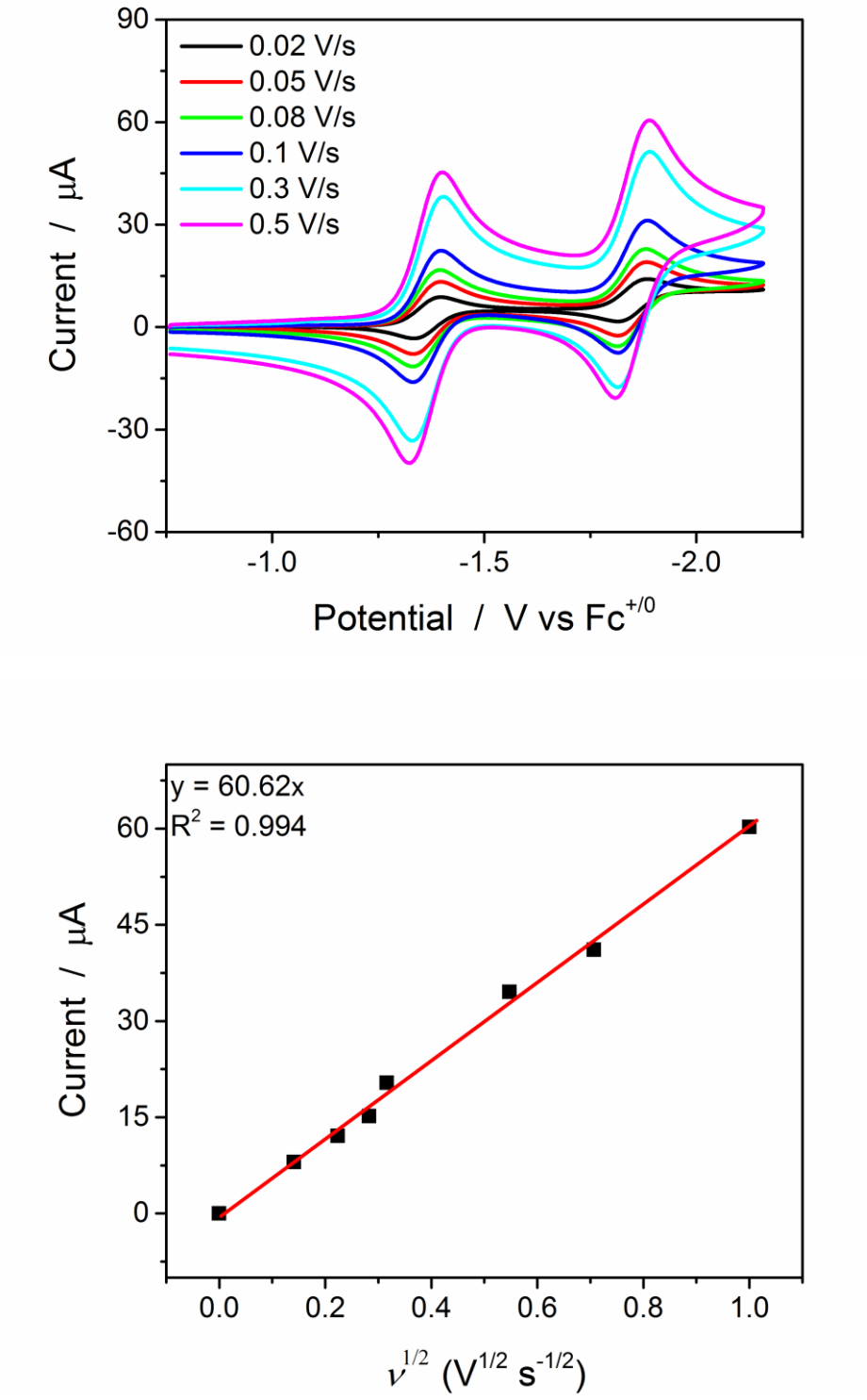


Figure S3. (Top) CVs of 1 mM **2-Ni** at different scan rates in CH_3CN containing 0.1 M Bu_4NPF_6 supporting electrolyte at a glass carbon working electrode under N_2. (Bottom) Dependence of the first reduction peak current versus $\nu^{1/2}$.

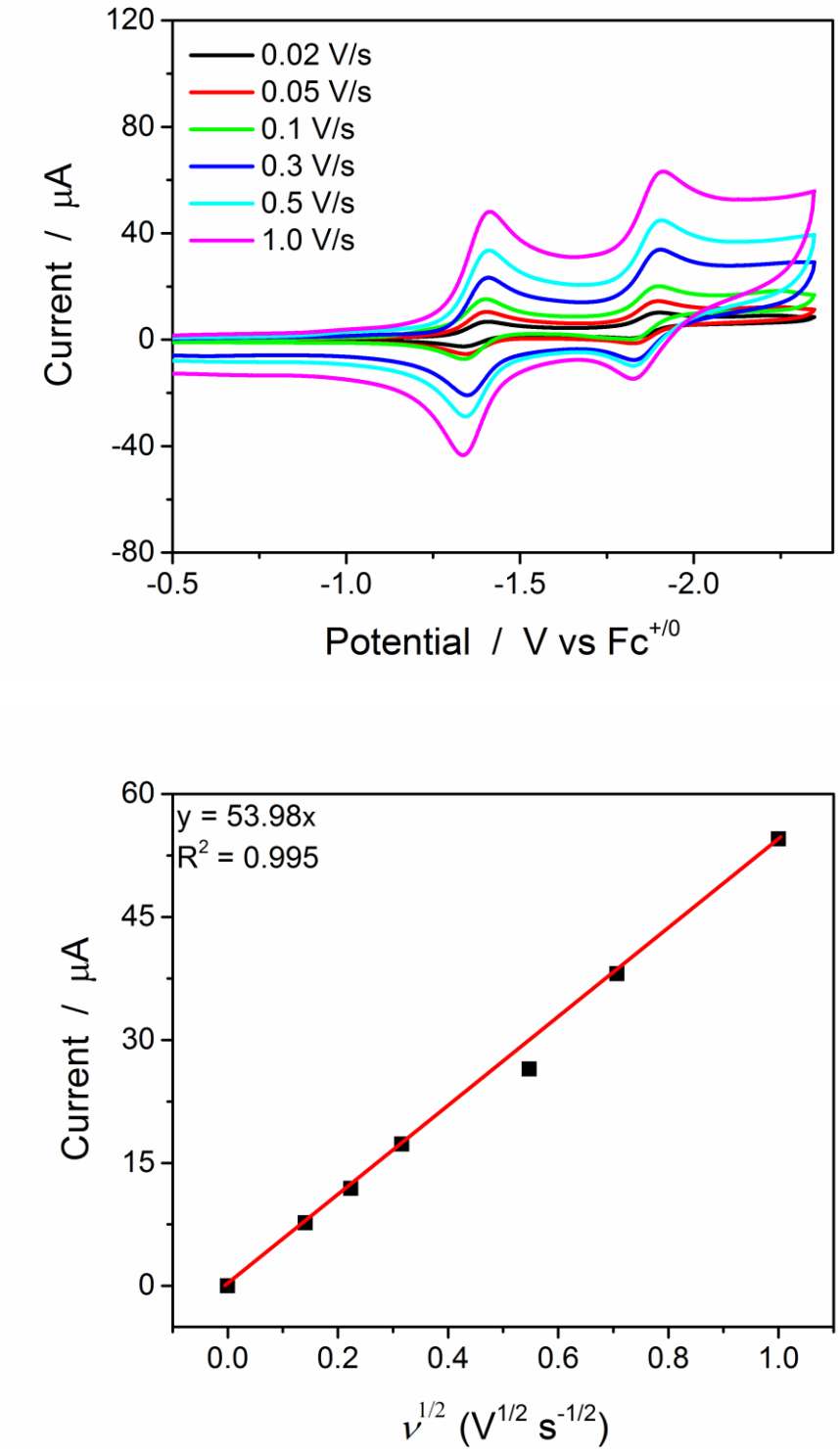


Figure S4. (Top) CVs of 1 mM **3-Ni** at different scan rates in CH_3CN containing 0.1 M Bu_4NPF_6 supporting electrolyte at a glass carbon working electrode under N_2. (Bottom) Dependence of the first reduction peak current versus $\nu^{1/2}$.

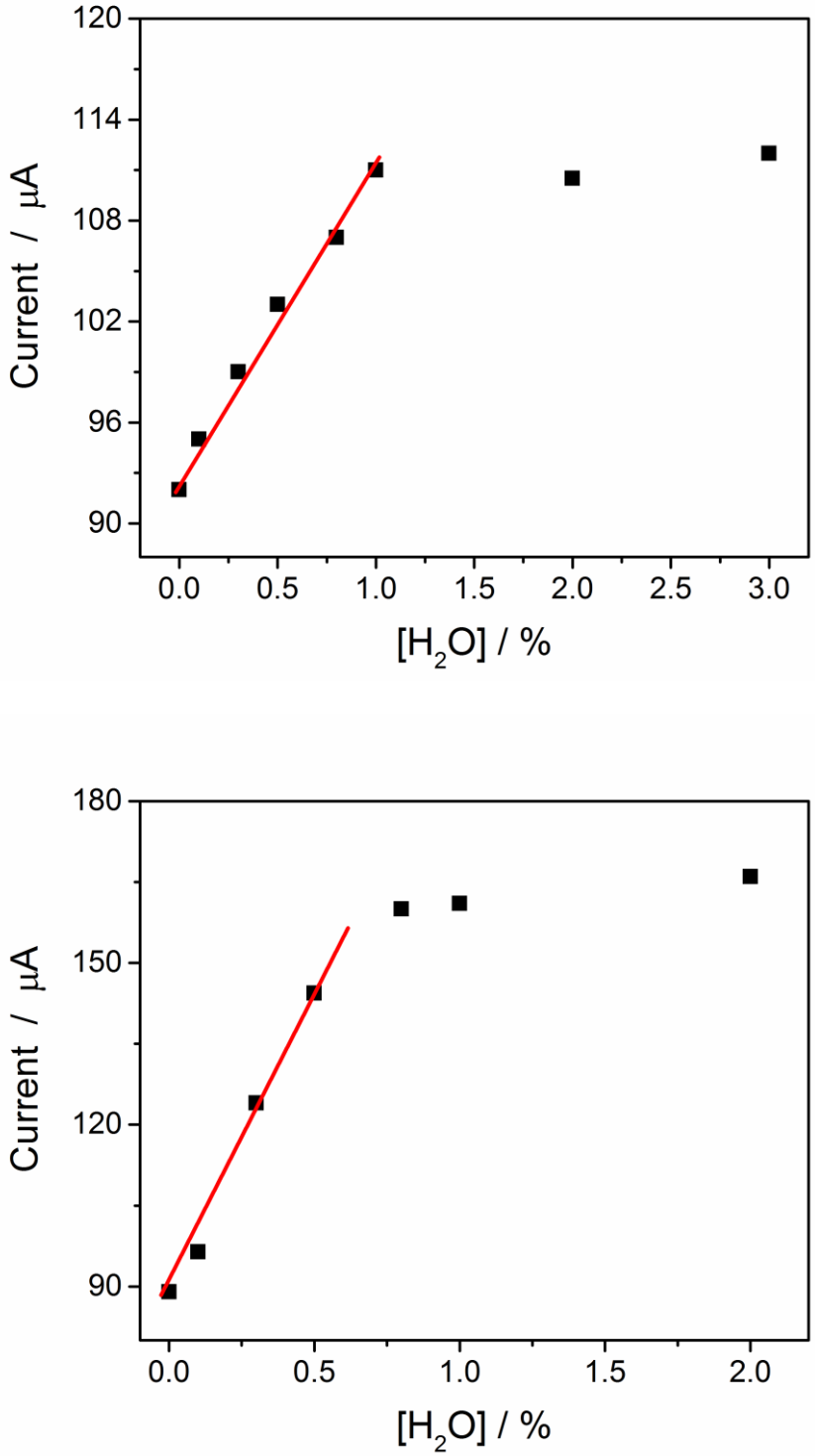


Figure S5. Dependence of catalytic current obtained from 1 mM of **2-Ni** (Top) and **3-Ni** (Bottom) versus the concentration of water. CVs were performed in CO_2 saturated-CH_3CN solutions containing 0.1 M Bu_4NPF_6 at ν = 100 mV/s. At low [H_2O], a linear dependence on [H_2O] is observed, consistent with a catalytic reaction that is second order in proton source. At higher [H_2O], the current reaches a limiting value, which is typical of saturation kinetics.

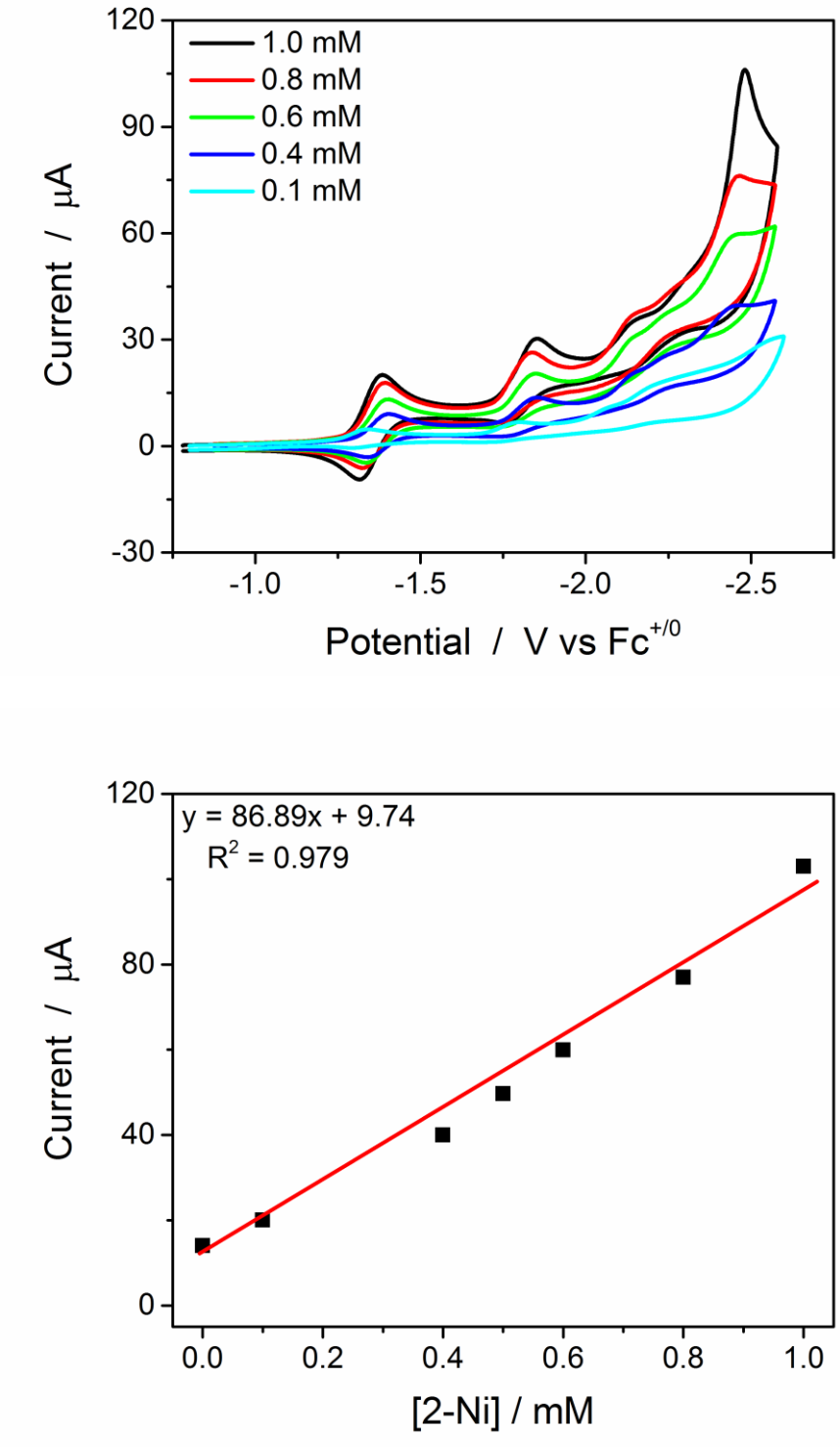


Figure S6. (Top) CVs of different concentrations of **2-Ni** at 100 mV/s in 0.1 M Bu_4NPF_6 CO_2-saturated CH_3CN solutions containing 2% water at a glass carbon working electrode. (Bottom) Dependence of the catalytic current versus catalyst concentration.

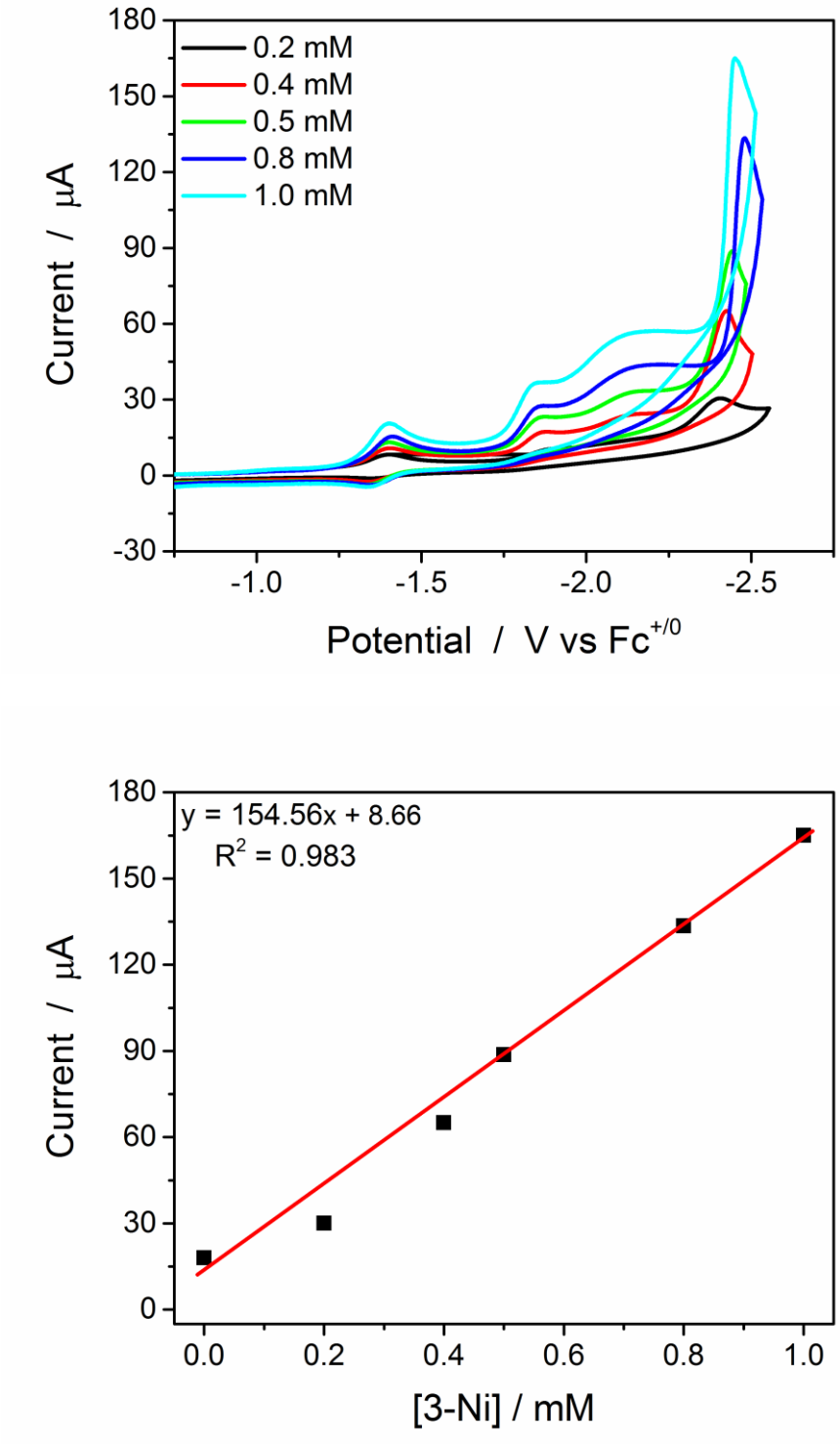


Figure S7. (Top) CVs of different concentration of **3-Ni** at 100 mV/s in 0.1 M Bu_4NPF_6 CO_2-saturated CH_3CN solutions containing 2% water at a glass carbon working electrode under CO_2. (Right) Dependence of the catalytic current versus catalyst concentration.

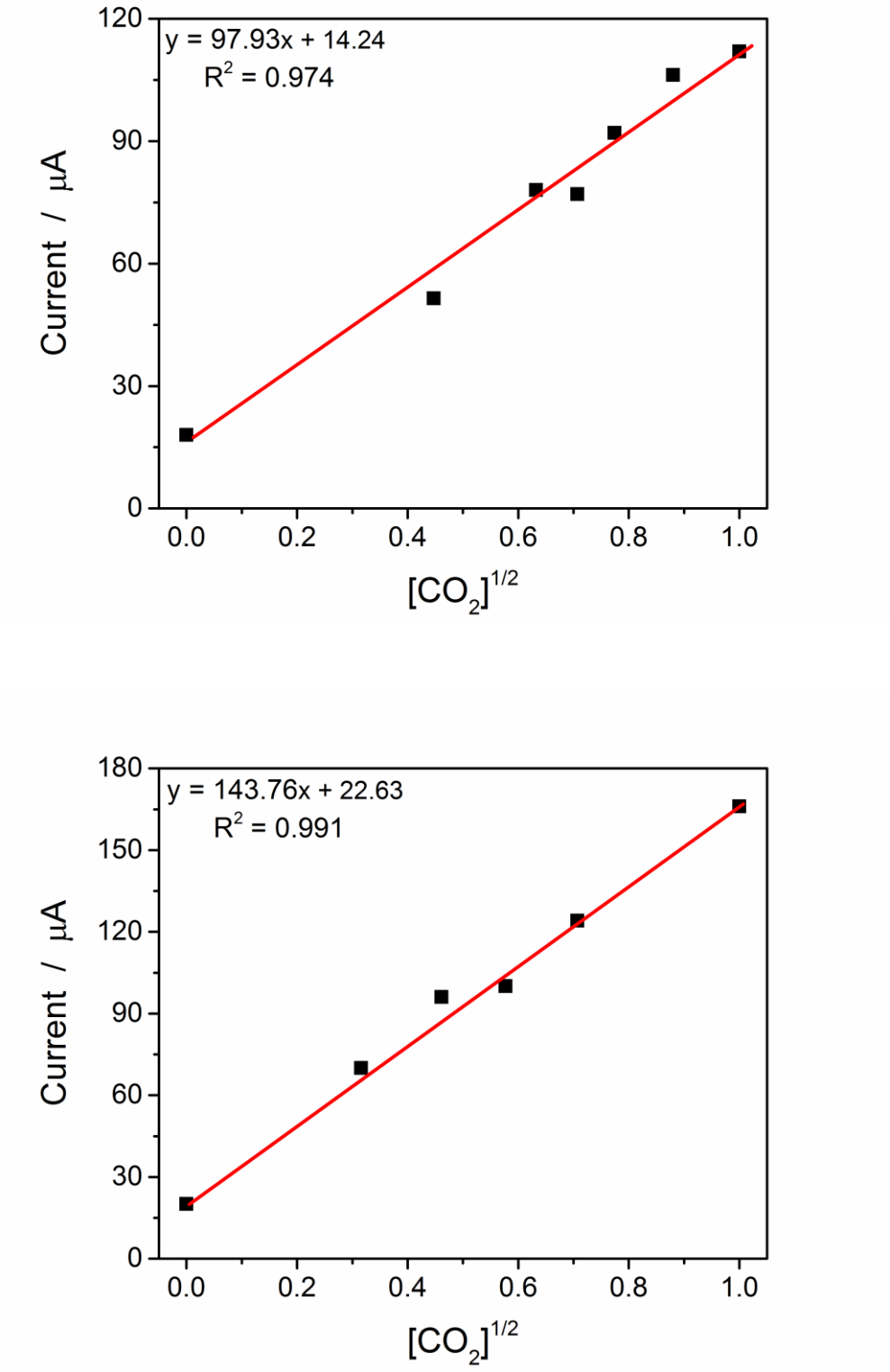


Figure S8. Dependence of catalytic current obtained from 1 mM of **2-Ni** (Top) and **3-Ni** (Bottom) versus the square root of CO_2 percentage. (CVs were performed in different ratios of N_2:CO_2 saturated-CH_3CN solutions containing 0.1 M Bu_4NPF_6 with the scan rate of 100 mV/s).

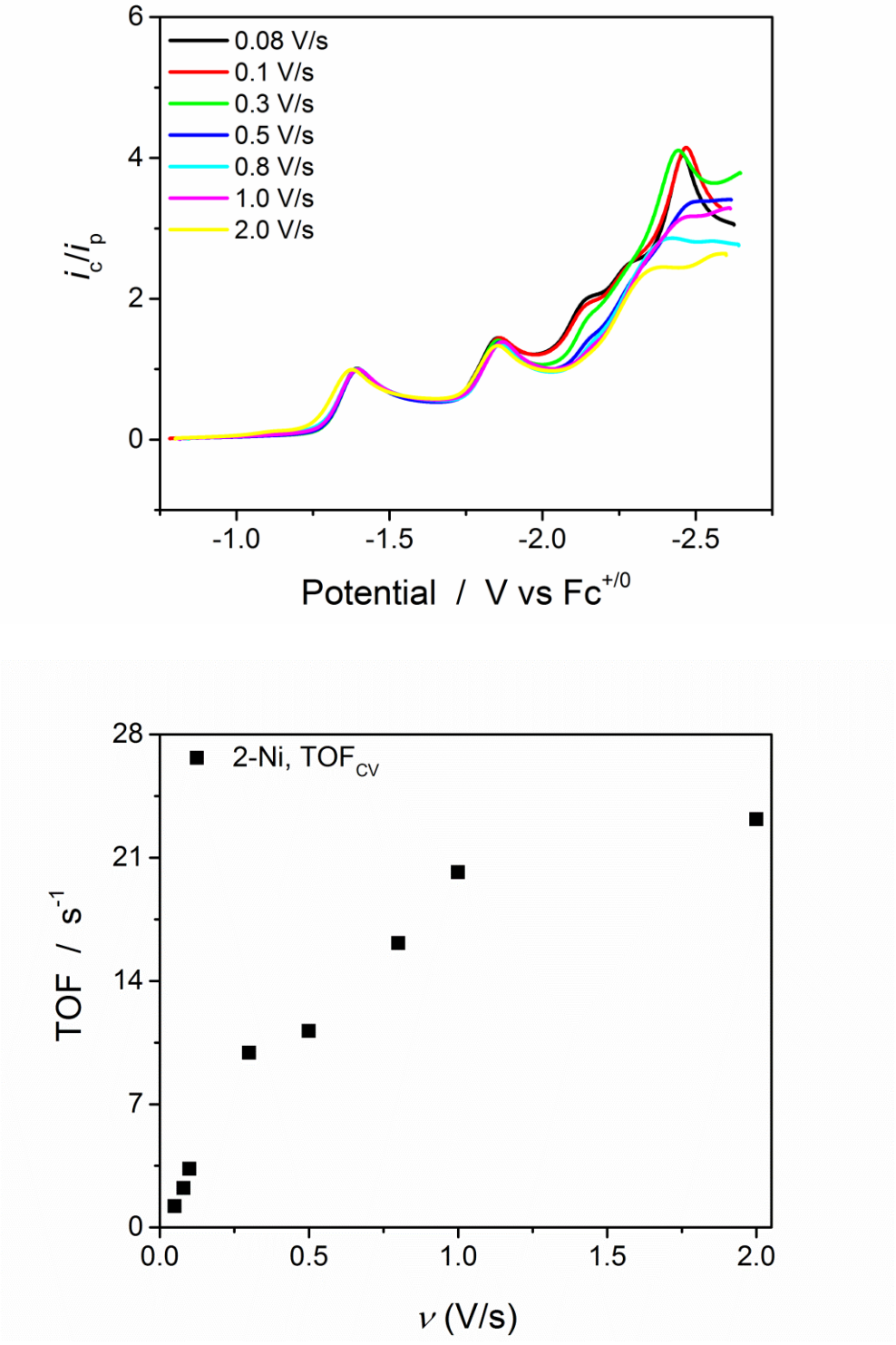


Figure S9. (Top) Linear sweep voltammograms of 1 mM **2-Ni** in CO_2-saturated CH_3CN/0.1 M Bu_4NPF_6 solutions containing 2% H_2O. (Bottom) Plot of turnover frequency (TOF, s^{-1}) versus scan rate.

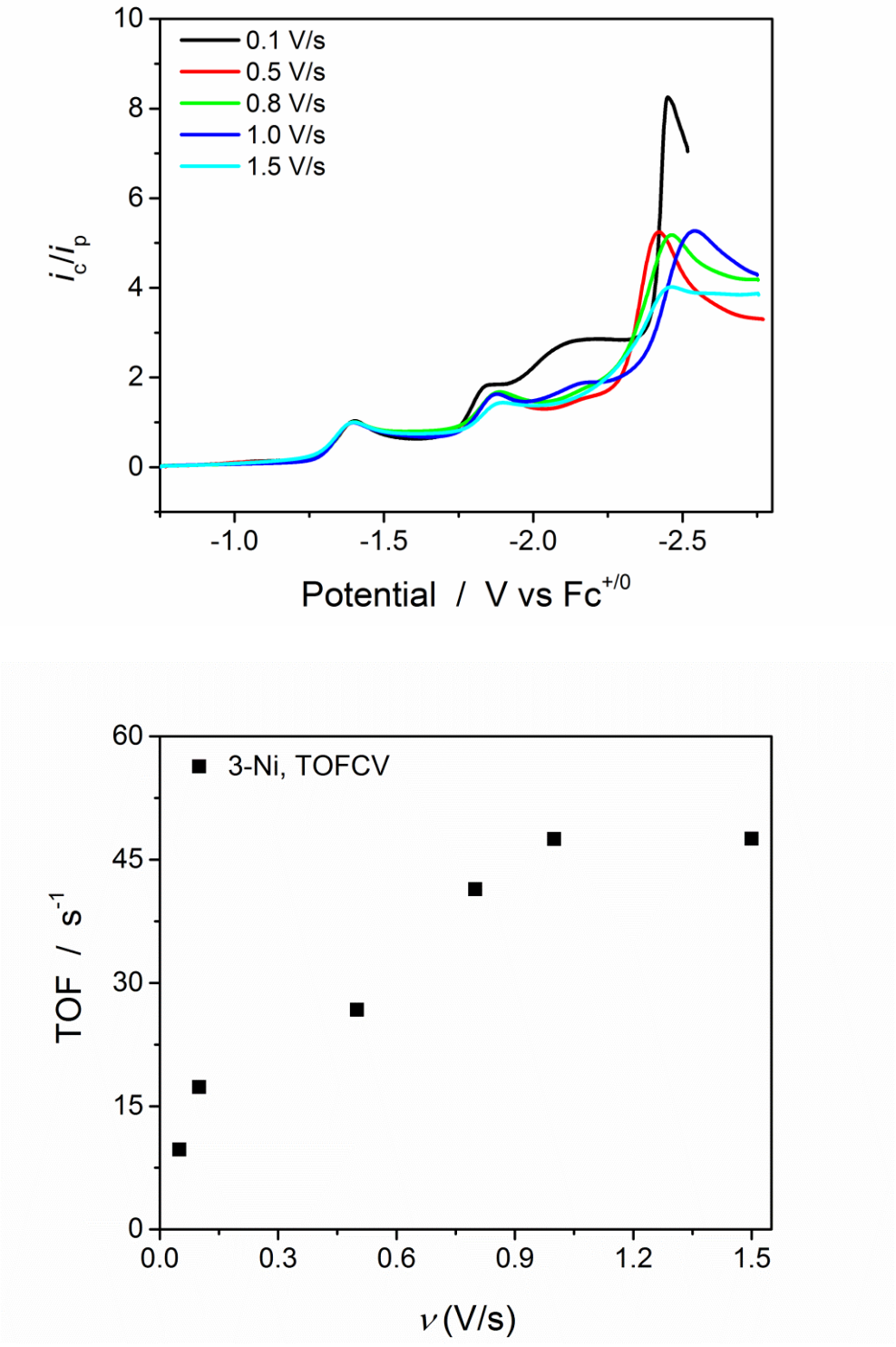


Figure S10. (Top) Linear sweep voltammograms of 1 mM **3-Ni** in CO_2-saturated CH_3CN/0.1 M Bu_4NPF_6 solutions containing 2% H_2O. (Bottom) Plot of TOF (s^{-1}) versus scan rate.

The effect of CO_2 binding on the redox behavior of the macrocyclic catalysts was investigated by CV in anhydrous CH_3CN solutions using different ratios of N_2:CO_2. Both **2-Ni** and **3-Ni** exhibit irreversible voltammetric behavior at the second redox couple as the concentration of dissolved CO_2 is increased. Small anodic shifts in the peak potentials of the second redox process are also observed in CO_2-saturated solutions (Figure S12). This behavior is characteristic of CO_2 binding.[20]

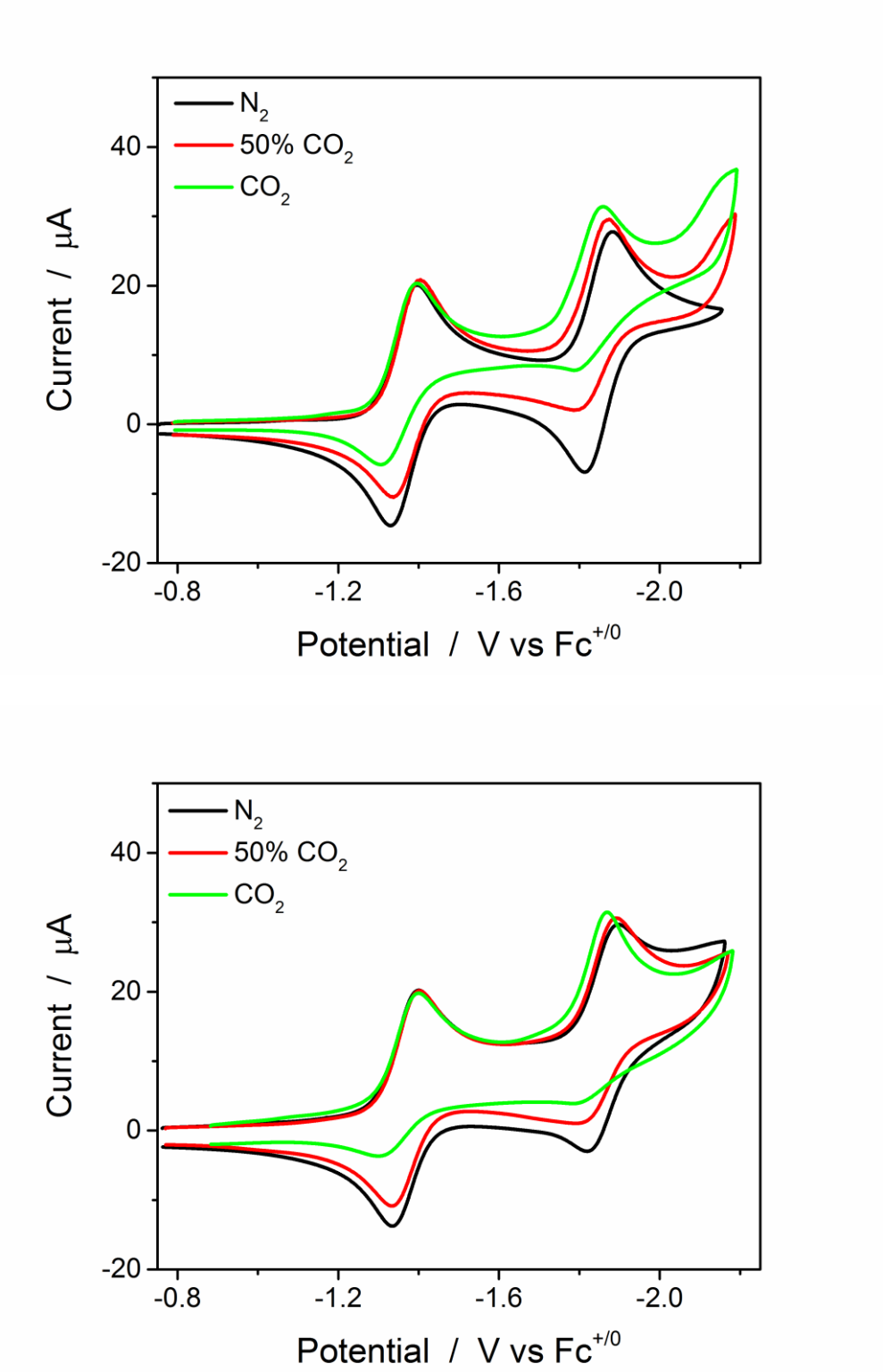


Figure S11. CVs of 1 mM **2-Ni** (Top) and 1 mM **3-Ni** (Bottom) under different ratios of N_2:CO_2 saturated-CH_3CN solutions containing 0.1 M Bu_4NPF_6.

Given the electronic structure of **2-Ni** which has nearly degenerate metal-centered and ligand-centered reduced states, we investigated whether the selectivity for this catalyst may be sensitive to relative substrate concentrations. Controlled potential electrolyses were performed at the same applied potential (E = -2.42 V vs $Fc^{+/0}$), but with a decrease in [H_2O] (from 2% to 1% H_2O) as shown in **Figure S12**. The selectivity for CO_2 reduction versus proton reduction is essentially unchanged relative to 2% H_2O (**Table S2**).

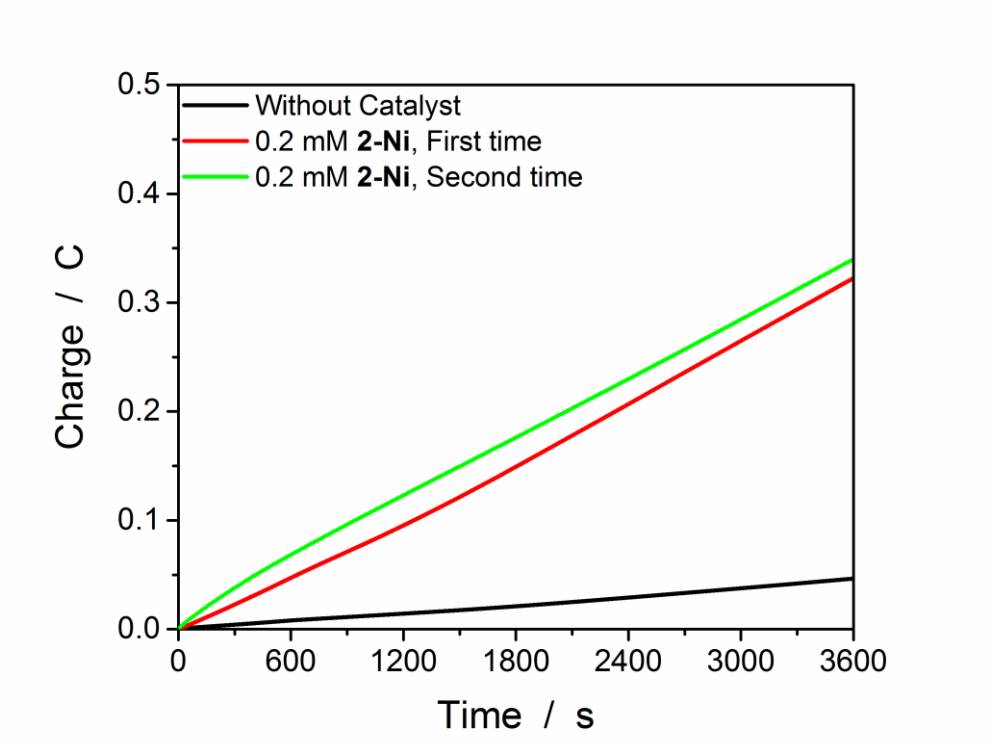


Figure S12. Charge versus time plots from controlled potential electrolyses with and without 0.2 mM **2-Ni** in CO_2-saturated CH_3CN/0.1 M Bu_4NPF_6 solutions containing 1% H_2O at E = -2.42 V vs $Fc^{+/0}$ with a glassy carbon rod.

Additional controlled potential electrolyses were performed with **3-Ni** at an applied potential of -2.13 V vs $Fc^{+/0}$ (corresponding to the peak of the broad feature following the 2nd reduction) in order to determine if catalytic activity occurs as less negative potentials and, if so, with the same high selectivity for CO_2 reduction as observed at E = -2.44 V. Indeed, catalysis occurs and with similar selectivity for CO_2 reduction vs H^+ reduction (**Table S2**).

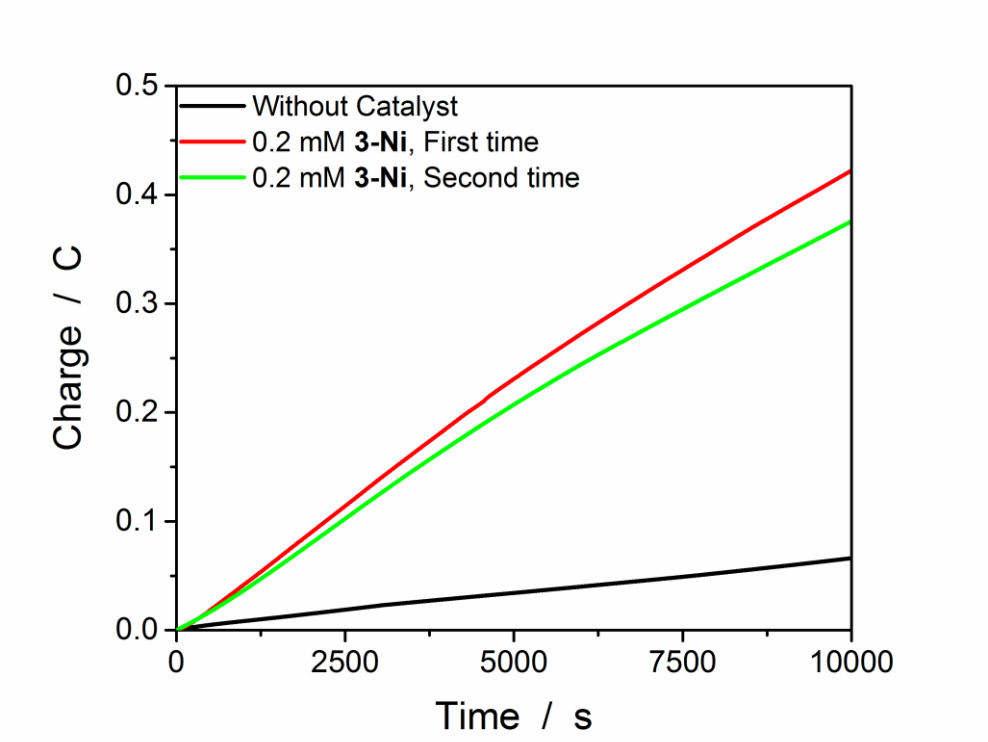


Figure S13. Charge versus time plots from controlled potential electrolyses with and without 0.2 mM **3-Ni** in CO_2-saturated CH_3CN/0.1 M Bu_4NPF_6 solutions containing 2% H_2O at E = -2.13 V vs $Fc^{+/0}$ with a glassy carbon rod.

Experiments were also conducted with **3-Ni** and methanol as the added proton source ($pK_{a(DMSO)}$ = 29.0), a slightly stronger acid than H_2O ($pK_{a(DMSO)}$ = 31.4).[21] These results (**Figure S14**) suggest that two different pathways are observed in cyclic voltammograms of **3-Ni**. Similar to reported observations with manganese-based catalysts,[22] the broad feature around -2.1 V in Figure 2 of the main text (**3-Ni** under CO_2 with 2% H_2O) likely corresponds to slow catalysis through a protonation-first pathway before further reduction, while the large catalytic wave at more negative potentials corresponds to a reduction-first pathway. With added CH_3OH, catalysis begins right at the second reduction due to more facile protonation of the metallocarboxylic acid intermediate, which allows for subsequent reduction at a lower overpotential. High selectivity for CO_2 conversion to CO is still observed in controlled potential electrolyses with added methanol (**Table S2**).

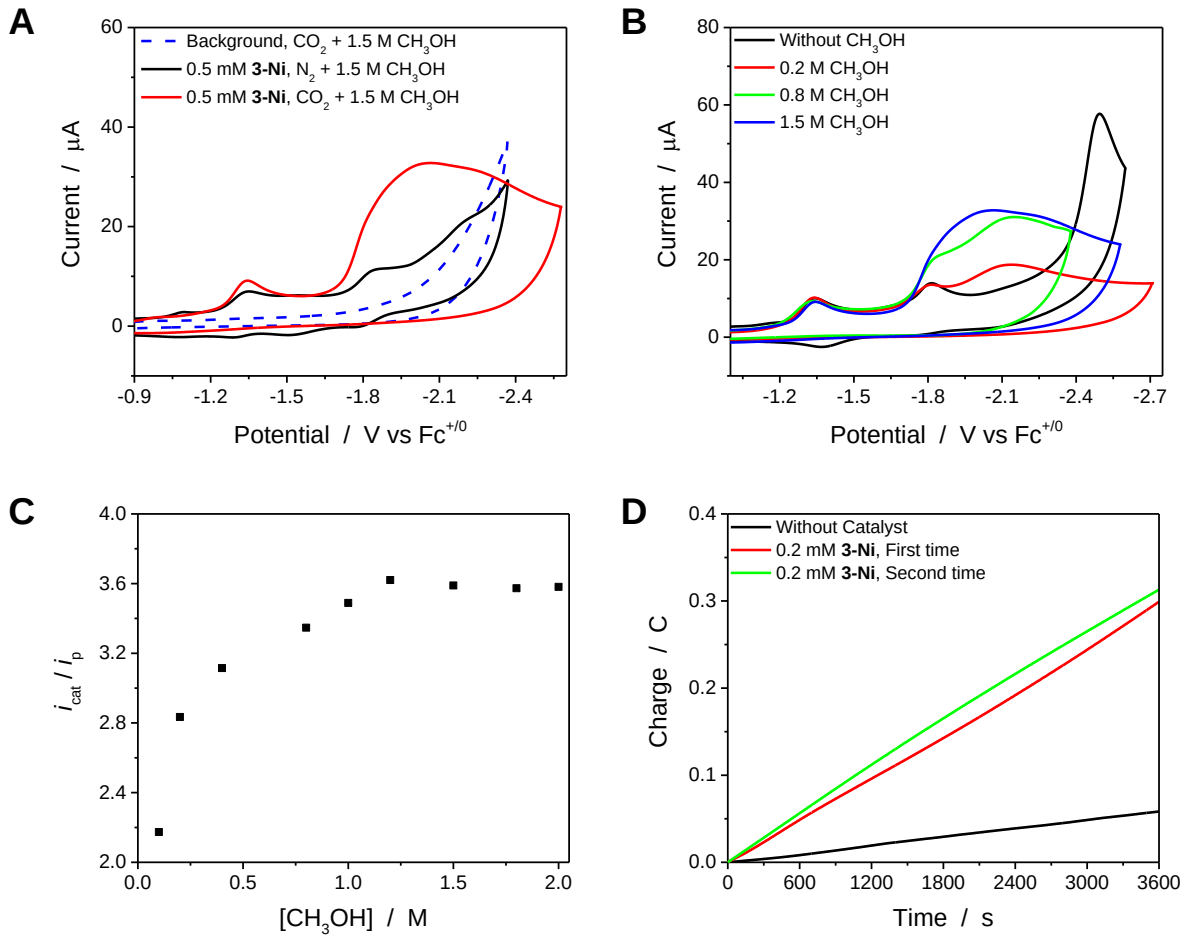


Figure S14. A) Cyclic voltammograms of 0.5 mM **3-Ni** in CH_3CN / 1.5 M CH_3OH containing 0.1 M Bu_4NPF_6, ν = 100 mV/s, glassy carbon disc. B) CVs of 0.5 mM **3-Ni** with different concentrations of added CH_3OH in CO_2-saturated CH_3CN / 0.1 M Bu_4NPF_6. C) Plot of i_{cat}/i_p as a function of [CH_3OH] obtained from CVs with 0.5 mM **3-Ni**. The current reaches a limiting value, consistent with saturated kinetics, at CH_3OH concentrations above 1 M. D) Controlled potential electrolyses of 0.2 mM **3-Ni** in CH_3CN / 2 M CH_3OH containing 0.1 M Bu_4NPF_6 at applied potential, E = -2.0 V vs $Fc^{+/0}$, using a glassy carbon rod.

Table S2. Summary of controlled potential electrolyses with 0.2 mM catalyst in the specified conditions at a glassy carbon rod. Faradaic efficiencies are reported as an average of two runs with standard deviations provided, all to the nearest whole number.

Catalyst	Solvent	E_{appl}	FE (%)	CO (%)	H_2 (%)
1-Ni	CH_3CN (2% H_2O)	-2.25	98	5 ± 2	93 ± 3
2-Ni	CH_3CN (1% H_2O)	-2.42	99	57 ± 2	42 ± 3
2-Ni	CH_3CN (2% H_2O)	-2.42	99	56 ± 3	43 ± 3
3-Ni	CH_3CN (2% H_2O)	-2.13	98	89 ± 2	9 ± 2
3-Ni	CH_3CN (2% H_2O)	-2.44	98	87 ± 4	11 ± 2
3-Ni	CH_3CN (2 M CH_3OH)	-2.00	98	92 ± 3	6 ± 3

Table S3. Experimental and calculated bond lengths (Ångströms, Å) and bond angles (degrees, °) for **1-Ni**, **2-Ni**, and **3-Ni** using the ωB97X-D functional in acetonitrile *via* the SMD approach. The calculated parameters are provided for the singlet-ground states.

Complexes	Bond Lengths/ Angles	Exptl.	Calc.
1-Ni	Ni-C(2)	1.859(3)	1.881
	Ni-N(3)	1.913(2)	1.935
	Ni-N(4)	1.915(2)	1.935
	Ni-C(17)	1.860(3)	1.881
	C(2)-Ni-N(4)	162.5°	161.4°
	N(3)-Ni-C(17)	160.4°	161.4°
2-Ni	Ni-C(2)	1.9163(17)	1.933
	Ni-N(3)	1.9279(15)	1.948
	Ni-N(4)	1.9270(14)	1.947
	Ni-C(16)	1.8768(18)	1.896
	C(2)-Ni-N(4)	175.3°	174.0°
	N(3)-Ni-C(17)	168.8°	166.5°
3-Ni	Ni-C(2)	1.864(3)	1.864
	Ni-N(3)	1.936(3)	1.926
	C(2)-Ni-N(3)	174.5°	175.0°

Table S4. Calculated relative energies between the singlet and triplet states for **1-Ni**, **2-Ni** and **3-Ni** using the ωB97X-D functional in acetonitrile *via* the SMD approach. The Mulliken spin population is given for nickel, ρ(Ni).

Complexes	Multiplicity	$<S^2>$	ρ(Ni)	ΔE	ΔZPE	ΔG
1-Ni	S = 0	0.00	0.00	0.0	0.0	0.0
	S = 1	2.01	1.67	14.5	13.2	11.3
2-Ni	S = 0	0.00	0.00	0.0	0.0	0.0
	S = 1	2.01	1.74	17.0	15.7	14.4
3-Ni	S = 0	0.00	0.00	0.0	0.0	0.0
	S = 1	2.01	1.69	28.2	26.8	25.2

Table S5. Calculated relative energies between the doublet and quartet states for **1-Ni + 1e$^-$**, **2-Ni + 1e$^-$**, and **3-Ni + 1e$^-$** using the ωB97X-D functional in acetonitrile *via* the SMD approach. The Mulliken spin population is given for nickel, ρ(Ni).

Complexes	Multiplicity	$<S^2>$	ρ(Ni)	ΔE	ΔZPE	ΔG
1-Ni + 1e$^-$	S = 1/2	0.77	0.04	0.0	0.0	0.0
		0.76	0.86	1.3	0.0	-3.0
	S = 3/2	3.77	1.74	21.8	19.8	17.1
2-Ni + 1e$^-$	S = 1/2	0.76	0.02	0.0	0.0	0.0
		0.76	0.84	3.1	2.4	0.2
	S = 3/2	3.77	1.74	20.8	19.5	18.3
3-Ni + 1e$^-$	S = 1/2	0.76	0.02	0.0	0.0	0.0
		0.76	0.81	12.1	11.4	9.8
	S = 3/2	3.77	1.70	31.0	29.6	28.3

Table S6. Calculated relative energies between the singlet and triplet states for **1-Ni + 2e⁻**, **2-Ni + 2e⁻**, and **3-Ni + 2e⁻** using the ωB97X-D functional in acetonitrile *via* the SMD approach. The Mulliken spin population is given for nickel, ρ(Ni). [a]The computed energies for the spin purified low-spin singlet were obtained by using Yamaguchi and co-workers' approach. [b]This species has a negative eigenvalue on the order of 14 cm^{-1}.

Complexes	Multiplicity	<S²>	ρ(Ni)	ΔE	ΔZPE	ΔG
1-Ni + 2e⁻	S = 0	0.00	0.00	0.0	0.0	0.0
		0.93	0.81	0.3/-2.0[a]	-1.5/-3.8[a]	-4.3/-6.7[a]
	S = 1	2.03	0.90	1.9	-0.1	-3.5
2-Ni + 2e⁻	S = 0	0.00	0.00	0.0	0.0	0.0
		1.00	0.79	1.6/1.2[a]	0.7/0.3[a]	-0.2/-0.7[a]
	S = 1	2.03	0.85	1.6	0.5	-1.2
3-Ni + 2e⁻	S = 0	0.00	0.00	0.0	0.0	0.0
		1.00	0.79	9.5/9.9[a]	8.3/8.7[a]	8.1/8.5[a,b]
	S = 1	2.03	0.85	9.1	8.0	6.2

The spin contaminated singlets were corrected by using the broken spin (BS) symmetry procedure reported by Yamaguchi and co-workers:

$$^{LS}E = \frac{^{BS}E\left(^{HS}\langle S^2\rangle - ^{LS}\langle S^2\rangle\right) - ^{HS}E\left(^{BS}\langle S^2\rangle - ^{LS}\langle S^2\rangle\right)}{^{HS}\langle S^2\rangle - ^{BS}\langle S^2\rangle} \quad (4)$$

Yamaguchi's approach allows one to calculate the energy of the spin purified low-spin (LS) state from the triplet state (HS) that is related to the low-spin state by spin flip and $\langle S^2\rangle$, which is the expected value of the total spin operator.

Table S7. Calculated relative energies between the doublet and quartet states for **1-Ni + 3e⁻**, **2-Ni + 3e⁻**, and **3-Ni + 3e⁻** using the ωB97X-D functional in acetonitrile *via* the SMD approach. The Mulliken spin population is given for nickel, ρ(Ni).

Complexes	Multiplicity	<S²>	ρ(Ni)	ΔE	ΔZPE	ΔG
1-Ni + 3e⁻	S = 1/2	0.77	0.85	0.0	0.0	0.0
	S = 3/2	3.78	0.91	16.8	15.2	14.7
2-Ni + 3e⁻	S = 1/2	0.76	0.80	0.0	0.0	0.0
	S = 3/2	3.78	0.86	15.6	14.2	13.6
3-Ni + 3e⁻	S = 1/2	0.76	0.77	0.0	0.0	0.0
	S = 3/2	3.79	0.81	16.9	15.3	15.0

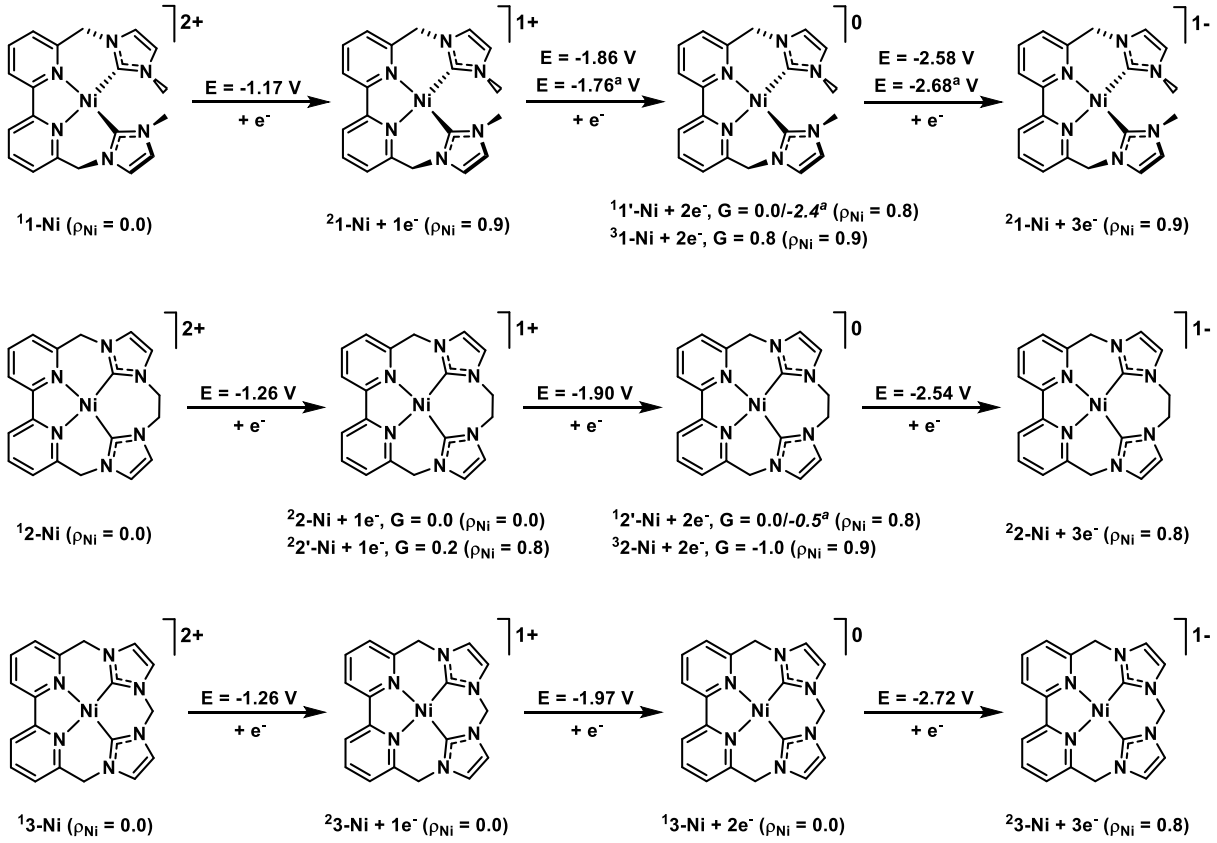


Figure S15. Calculated redox potentials (in V versus the $Fc^{+/0}$ redox couple) are displayed for the first three-reduction events. The superscript represents the spin multiplicity of a given species and the spin on the nickel is denoted as ρ_{Ni}. [a]The computed energies for the spin purified low-spin singlet were obtained by using Yamaguchi and co-workers' approach.

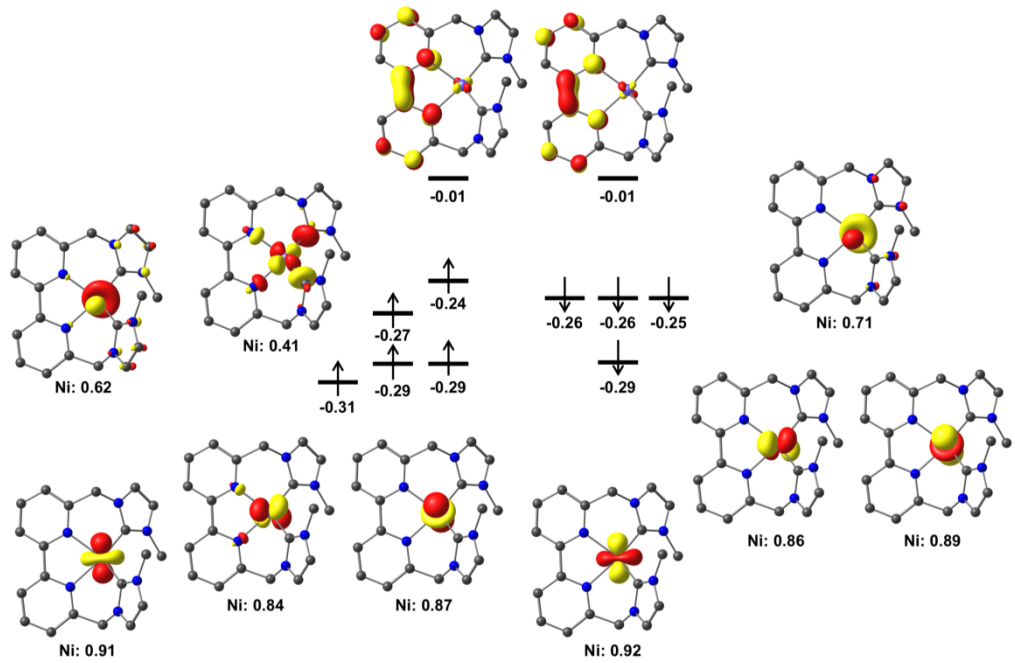


Figure S16. Isosurface (0.07 au) plots of the canonical molecular orbitals for ^{2}**1-Ni + 1e**$^{-}$ at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. Hydrogen atoms have been omitted for clarity.

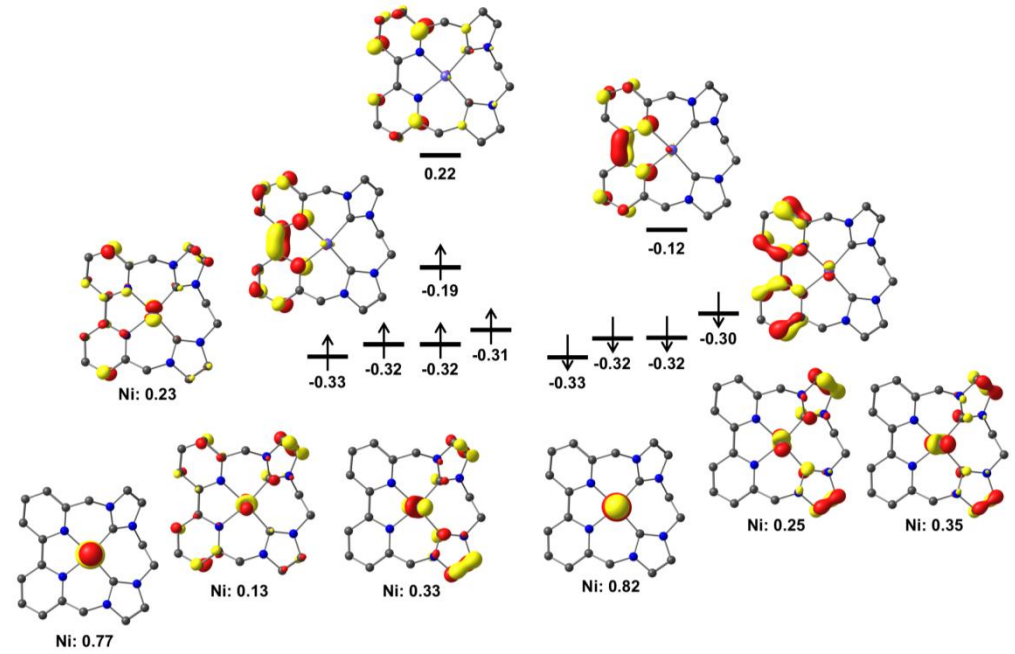


Figure S17. Isosurface (0.07 au) plots of the canonical molecular orbitals for ^{2}**2-Ni + 1e**$^{-}$ at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. Hydrogen atoms have been omitted for clarity. Hydrogen atoms have been omitted for clarity.

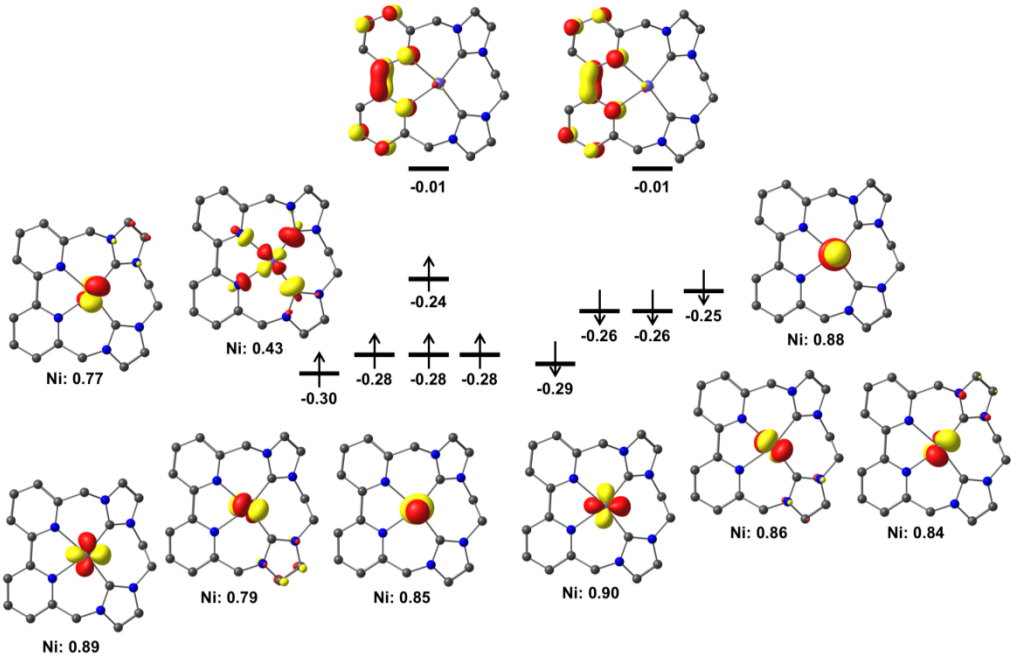


Figure S18. Isosurface (0.07 au) plots of the canonical molecular orbitals for ^{2}**2'-Ni + 1e**$^{-}$ at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. Hydrogen atoms have been omitted for clarity.

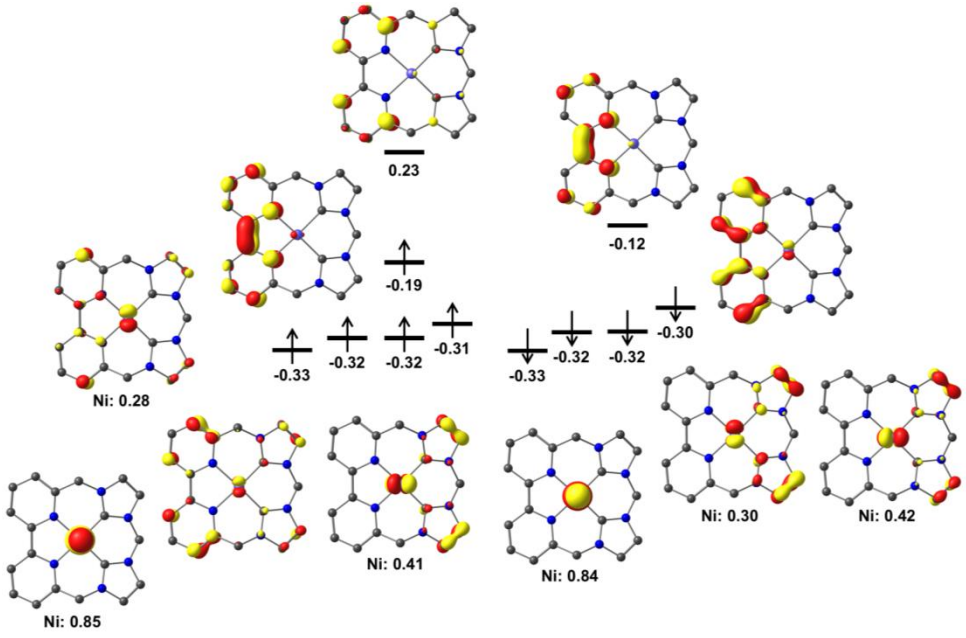


Figure S19. Isosurface (0.07 au) plots of the canonical molecular orbitals for ^{2}**3-Ni + 1e**$^{-}$ at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. Hydrogen atoms have been omitted for clarity.

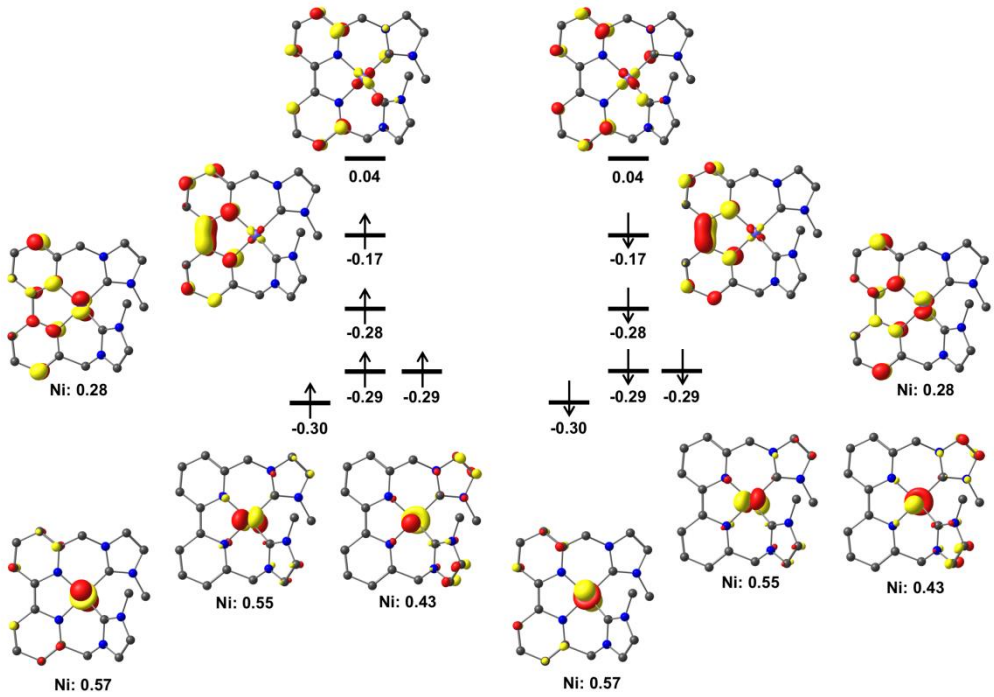


Figure S20. Isosurface (0.07 au) plots of the canonical molecular orbitals for **^{1}1-Ni + 2e$^-$** at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. Hydrogen atoms have been omitted for clarity.

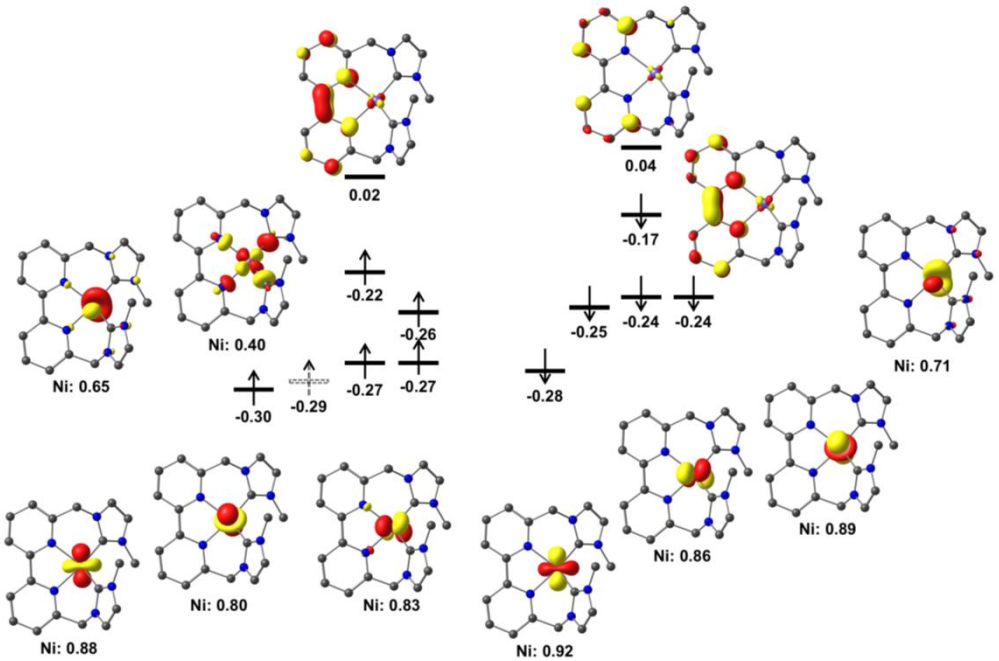


Figure S21. Isosurface (0.07 au) plots of the canonical molecular orbitals for **^{1}1'-Ni + 2e$^-$** at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. The α-HOMO-4, which is mainly ligand-centered, as well as the hydrogen atoms have been omitted for clarity.

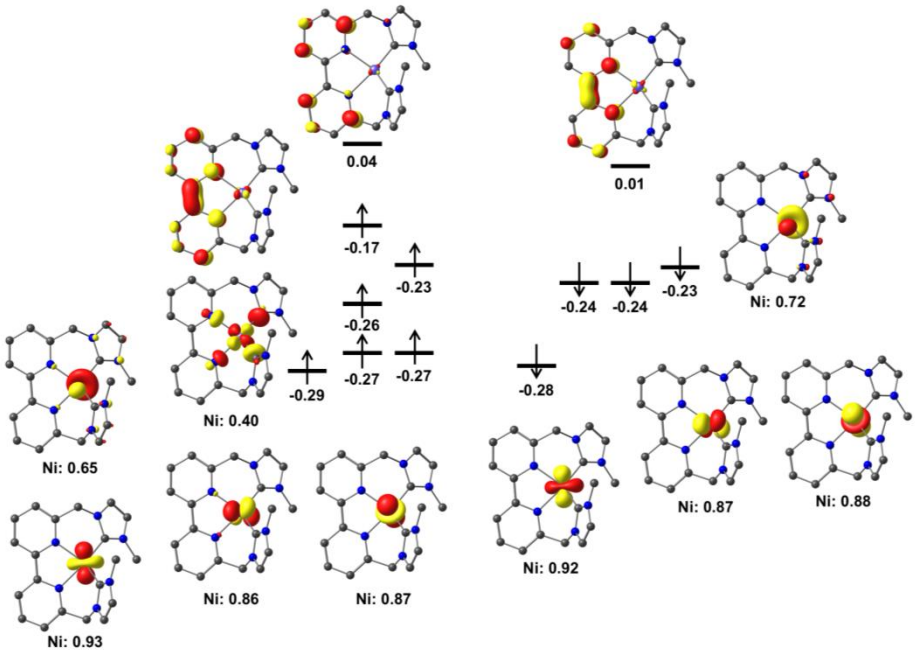


Figure S22. Isosurface (0.07 au) plots of the canonical molecular orbitals for ^{3}**1-Ni + 2e**$^{-}$ at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. Hydrogen atoms have been omitted for clarity.

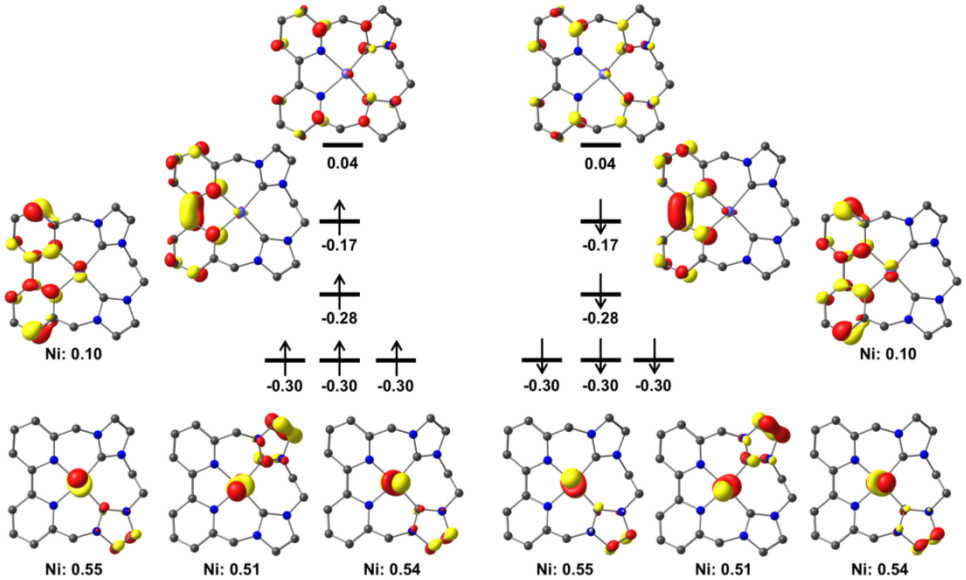


Figure S23. Isosurface (0.07 au) plots of the canonical molecular orbitals for ^{1}**2-Ni + 2e**$^{-}$ at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. The α-HOMO-4, which is mainly ligand-centered, as well as the hydrogen atoms have been omitted for clarity.

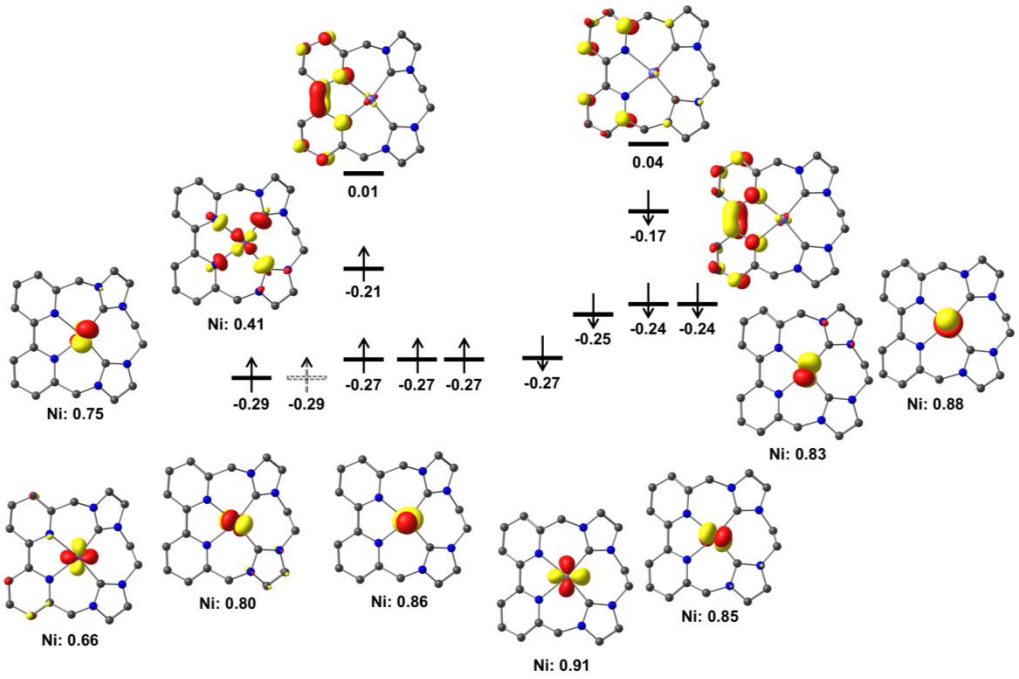


Figure S24. Isosurface (0.07 au) plots of the canonical molecular orbitals for **^{1}2'-Ni + 2e^{-}** at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. The α-HOMO-4, which is mainly ligand-centered, as well as the hydrogen atoms have been omitted for clarity.

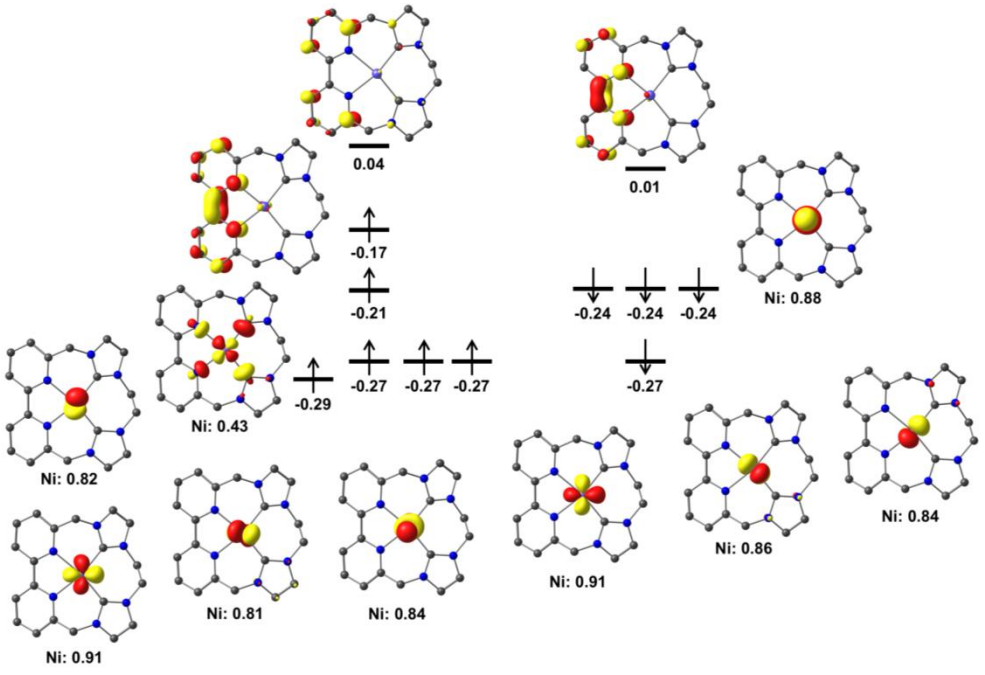


Figure S25. Isosurface (0.07 au) plots of the canonical molecular orbitals for **^{3}2-Ni + 2e^{-}** at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. Hydrogen atoms have been omitted for clarity.

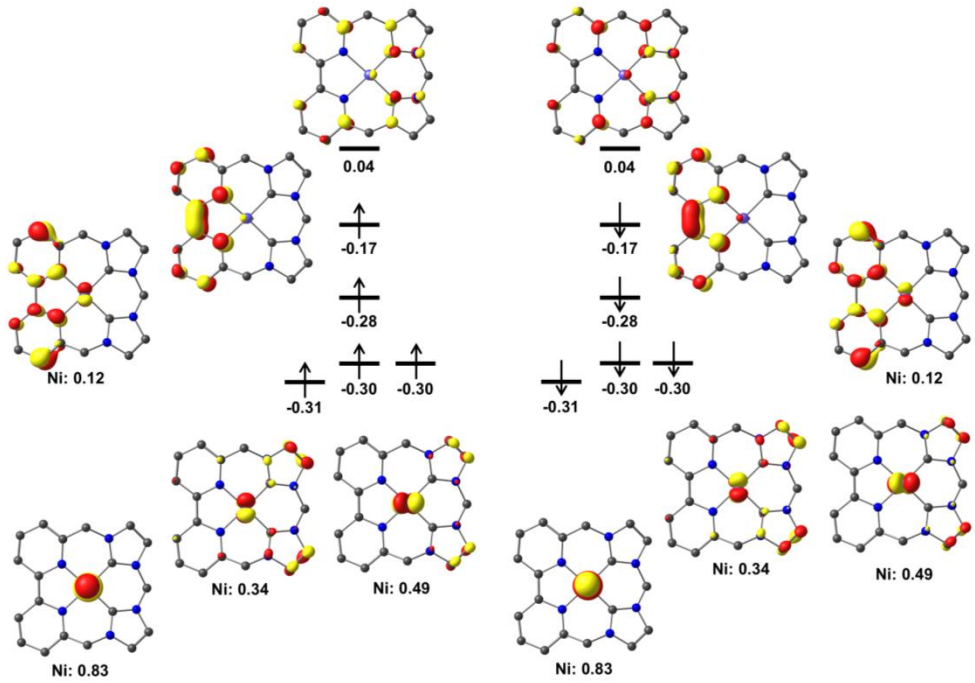


Figure S26. Isosurface (0.07 au) plots of the canonical molecular orbitals for **^{1}3-Ni + 2e^{-}** at the ωB97X-D/Def2TZVPP level of theory in solution (SMD). The atomic contributions to the molecular orbitals are given for nickel. All energies are in atomic units. Hydrogen atoms have been omitted for clarity.

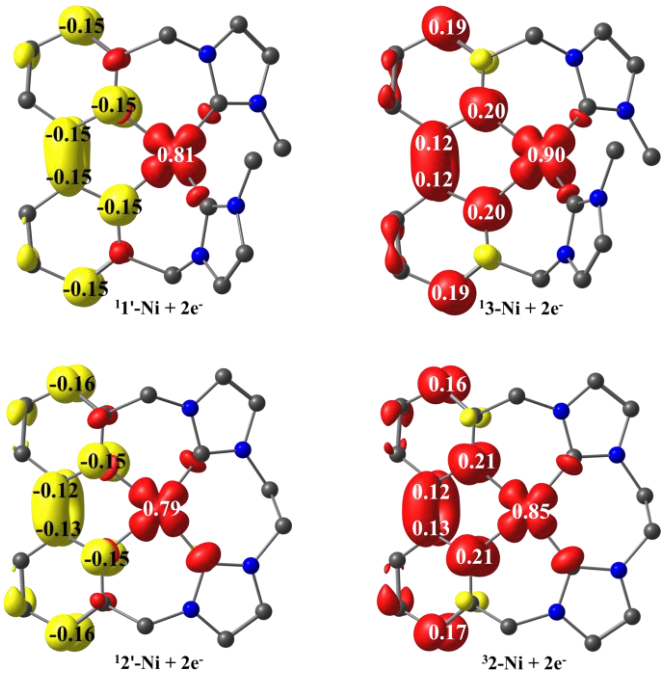


Figure S27. Isosurface (0.005 au) plots of the Mulliken spin population for the two-electron reduced species: **^{1}1'-Ni + 2e^{-}**, **^{3}1-Ni + 2e^{-}**, **^{1}2'-Ni + 2e^{-}**, and **^{3}2-Ni + 2e^{-}**.

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Tables of Cartesian Coordinates (Å) and Computed Energies (a.u.) for all Stationary.

^{1}1-Ni

Energy = -2610.935710
Enthalpy 0K = -2610.549802
Enthalpy 298K = -2610.527400
Free Energy 298K = -2610.599097
Nimag = 0 (40.5574 cm-1)

C	3.00631	0.07697	-1.83506
H	3.70121	-0.40959	-1.15203
H	3.53721	0.36942	-2.73703
H	2.20745	-0.60892	-2.09932
C	1.35767	1.32406	-0.43582
C	2.97930	2.52722	-1.39350
H	3.85168	2.69770	-1.99866
C	2.19765	3.38365	-0.70593
H	2.24902	4.45005	-0.57815
C	0.15629	3.14998	0.71089
H	0.12847	4.22741	0.57898
H	0.40246	2.94955	1.75632
C	-1.21140	2.58040	0.44645
C	-2.32168	3.39210	0.62253
H	-2.18546	4.44193	0.83808
C	-3.58270	2.83991	0.52780
H	-4.46149	3.45615	0.65784
C	-3.71336	1.48323	0.28599
H	-4.68999	1.02646	0.24633
C	-2.57024	0.72911	0.11063
C	-2.57024	-0.72911	-0.11063
C	-3.71336	-1.48323	-0.28599
H	-4.68999	-1.02646	-0.24633
C	-3.58270	-2.83992	-0.52780
H	-4.46149	-3.45615	-0.65785
C	-2.32168	-3.39210	-0.62253
H	-2.18546	-4.44193	-0.83808
C	-1.21140	-2.58040	-0.44645
C	0.15629	-3.14998	-0.71089
H	0.12847	-4.22742	-0.57897
H	0.40246	-2.94956	-1.75632
C	1.35767	-1.32406	0.43582
C	2.19765	-3.38365	0.70592
H	2.24903	-4.45005	0.57814
C	2.97930	-2.52722	1.39351
H	3.85167	-2.69770	1.99868
C	3.00631	-0.07697	1.83505
H	3.70121	0.40959	1.15203
H	3.53721	-0.36941	2.73703
H	2.20745	0.60892	2.09931
N	2.44495	1.27046	-1.22399
N	1.20518	2.62277	-0.13363
N	-1.34363	1.28495	0.15764
N	-1.34363	-1.28496	-0.15764
N	1.20518	-2.62277	0.13363
N	2.44495	-1.27046	1.22399
Ni	0.09478	-0.00000	0.00000

^{3}1-Ni

Energy = -2610.912568
Enthalpy 0K = -2610.528753
Enthalpy 298K = -2610.505513
Free Energy 298K = -2610.581075
Nimag = 0 (27.9830 cm-1)

C	0.75281	-2.47094	2.41949
H	1.20252	-3.45454	2.53663
H	0.51598	-2.06028	3.39953
H	1.44913	-1.81248	1.90794
C	-0.74645	-1.79992	0.57462
C	-1.46376	-3.48472	1.85814
H	-1.41678	-4.19842	2.66154
C	-2.41272	-3.26114	0.92410
H	-3.35659	-3.74348	0.74135
C	-2.65218	-1.65706	-1.00341
H	-3.61595	-2.14945	-1.08861
H	-2.07910	-1.86860	-1.90676
C	-2.84088	-0.16959	-0.85179
C	-4.08145	0.43674	-0.93909
H	-4.95895	-0.15506	-1.15630
C	-4.16953	1.80139	-0.72221

H	-5.12615	2.30169	-0.78377
C	-3.03513	2.51781	-0.38121
H	-3.10022	3.57128	-0.15537
C	-1.82667	1.84617	-0.30839
C	-0.55879	2.46388	0.15344
C	-0.38426	3.82575	0.32971
H	-1.17705	4.52106	0.09904
C	0.83415	4.28037	0.80126
H	0.99951	5.33961	0.94292
C	1.84113	3.37380	1.08391
H	2.80217	3.70241	1.45219
C	1.60393	2.02536	0.88136
C	2.64542	0.98808	1.21173
H	3.55610	1.47845	1.54167
H	2.27693	0.36987	2.03172
C	2.08574	-0.54653	-0.65385
C	4.27030	-0.18469	-0.29856
H	5.13415	0.24533	0.17635
C	4.15885	-1.06546	-1.31576
H	4.90803	-1.55518	-1.91228
C	2.25677	-2.14655	-2.52800
H	2.61640	-3.16234	-2.37585
H	2.54907	-1.80168	-3.51804
H	1.17337	-2.12830	-2.44300
N	-0.45328	-2.58004	1.62051
N	-1.95291	-2.22295	0.14752
N	-1.74612	0.54129	-0.58926
N	0.42414	1.59464	0.43013
N	2.98674	0.12245	0.08954
N	2.81282	-1.26993	-1.51452
Ni	0.12443	-0.26338	-0.38755

^{1}2-Ni

Energy = -2609.728030
Enthalpy 0K = -2609.361258
Enthalpy 298K = -2609.341171
Free Energy 298K = -2609.407602
Nimag = 0 (41.4011 cm-1)

C	1.92071	0.66107	-0.21727
C	4.11405	1.14234	-0.08252
H	5.14933	0.95115	0.13635
C	3.49566	2.24236	-0.54313
H	3.87348	3.21104	-0.81666
C	1.18333	2.88561	-1.09917
H	0.92192	2.63828	-2.12967
H	1.64541	3.86770	-1.09437
C	-0.07237	2.90669	-0.28785
C	-0.63876	4.09152	0.15055
H	-0.12439	5.02590	-0.02085
C	-1.85812	4.04955	0.80026
H	-2.31088	4.95768	1.17335
C	-2.51488	2.83831	0.93575
H	-3.49257	2.78730	1.39017
C	-1.90252	1.69901	0.45284
C	-2.55195	0.38302	0.33022
C	-3.88410	0.13600	0.60065
H	-4.50272	0.89165	1.06093
C	-4.41533	-1.08885	0.23609
H	-5.45518	-1.31004	0.43305
C	-3.61388	-2.01357	-0.40838
H	-4.00660	-2.96329	-0.74106
C	-2.28044	-1.71280	-0.62082
C	-1.35522	-2.65243	-1.33952
H	-1.83681	-3.61092	-1.50301
H	-1.09097	-2.22656	-2.30796
C	0.57986	-1.86827	-0.03938
C	0.29649	-4.09248	-0.12981
H	-0.16747	-5.01264	-0.43653
C	1.34472	-3.84567	0.68080
H	1.99116	-4.50799	1.22818
C	2.51567	-1.79617	1.49637
H	3.02056	-2.54841	2.09621
H	2.04760	-1.08061	2.16981
C	3.53264	-1.13001	0.60521
H	4.44644	-0.98229	1.17508
H	3.76473	-1.77109	-0.24523
N	3.14227	0.18970	0.11671
N	2.16114	1.93165	-0.61160
N	-0.67323	1.73613	-0.09297
N	-1.76143	-0.54990	-0.22608
N	-0.15453	-2.86666	-0.55796
N	1.49243	-2.47856	0.72743

Ni 0.11811 -0.03803 -0.22078

^{3}2-Ni

Energy = -2609.701011
Enthalpy 0K = -2609.336241
Enthalpy 298K = -2609.315456
Free Energy 298K = -2609.384651
Nimag = 0 (45.8192 cm-1)

C 2.11655 0.49419 -0.32877
C 4.31082 0.70473 0.08944
H 5.30190 0.36945 0.33846
C 3.83398 1.93685 -0.17736
H 4.32066 2.89510 -0.21217
C 1.63522 2.87030 -0.87582
H 1.46008 2.75331 -1.94670
H 2.18255 3.79627 -0.72889
C 0.29779 2.97292 -0.19312
C -0.13231 4.19142 0.30633
H 0.53068 5.04447 0.28941
C -1.41332 4.28998 0.81651
H -1.77028 5.22663 1.22207
C -2.24168 3.18307 0.79268
H -3.25006 3.25251 1.17026
C -1.74873 1.99487 0.27921
C -2.57075 0.76246 0.15487
C -3.92526 0.72361 0.44347
H -4.44412 1.59721 0.80572
C -4.61212 -0.46016 0.24645
H -5.66929 -0.51708 0.46673
C -3.93780 -1.56651 -0.23697
H -4.44758 -2.50393 -0.40684
C -2.58346 -1.45939 -0.50299
C -1.82020 -2.62153 -1.08441
H -2.45814 -3.49959 -1.11328
H -1.53140 -2.37941 -2.10778
C 0.34475 -2.07988 -0.03498
C -0.32790 -4.21209 0.15880
H -0.98100 -5.05521 0.02042
C 0.86794 -4.10181 0.77482
H 1.46872 -4.83141 1.28811
C 2.49310 -2.24254 1.19585
H 3.02266 -3.07595 1.64923
H 2.25359 -1.53044 1.98396
C 3.40036 -1.60628 0.15232
H 4.43210 -1.76382 0.45436
H 3.26020 -2.08836 -0.81401
N 3.24583 -0.16243 -0.00683
N 2.49008 1.78287 -0.42565
N -0.49338 1.89931 -0.17953
N -1.92595 -0.31635 -0.30336
N -0.62612 -2.95980 -0.32655
N 1.25823 -2.78754 0.64475
Ni 0.16985 -0.09026 -0.35846

^{1}3-Ni

Energy = -2570.413937
Enthalpy 0K = -2570.076303
Enthalpy 298K = -2570.057325
Free Energy 298K = -2570.121306
Nimag = 0 (50.9048 cm-1)

C -1.50850 1.28212 0.04242
C -3.44724 2.35477 -0.28698
H -4.48140 2.45658 -0.56349
C -2.54768 3.26049 0.14488
H -2.64019 4.31419 0.33835
C -0.15670 3.18433 0.86525
H -0.13506 3.04150 1.94771
H -0.20545 4.25117 0.66898
C 1.11972 2.62945 0.29555
C 2.18008 3.48174 0.03096
H 2.05205 4.54704 0.15750
C 3.38212 2.95066 -0.39361
H 4.21621 3.59983 -0.62113
C 3.51696 1.57807 -0.51230
H 4.45453 1.14253 -0.82137
C 2.42834 0.78069 -0.22135
C 2.45916 -0.69522 -0.20823
C 3.58901 -1.44943 -0.45305
H 4.51984 -0.97864 -0.72982
C 3.50667 -2.82542 -0.32377

H	4.37374	-3.44170	-0.51694
C	2.31423	-3.40147	0.06692
H	2.22497	-4.47026	0.19739
C	1.21398	-2.59010	0.29750
C	-0.05066	-3.19653	0.83975
H	-0.05751	-4.26147	0.62867
H	-0.04880	-3.06897	1.92440
C	-1.46229	-1.33457	0.02530
C	-2.43129	-3.34946	0.09977
H	-2.48703	-4.40801	0.28020
C	-3.36084	-2.47069	-0.32387
H	-4.39005	-2.60534	-0.60485
C	-3.36668	-0.05277	-0.90471
H	-3.23328	-0.04123	-1.98508
H	-4.42631	-0.07443	-0.66861
N	-2.78754	1.14624	-0.33954
N	-1.36545	2.58030	0.33579
N	1.24543	1.31050	0.14452
N	1.29057	-1.26852	0.13881
N	-1.27430	-2.63030	0.30338
N	-2.74418	-1.23901	-0.35899
Ni	-0.16280	-0.00419	0.15421

^{3}3-Ni

Energy	= -2570.368959
Enthalpy 0K	= -2570.033660
Enthalpy 298K	= -2570.013942
Free Energy 298K	= -2570.081216
Nimag	= 0 (40.7640 cm-1)

C	-1.53983	1.48522	0.34172
C	-3.21124	2.52810	-0.72574
H	-4.17910	2.62805	-1.18401
C	-2.21567	3.42337	-0.55131
H	-2.14109	4.45951	-0.82978
C	0.04741	3.34259	0.55850
H	0.01276	3.41059	1.64708
H	0.09841	4.35473	0.16890
C	1.31532	2.61082	0.17269
C	2.43581	3.36220	-0.14895
H	2.36746	4.43986	-0.18783
C	3.62533	2.71278	-0.41195
H	4.51429	3.27799	-0.65622
C	3.67047	1.33023	-0.37795
H	4.59354	0.81664	-0.59571
C	2.51381	0.63427	-0.07280
C	2.44221	-0.85494	-0.08605
C	3.51342	-1.65016	-0.45568
H	4.46768	-1.21998	-0.71540
C	3.33788	-3.02130	-0.50681
H	4.15779	-3.66180	-0.80141
C	2.10534	-3.56222	-0.19795
H	1.93492	-4.62805	-0.24790
C	1.07438	-2.71556	0.17958
C	-0.24497	-3.32418	0.60421
H	-0.29090	-4.34804	0.24604
H	-0.27143	-3.35447	1.69459
C	-1.66548	-1.34038	0.36188
C	-2.51029	-3.22398	-0.50333
H	-2.52759	-4.26651	-0.76683
C	-3.42282	-2.24665	-0.69167
H	-4.39604	-2.26687	-1.14896
C	-3.60940	0.15843	-0.04309
H	-4.36127	0.18658	-0.82608
H	-4.09930	0.18655	0.92788
N	-2.77074	1.34013	-0.17806
N	-1.20014	2.75461	0.09699
N	1.37334	1.27882	0.21942
N	1.25854	-1.39490	0.24256
N	-1.44008	-2.63846	0.13692
N	-2.87864	-1.09449	-0.16119
Ni	-0.22308	0.01333	0.57526

^{2}1-Ni + 1e^{-}

Energy	= -2611.048715
Enthalpy 0K	= -2610.665293
Enthalpy 298K	= -2610.642965
Free Energy 298K	= -2610.714533
Nimag	= 0 (47.8587 cm-1)

C	3.01123	0.14896	-1.83040
H	3.69558	-0.36609	-1.15704

H	3.55405	0.46657	-2.71692
H	2.21184	-0.52448	-2.12445
C	1.35438	1.34698	-0.40210
C	2.98802	2.58390	-1.30670
H	3.86461	2.77489	-1.89969
C	2.20397	3.41530	-0.59087
H	2.25773	4.47615	-0.42316
C	0.14582	3.11611	0.80985
H	0.14201	4.20121	0.76622
H	0.37180	2.81993	1.83696
C	-1.21692	2.58462	0.45437
C	-2.30663	3.41020	0.53490
H	-2.17084	4.46063	0.74881
C	-3.59575	2.85902	0.36628
H	-4.46907	3.49544	0.41710
C	-3.72967	1.51813	0.15834
H	-4.70919	1.07441	0.05117
C	-2.57986	0.70364	0.08053
C	-2.57986	-0.70362	-0.08053
C	-3.72968	-1.51810	-0.15834
H	-4.70920	-1.07437	-0.05117
C	-3.59577	-2.85899	-0.36628
H	-4.46910	-3.49541	-0.41709
C	-2.30666	-3.41018	-0.53490
H	-2.17088	-4.46061	-0.74881
C	-1.21694	-2.58461	-0.45437
C	0.14579	-3.11611	-0.80985
H	0.14197	-4.20122	-0.76621
H	0.37177	-2.81993	-1.83696
C	1.35437	-1.34699	0.40209
C	2.20393	-3.41532	0.59088
H	2.25767	-4.47617	0.42318
C	2.98801	-2.58392	1.30669
H	3.86460	-2.77492	1.89967
C	3.01122	-0.14899	1.83041
H	3.69556	0.36607	1.15704
H	3.55405	-0.46660	2.71692
H	2.21184	0.52446	2.12447
N	2.44863	1.32263	-1.18629
N	1.20774	2.63515	-0.05253
N	-1.32740	1.26714	0.18604
N	-1.32741	-1.26713	-0.18604
N	1.20772	-2.63516	0.05253
N	2.44861	-1.32265	1.18630
Ni	0.09301	-0.00000	-0.00000

^{2}1'-Ni + 1e^{-}

Energy	= -2611.046579
Enthalpy 0K	= -2610.665234
Enthalpy 298K	= -2610.641372
Free Energy 298K	= -2610.719259
Nimag	= 0 (20.8936 cm-1)

C	-0.93492	-2.89424	2.36549
H	-1.01946	-3.97980	2.35953
H	-1.09574	-2.52698	3.37857
H	0.05903	-2.60575	2.03447
C	-1.61859	-1.41193	0.50236
C	-3.25490	-2.60834	1.49827
H	-3.67343	-3.30854	2.19969
C	-3.83570	-1.86623	0.53414
H	-4.86114	-1.79115	0.21755
C	-2.99957	-0.22594	-1.17054
H	-4.05789	-0.18886	-1.41292
H	-2.46493	-0.61320	-2.03924
C	-2.49598	1.16087	-0.86346
C	-3.31359	2.26970	-0.99808
H	-4.34192	2.14822	-1.30828
C	-2.79000	3.52230	-0.72402
H	-3.40716	4.40598	-0.81330
C	-1.47192	3.63111	-0.32346
H	-1.05116	4.59802	-0.09181
C	-0.71002	2.47567	-0.21266
C	0.71000	2.47567	0.21266
C	1.47189	3.63112	0.32346
H	1.05113	4.59803	0.09181
C	2.78998	3.52232	0.72402
H	3.40713	4.40599	0.81330
C	3.31358	2.26972	0.99808
H	4.34191	2.14824	1.30828
C	2.49597	1.16089	0.86346
C	2.99957	-0.22592	1.17054
H	4.05789	-0.18884	1.41292

H	2.46493	-0.61318	2.03924
C	1.61860	-1.41192	-0.50236
C	3.83571	-1.86621	-0.53414
H	4.86115	-1.79113	-0.21755
C	3.25491	-2.60834	-1.49826
H	3.67345	-3.30854	-2.19968
C	0.93493	-2.89423	-2.36549
H	1.01948	-3.97979	-2.35952
H	1.09576	-2.52697	-3.37857
H	-0.05901	-2.60575	-2.03448
N	-1.90716	-2.31779	1.46010
N	-2.82201	-1.14615	-0.05920
N	-1.22184	1.26869	-0.48151
N	1.22183	1.26869	0.48150
N	2.82202	-1.14614	0.05920
N	1.90717	-2.31778	-1.46010
Ni	0.00000	-0.36354	-0.00000

^{4}1-Ni + 1e^{-}

Energy	= -2611.013911
Enthalpy 0K	= -2610.633779
Enthalpy 298K	= -2610.609919
Free Energy 298K	= -2610.687347
Nimag	= 0 (32.9187 cm-1)

C	-0.39552	-3.24159	1.87782
H	-0.27357	-4.26469	1.52604
H	-0.54936	-3.24626	2.95543
H	0.49648	-2.66884	1.64280
C	-1.47004	-1.53618	0.43678
C	-2.82196	-3.09530	1.31765
H	-3.07556	-3.95907	1.90643
C	-3.58867	-2.27237	0.57226
H	-4.64514	-2.27701	0.36999
C	-3.14309	-0.30283	-0.90938
H	-4.22785	-0.31515	-0.96596
H	-2.75506	-0.58514	-1.89046
C	-2.67149	1.09590	-0.59736
C	-3.54569	2.14527	-0.73018
H	-4.58589	1.96236	-0.95786
C	-3.04506	3.45931	-0.58704
H	-3.70811	4.30707	-0.70017
C	-1.72388	3.65298	-0.31589
H	-1.33328	4.65575	-0.22096
C	-0.86462	2.53762	-0.15315
C	0.51979	2.63059	0.15279
C	1.22122	3.85058	0.32105
H	0.69929	4.79197	0.23010
C	2.55636	3.83481	0.59267
H	3.09926	4.76350	0.71059
C	3.22909	2.59953	0.73074
H	4.28437	2.55829	0.95895
C	2.50364	1.44263	0.59333
C	3.15929	0.11960	0.90423
H	4.23601	0.25268	0.95538
H	2.81758	-0.20958	1.88796
C	1.66271	-1.32618	-0.43856
C	3.85876	-1.78318	-0.56599
H	4.90649	-1.64985	-0.36210
C	3.20679	-2.70118	-1.30969
H	3.57164	-3.52653	-1.89515
C	0.81922	-3.16217	-1.87087
H	0.78357	-4.17177	-1.46451
H	1.01099	-3.21009	-2.94118
H	-0.13110	-2.66685	-1.69619
N	-1.53128	-2.62588	1.21900
N	-2.74126	-1.32394	0.04713
N	-1.37276	1.26681	-0.29776
N	1.19394	1.43927	0.29289
N	2.89454	-0.94945	-0.04753
N	1.86626	-2.40123	-1.21682
Ni	0.01472	-0.21667	-0.00553

^{2}2-Ni + 1e^{-}

Energy	= -2609.840863
Enthalpy 0K	= -2609.477192
Enthalpy 298K	= -2609.456876
Free Energy 298K	= -2609.524146
Nimag	= 0 (46.4592 cm-1)

C	1.89393	0.75062	-0.20899
C	4.06325	1.33662	-0.03883
H	5.10358	1.19405	0.19284
C	3.39750	2.40901	-0.49950
H	3.73156	3.39724	-0.76015
C	1.05824	2.93270	-1.09367
H	0.81735	2.64861	-2.12024
H	1.47688	3.93438	-1.10846
C	-0.19906	2.90592	-0.28436
C	-0.81958	4.06345	0.10302
H	-0.35224	5.01770	-0.09194
C	-2.07897	3.97688	0.73885
H	-2.57927	4.87432	1.07747
C	-2.67388	2.75869	0.88439
H	-3.65900	2.67471	1.32092
C	-2.00787	1.59753	0.43505
C	-2.56490	0.30423	0.33749
C	-3.89691	-0.05521	0.63874
H	-4.54953	0.65993	1.11939
C	-4.35730	-1.29003	0.28936
H	-5.37861	-1.57414	0.50510
C	-3.49852	-2.18930	-0.38463
H	-3.84730	-3.15549	-0.71909
C	-2.20120	-1.81658	-0.60745
C	-1.24353	-2.70071	-1.35303
H	-1.68031	-3.67802	-1.53320
H	-0.99705	-2.24514	-2.31326
C	0.66222	-1.84671	-0.06114
C	0.48079	-4.08323	-0.16553
H	0.05933	-5.02178	-0.47797
C	1.51930	-3.79631	0.64443
H	2.19666	-4.43343	1.18439
C	2.58950	-1.70046	1.48132
H	3.12784	-2.43363	2.07614
H	2.08345	-1.01660	2.16056
C	3.58059	-0.97140	0.60877
H	4.48283	-0.79184	1.18829
H	3.84856	-1.58901	-0.24889
N	3.13489	0.33603	0.13785
N	2.08109	2.03384	-0.59009
N	-0.72589	1.68917	-0.06446
N	-1.71029	-0.62598	-0.21153
N	-0.02580	-2.87589	-0.58421
N	1.60550	-2.42341	0.69962
Ni	0.12061	-0.03259	-0.21242

^{2}2'-Ni + 1e^{-}

Energy = -2609.835918
Enthalpy 0K = -2609.473327
Enthalpy 298K = -2609.452032
Free Energy 298K = -2609.523763
Nimag = 0 (8.5863 cm-1)

C	2.15403	0.28133	-0.41922
C	4.30262	0.30516	0.28833
H	5.22773	-0.11660	0.63961
C	3.95453	1.58120	0.03268
H	4.51106	2.49834	0.11148
C	1.91886	2.70366	-0.87163
H	1.75024	2.59394	-1.94452
H	2.55198	3.57423	-0.72498
C	0.58273	2.94265	-0.21577
C	0.26249	4.20720	0.25380
H	1.00290	4.99449	0.23523
C	-1.01357	4.43662	0.73392
H	-1.29250	5.41177	1.10956
C	-1.93560	3.40713	0.71561
H	-2.94225	3.57877	1.06359
C	-1.54073	2.16392	0.24232
C	-2.47011	1.00518	0.15505
C	-3.79589	1.06752	0.56449
H	-4.20984	1.96955	0.98831
C	-4.59029	-0.05417	0.42085
H	-5.62539	-0.03177	0.73358
C	-4.04490	-1.20452	-0.12176
H	-4.63609	-2.10087	-0.24633
C	-2.71355	-1.19412	-0.50283
C	-2.07130	-2.41482	-1.10867
H	-2.79167	-3.22662	-1.15536
H	-1.75054	-2.18441	-2.12514
C	0.13473	-2.08630	-0.05590
C	-0.75903	-4.15477	0.13942
H	-1.49636	-4.92579	0.00144

C	0.44159	-4.17202	0.75338
H	0.96198	-4.96256	1.26474
C	2.25793	-2.49995	1.16090
H	2.71036	-3.39332	1.58485
H	2.10816	-1.78587	1.97006
C	3.20934	-1.92309	0.11772
H	4.22516	-2.19786	0.39110
H	3.00064	-2.35907	-0.85806
N	3.19728	-0.47000	0.00662
N	2.64556	1.54191	-0.39576
N	-0.29580	1.94028	-0.19466
N	-1.94935	-0.10892	-0.36724
N	-0.92234	-2.87511	-0.34476
N	0.96759	-2.90348	0.62138
Ni	0.19610	-0.12843	-0.42908

^{4}2-Ni + 1e^{-}

Energy = -2609.807766
Enthalpy 0K = -2609.446145
Enthalpy 298K = -2609.425104
Free Energy 298K = -2609.495011
Nimag = 0 (43.9558 cm-1)

C	2.13189	0.45197	-0.33937
C	4.32179	0.62016	0.13729
H	5.30026	0.26486	0.40789
C	3.87182	1.86277	-0.12870
H	4.37590	2.81267	-0.14134
C	1.69929	2.83881	-0.86898
H	1.52746	2.71197	-1.93967
H	2.26878	3.75296	-0.72909
C	0.36371	2.96918	-0.18686
C	-0.03648	4.19229	0.28544
H	0.63997	5.03437	0.25777
C	-1.35309	4.32545	0.78451
H	-1.69450	5.27729	1.16962
C	-2.19110	3.25156	0.76217
H	-3.20437	3.34819	1.12478
C	-1.73281	2.00691	0.26519
C	-2.53802	0.84062	0.15857
C	-3.91642	0.78377	0.48072
H	-4.42049	1.66225	0.85683
C	-4.60846	-0.37684	0.30344
H	-5.66213	-0.42595	0.54507
C	-3.94401	-1.51635	-0.20490
H	-4.46747	-2.44812	-0.36362
C	-2.60905	-1.41485	-0.49890
C	-1.87012	-2.58158	-1.10253
H	-2.51949	-3.45107	-1.14527
H	-1.56899	-2.32992	-2.12046
C	0.31074	-2.08998	-0.06353
C	-0.41815	-4.20381	0.15441
H	-1.09271	-5.03120	0.02339
C	0.77653	-4.11832	0.77666
H	1.35448	-4.85707	1.30302
C	2.44469	-2.29833	1.18801
H	2.95667	-3.14370	1.64001
H	2.21819	-1.58400	1.97829
C	3.36769	-1.67377	0.15072
H	4.39548	-1.85721	0.45210
H	3.21774	-2.14614	-0.81901
N	3.24425	-0.22698	0.00366
N	2.53251	1.73430	-0.41287
N	-0.43362	1.88470	-0.17436
N	-1.90745	-0.28150	-0.31922
N	-0.67987	-2.95082	-0.34901
N	1.20181	-2.81605	0.63137
Ni	0.15175	-0.07905	-0.37419

^{2}3-Ni + 1e^{-}

Energy = -2570.526508
Enthalpy 0K = -2570.192106
Enthalpy 298K = -2570.172848
Free Energy 298K = -2570.238120
Nimag = 0 (38.2907 cm-1)

C	-1.49175	1.30136	0.04424
C	-3.41977	2.39213	-0.31181
H	-4.45025	2.50278	-0.59861
C	-2.51442	3.29162	0.12201

H	-2.59931	4.34742	0.30757
C	-0.12480	3.17996	0.87641
H	-0.11485	3.00051	1.95382
H	-0.16564	4.25283	0.71329
C	1.14455	2.62330	0.28915
C	2.19444	3.46409	0.02764
H	2.07504	4.53059	0.15185
C	3.42651	2.90923	-0.38607
H	4.26472	3.55665	-0.60651
C	3.55560	1.55611	-0.48903
H	4.49652	1.11401	-0.78406
C	2.45078	0.72447	-0.20390
C	2.46244	-0.69026	-0.19944
C	3.58445	-1.50479	-0.46631
H	4.52362	-1.04843	-0.74508
C	3.47550	-2.85956	-0.36118
H	4.32715	-3.49405	-0.56721
C	2.24716	-3.43287	0.03768
H	2.14274	-4.50100	0.16150
C	1.18216	-2.60779	0.28895
C	-0.08232	-3.18499	0.86693
H	-0.10714	-4.25736	0.69737
H	-0.07928	-3.01195	1.94544
C	-1.47348	-1.32200	0.03940
C	-2.46817	-3.32675	0.10666
H	-2.53843	-4.38446	0.28729
C	-3.38548	-2.43808	-0.32422
H	-4.41398	-2.56185	-0.61279
C	-3.35373	-0.02125	-0.91492
H	-3.20431	-0.01746	-1.99364
H	-4.41752	-0.02961	-0.69640
N	-2.77133	1.17571	-0.34836
N	-1.34101	2.60092	0.32905
N	1.24008	1.28744	0.14360
N	1.25839	-1.27098	0.14222
N	-1.30481	-2.62059	0.31841
N	-2.75420	-1.21252	-0.35425
Ni	-0.16025	-0.00150	0.16137

^{2}3'-Ni + 1e^{-}

Energy = -2570.507214
Enthalpy 0K = -2570.173954
Enthalpy 298K = -2570.153881
Free Energy 298K = -2570.222460
Nimag = 0 (18.1633 cm-1)

C	-1.12355	-1.86384	-0.46165
C	-2.37299	-3.11704	0.95106
H	-3.24371	-3.38498	1.52327
C	-1.17926	-3.73010	0.81527
H	-0.79878	-4.63840	1.24816
C	0.90005	-3.23536	-0.51644
H	0.87300	-3.34627	-1.60190
H	1.20872	-4.18984	-0.09872
C	1.94405	-2.19238	-0.17721
C	3.23573	-2.62155	0.09403
H	3.45684	-3.67946	0.12004
C	4.21983	-1.68075	0.32194
H	5.23808	-1.98643	0.52054
C	3.88467	-0.33912	0.30931
H	4.64244	0.40585	0.49466
C	2.56891	0.01959	0.05999
C	2.10698	1.43403	0.11170
C	2.91888	2.45866	0.57735
H	3.93338	2.26939	0.89151
C	2.40070	3.73708	0.65729
H	3.01105	4.55108	1.02415
C	1.08865	3.95586	0.28303
H	0.64560	4.93956	0.34943
C	0.33436	2.88812	-0.17877
C	-1.08232	3.14121	-0.64572
H	-1.39510	4.12707	-0.31362
H	-1.09261	3.13983	-1.73670
C	-1.95978	0.86583	-0.46820
C	-3.18744	2.45446	0.56587
H	-3.43608	3.44797	0.89517
C	-3.82228	1.27717	0.74481
H	-4.73663	1.03874	1.25925
C	-3.43080	-1.07440	-0.04330
H	-4.20343	-1.30378	0.68386
H	-3.82695	-1.22394	-1.04559
N	-2.32000	-1.98203	0.16593
N	-0.43925	-2.94934	-0.04995

N	1.62760	-0.89774	-0.20864
N	0.84333	1.65697	-0.27240
N	-2.05688	2.17551	-0.17527
N	-3.05451	0.32080	0.10948
Ni	-0.25515	-0.09645	-0.68570

^{4}3-Ni + 1e^{-}

Energy	= -2570.477033
Enthalpy 0K	= -2570.144966
Enthalpy 298K	= -2570.124979
Free Energy 298K	= -2570.193047
Nimag	= 0 (36.0049 cm-1)

C	-1.59398	1.43513	0.37499
C	-3.26139	2.41986	-0.76011
H	-4.21493	2.48619	-1.25322
C	-2.30138	3.34734	-0.55470
H	-2.24992	4.38377	-0.83745
C	-0.06284	3.32896	0.62508
H	-0.10220	3.32701	1.71552
H	-0.05619	4.36302	0.29388
C	1.21913	2.65475	0.18532
C	2.27125	3.43980	-0.21218
H	2.15397	4.51149	-0.28397
C	3.50614	2.81837	-0.50345
H	4.35994	3.41750	-0.79159
C	3.61198	1.46198	-0.43172
H	4.55097	0.98188	-0.66537
C	2.48578	0.68321	-0.06814
C	2.46836	-0.74071	-0.06986
C	3.57354	-1.54515	-0.44127
H	4.52120	-1.08642	-0.68213
C	3.43578	-2.89860	-0.51412
H	4.27349	-3.51699	-0.80869
C	2.18824	-3.49126	-0.21688
H	2.04549	-4.55984	-0.28891
C	1.15618	-2.68217	0.18492
C	-0.14035	-3.32624	0.62735
H	-0.15871	-4.36042	0.29673
H	-0.17793	-3.32268	1.71787
C	-1.62658	-1.39689	0.37502
C	-2.38164	-3.29469	-0.54647
H	-2.35546	-4.33291	-0.82608
C	-3.32000	-2.34541	-0.75226
H	-4.27605	-2.39057	-1.24285
C	-3.60467	0.04209	-0.07471
H	-4.34391	0.04997	-0.87026
H	-4.11275	0.04871	0.88754
N	-2.80220	1.24960	-0.18937
N	-1.29091	2.71535	0.13564
N	1.31214	1.31419	0.28008
N	1.28103	-1.34413	0.28088
N	-1.35455	-2.68470	0.13915
N	-2.83131	-1.18453	-0.18707
Ni	-0.20706	0.00278	0.60939

^{1}1-Ni + 2e^{-}

Energy	= -2611.138721
Enthalpy 0K	= -2610.758103
Enthalpy 298K	= -2610.735387
Free Energy 298K	= -2610.807059
Nimag	= 0 (51.4608 cm-1)

C	3.01038	0.17952	-1.82905
H	3.69001	-0.35078	-1.16198
H	3.55721	0.50251	-2.71164
H	2.20714	-0.48697	-2.13009
C	1.34072	1.35814	-0.40393
C	3.00732	2.60369	-1.25361
H	3.89561	2.80031	-1.82728
C	2.22001	3.42489	-0.52965
H	2.28258	4.48108	-0.33639
C	0.13972	3.10380	0.84493
H	0.14595	4.19031	0.83775
H	0.36230	2.76520	1.86090
C	-1.21797	2.58570	0.45644
C	-2.28835	3.42557	0.47816
H	-2.14719	4.47739	0.68445
C	-3.60337	2.87677	0.28858
H	-4.46790	3.52851	0.29447
C	-3.74602	1.54442	0.10955
H	-4.72892	1.11442	-0.03638

C	-2.60150	0.68199	0.08276
C	-2.60150	-0.68199	-0.08276
C	-3.74602	-1.54442	-0.10955
H	-4.72892	-1.11442	0.03638
C	-3.60337	-2.87677	-0.28858
H	-4.46790	-3.52851	-0.29447
C	-2.28835	-3.42557	-0.47816
H	-2.14719	-4.47739	-0.68445
C	-1.21797	-2.58570	-0.45644
C	0.13972	-3.10380	-0.84493
H	0.14595	-4.19031	-0.83775
H	0.36230	-2.76520	-1.86090
C	1.34072	-1.35814	0.40393
C	2.22001	-3.42489	0.52965
H	2.28258	-4.48108	0.33639
C	3.00732	-2.60369	1.25362
H	3.89561	-2.80031	1.82728
C	3.01038	-0.17952	1.82905
H	3.69001	0.35077	1.16198
H	3.55721	-0.50251	2.71164
H	2.20714	0.48697	2.13009
N	2.45139	1.34507	-1.17193
N	1.20676	2.64257	-0.02638
N	-1.31458	1.24675	0.24016
N	-1.31458	-1.24675	-0.24016
N	1.20676	-2.64257	0.02638
N	2.45139	-1.34507	1.17193
Ni	0.08804	0.00000	0.00000

^{1}1'-Ni + 2e^{-}

Energy	= -2611.138254
Enthalpy 0K	= -2610.760455
Enthalpy 298K	= -2610.736321
Free Energy 298K	= -2610.813958
Nimag	= 0 (22.0701 cm-1)

C	0.91015	-2.87920	-2.39160
H	1.00163	-3.96441	-2.40694
H	1.05548	-2.49324	-3.40048
H	-0.08239	-2.60400	-2.04504
C	1.60340	-1.40991	-0.51936
C	3.23483	-2.60165	-1.53860
H	3.64844	-3.29643	-2.24840
C	3.82196	-1.86552	-0.57375
H	4.85035	-1.79209	-0.26605
C	3.00340	-0.23814	1.15273
H	4.06468	-0.21127	1.38585
H	2.47315	-0.63978	2.01872
C	2.49739	1.15304	0.86749
C	3.31716	2.24550	1.02042
H	4.34762	2.11919	1.32173
C	2.76977	3.52823	0.78529
H	3.38348	4.41215	0.90368
C	1.46904	3.64127	0.39037
H	1.04988	4.61642	0.18400
C	0.67342	2.47833	0.22636
C	-0.67340	2.47834	-0.22636
C	-1.46901	3.64128	-0.39037
H	-1.04984	4.61642	-0.18400
C	-2.76974	3.52825	-0.78529
H	-3.38344	4.41218	-0.90368
C	-3.31714	2.24553	-1.02042
H	-4.34760	2.11923	-1.32173
C	-2.49738	1.15306	-0.86749
C	-3.00340	-0.23812	-1.15273
H	-4.06468	-0.21124	-1.38585
H	-2.47316	-0.63976	-2.01872
C	-1.60341	-1.40989	0.51936
C	-3.82198	-1.86548	0.57375
H	-4.85037	-1.79204	0.26606
C	-3.23485	-2.60164	1.53859
H	-3.64847	-3.29643	2.24838
C	-0.91017	-2.87920	2.39159
H	-1.00158	-3.96442	2.40683
H	-1.05559	-2.49335	3.40050
H	0.08236	-2.60391	2.04511
N	1.88688	-2.31205	-1.48670
N	2.81400	-1.14932	0.03349
N	1.20916	1.24147	0.50447
N	-1.20915	1.24148	-0.50447
N	-2.81400	-1.14929	-0.03349
N	-1.88690	-2.31203	1.48670
Ni	-0.00000	-0.35141	0.00000

^{3}1-Ni + 2e$^-$

Energy = -2611.135642
Enthalpy 0K = -2610.758212
Enthalpy 298K = -2610.733992
Free Energy 298K = -2610.812667
Nimag = 0 (22.1248 cm-1)

C	0.99467	-2.85444	-2.45942
H	1.17303	-3.92408	-2.55996
H	1.06994	-2.38522	-3.44021
H	-0.00301	-2.68909	-2.06171
C	1.64282	-1.44646	-0.52548
C	3.31885	-2.47535	-1.64521
H	3.75655	-3.10459	-2.40025
C	3.88372	-1.75562	-0.65489
H	4.91316	-1.63409	-0.36647
C	3.01115	-0.26364	1.16254
H	4.06928	-0.22450	1.40788
H	2.48302	-0.70289	2.01076
C	2.48167	1.13056	0.92367
C	3.26362	2.23191	1.19934
H	4.27998	2.11224	1.54698
C	2.68999	3.50992	1.01638
H	3.26493	4.40041	1.23774
C	1.41008	3.61786	0.55608
H	0.96942	4.59485	0.41488
C	0.66158	2.44710	0.25915
C	-0.66158	2.44710	-0.25915
C	-1.41009	3.61786	-0.55608
H	-0.96943	4.59485	-0.41487
C	-2.69000	3.50991	-1.01637
H	-3.26494	4.40040	-1.23774
C	-3.26362	2.23190	-1.19933
H	-4.27998	2.11223	-1.54698
C	-2.48167	1.13055	-0.92367
C	-3.01115	-0.26365	-1.16254
H	-4.06929	-0.22450	-1.40787
H	-2.48304	-0.70290	-2.01076
C	-1.64281	-1.44646	0.52548
C	-3.88372	-1.75557	0.65494
H	-4.91316	-1.63400	0.36655
C	-3.31883	-2.47544	1.64515
H	-3.75652	-3.10473	2.40014
C	-0.99467	-2.85442	2.45943
H	-1.17299	-3.92408	2.55994
H	-1.06997	-2.38524	3.44023
H	0.00302	-2.68904	2.06175
N	1.95741	-2.27654	-1.54597
N	2.84874	-1.14081	0.01463
N	1.22685	1.21234	0.47730
N	-1.22686	1.21233	-0.47730
N	-2.84874	-1.14082	-0.01463
N	-1.95741	-2.27654	1.54597
Ni	0.00000	-0.41847	-0.00000

^{1}2-Ni + 2e$^-$

Energy = -2609.929885
Enthalpy 0K = -2609.568976
Enthalpy 298K = -2609.548294
Free Energy 298K = -2609.615576
Nimag = 0 (50.4879 cm-1)

C	1.81942	0.91984	-0.20911
C	3.92715	1.71124	-0.02932
H	4.97579	1.66785	0.20470
C	3.16356	2.71463	-0.49408
H	3.40365	3.72992	-0.75452
C	0.77826	2.99770	-1.10522
H	0.56163	2.65590	-2.12071
H	1.09983	4.03425	-1.15440
C	-0.46436	2.86826	-0.28197
C	-1.18969	3.97316	0.04750
H	-0.82196	4.95889	-0.19995
C	-2.45832	3.78826	0.70413
H	-3.03105	4.64844	1.02804
C	-2.94113	2.53828	0.87212
H	-3.91560	2.37885	1.31707
C	-2.18393	1.39776	0.43024
C	-2.60450	0.10510	0.33244
C	-3.90493	-0.42459	0.64317
H	-4.62524	0.21426	1.13915
C	-4.23428	-1.68560	0.28959

H	-5.21896	-2.07947	0.50882
C	-3.27196	-2.50197	-0.40489
H	-3.52577	-3.48950	-0.76310
C	-2.01938	-2.00468	-0.59918
C	-0.98998	-2.79396	-1.35594
H	-1.33572	-3.80550	-1.54827
H	-0.78006	-2.30465	-2.30963
C	0.82904	-1.78167	-0.06349
C	0.86555	-4.02726	-0.18864
H	0.53410	-4.99938	-0.50729
C	1.87741	-3.65056	0.61826
H	2.61647	-4.22558	1.14703
C	2.74001	-1.46534	1.47172
H	3.34679	-2.14489	2.06467
H	2.17012	-0.83578	2.15353
C	3.65939	-0.63694	0.60683
H	4.54061	-0.38051	1.19006
H	3.98556	-1.22314	-0.25314
N	3.09600	0.62575	0.14352
N	1.88895	2.21510	-0.59108
N	-0.84397	1.60143	0.00342
N	-1.61906	-0.78102	-0.17635
N	0.24285	-2.86990	-0.59311
N	1.83111	-2.27480	0.68649
Ni	0.12374	-0.02378	-0.18419

^{1}2'-Ni + 2e^{-}

Energy	= -2609.927269
Enthalpy 0K	= -2609.567826
Enthalpy 298K	= -2609.546477
Free Energy 298K	= -2609.615936
Nimag	= 0 (41.3297 cm-1)

C	1.91650	1.02032	-0.47000
C	3.89373	1.79694	0.32455
H	4.89916	1.72562	0.70046
C	3.11266	2.86777	0.08540
H	3.29637	3.92065	0.20820
C	0.82991	3.21413	-0.85447
H	0.70552	3.05871	-1.92830
H	1.12445	4.24899	-0.70135
C	-0.50324	2.96312	-0.19355
C	-1.25329	4.03649	0.23172
H	-0.84809	5.03776	0.19283
C	-2.56488	3.79097	0.69513
H	-3.18525	4.60995	1.03646
C	-3.05093	2.51704	0.68464
H	-4.06550	2.32542	1.00450
C	-2.22937	1.44754	0.24293
C	-2.66352	0.09662	0.14672
C	-3.93953	-0.36173	0.56608
H	-4.65193	0.33161	0.99042
C	-4.26779	-1.67942	0.44147
H	-5.23951	-2.03327	0.76163
C	-3.32388	-2.58108	-0.10005
H	-3.54641	-3.63336	-0.20760
C	-2.10439	-2.08272	-0.49458
C	-1.06765	-2.99326	-1.09718
H	-1.44267	-4.01210	-1.14376
H	-0.84146	-2.66378	-2.11280
C	0.86703	-1.89078	-0.02412
C	0.79815	-4.14914	0.12149
H	0.39214	-5.13343	-0.03248
C	1.92823	-3.74033	0.73305
H	2.70710	-4.29566	1.22535
C	3.02325	-1.53128	1.14724
H	3.76949	-2.20439	1.56267
H	2.64802	-0.90616	1.95716
C	3.68397	-0.66542	0.07817
H	4.73944	-0.56302	0.31852
H	3.61109	-1.15452	-0.89191
N	3.15463	0.68557	-0.02324
N	1.92094	2.37426	-0.39836
N	-0.93539	1.69681	-0.15369
N	-1.76288	-0.78931	-0.39604
N	0.17064	-3.00863	-0.33019
N	1.94929	-2.36440	0.63289
Ni	0.21206	-0.04549	-0.42312

^{3}2-Ni + 2e^{-}

Energy	= -2609.927270
Enthalpy 0K	= -2609.568119

Enthalpy 298K = -2609.546667
Free Energy 298K = -2609.617506
Nimag = 0 (42.8878 cm-1)

C	2.16762	0.22270	-0.44697
C	4.31332	0.17785	0.27893
H	5.22362	-0.27343	0.63263
C	4.00116	1.46590	0.03589
H	4.58226	2.36621	0.13165
C	1.99939	2.65804	-0.86303
H	1.82630	2.55943	-1.93659
H	2.66211	3.50572	-0.71006
C	0.67321	2.92334	-0.19422
C	0.41003	4.18061	0.30053
H	1.17474	4.94449	0.29025
C	-0.88566	4.44360	0.79948
H	-1.12898	5.41979	1.19942
C	-1.82875	3.45998	0.76125
H	-2.82661	3.65726	1.12663
C	-1.50030	2.17910	0.24524
C	-2.42767	1.10526	0.13966
C	-3.79832	1.19811	0.49898
H	-4.19771	2.12620	0.88294
C	-4.61656	0.11660	0.35437
H	-5.66232	0.18348	0.62663
C	-4.08960	-1.09163	-0.15334
H	-4.70815	-1.96943	-0.27646
C	-2.75562	-1.12326	-0.49111
C	-2.15094	-2.37486	-1.07742
H	-2.89084	-3.17048	-1.10466
H	-1.82970	-2.17280	-2.10043
C	0.09696	-2.10625	-0.09562
C	-0.90421	-4.10908	0.24160
H	-1.68409	-4.84580	0.16094
C	0.30359	-4.15654	0.83941
H	0.78914	-4.94279	1.39037
C	2.20862	-2.56716	1.13250
H	2.64234	-3.47495	1.54556
H	2.09903	-1.85029	1.94631
C	3.15593	-2.01452	0.07271
H	4.16773	-2.32736	0.31950
H	2.90935	-2.43373	-0.90156
N	3.18951	-0.56245	-0.02338
N	2.69591	1.46845	-0.40461
N	-0.22393	1.92827	-0.20611
N	-1.93295	-0.07554	-0.35713
N	-1.00551	-2.85551	-0.32083
N	0.89630	-2.92991	0.61961
Ni	0.18869	-0.13006	-0.45175

^{1}3-Ni + 2e^{-}

Energy = -2570.615306
Enthalpy 0K = -2570.283491
Enthalpy 298K = -2570.263970
Free Energy 298K = -2570.328768
Nimag = 0 (52.1156 cm-1)

C	1.48029	1.31248	-0.04863
C	3.40407	2.41605	0.32357
H	4.43203	2.53262	0.61729
C	2.49590	3.31084	-0.11412
H	2.57687	4.36762	-0.29640
C	0.10452	3.17157	-0.88740
H	0.09795	2.95800	-1.95963
H	0.14031	4.24929	-0.75480
C	-1.15717	2.61500	-0.28148
C	-2.19757	3.45830	-0.03068
H	-2.07973	4.52351	-0.17016
C	-3.45832	2.89441	0.37807
H	-4.29674	3.54633	0.58979
C	-3.59238	1.55430	0.47209
H	-4.54217	1.11793	0.75456
C	-2.48252	0.68324	0.19280
C	-2.48232	-0.68398	0.19276
C	-3.59194	-1.55538	0.47192
H	-4.54193	-1.11930	0.75421
C	-3.45747	-2.89545	0.37795
H	-4.29573	-3.54762	0.58954
C	-2.19650	-3.45897	-0.03064
H	-2.07830	-4.52414	-0.17006
C	-1.15636	-2.61534	-0.28143

C	0.10553	-3.17153	-0.88730
H	0.14164	-4.24923	-0.75468
H	0.09890	-2.95798	-1.95954
C	1.48078	-1.31199	-0.04867
C	2.49692	-3.31012	-0.11400
H	2.57815	-4.36689	-0.29624
C	3.40485	-2.41510	0.32369
H	4.43283	-2.53141	0.61743
C	3.34049	0.00053	0.92737
H	3.16937	0.00031	2.00365
H	4.40925	0.00057	0.73275
N	2.76193	1.19443	0.35163
N	1.32747	2.61387	-0.33015
N	-1.22812	1.27044	-0.12671
N	-1.22773	-1.27080	-0.12672
N	1.32831	-2.61345	-0.33006
N	2.76242	-1.19363	0.35157
Ni	0.15866	0.00004	-0.15856

^{1}3'-Ni + 2e^{-}

Energy = -2570.600175
Enthalpy 0K = -2570.270222
Enthalpy 298K = -2570.250779
Free Energy 298K = -2570.315937
Nimag = 0 (14.2793 cm-1)

C	1.63066	1.43007	-0.48861
C	3.19658	2.30980	0.89352
H	4.10490	2.32797	1.46985
C	2.24270	3.24680	0.71251
H	2.15150	4.24497	1.10353
C	0.10001	3.33241	-0.61822
H	0.13620	3.33936	-1.70898
H	0.10762	4.36472	-0.27836
C	-1.18880	2.66604	-0.18302
C	-2.23477	3.46507	0.22182
H	-2.10913	4.53637	0.29136
C	-3.46793	2.84890	0.52228
H	-4.32059	3.44812	0.81554
C	-3.57262	1.49146	0.45276
H	-4.51173	1.01508	0.69403
C	-2.44787	0.70917	0.08073
C	-2.44587	-0.71533	0.08114
C	-3.56802	-1.50048	0.45491
H	-4.50782	-1.02644	0.69801
C	-3.45985	-2.85764	0.52431
H	-4.31055	-3.45897	0.81891
C	-2.22550	-3.47069	0.22231
H	-2.09707	-4.54168	0.29159
C	-1.18189	-2.66899	-0.18328
C	0.10844	-3.33198	-0.61921
H	0.11883	-4.36444	-0.27985
H	0.14439	-3.33827	-1.70998
C	1.63450	-1.42596	-0.48950
C	2.25070	-3.24110	0.71195
H	2.16185	-4.23950	1.10292
C	3.20215	-2.30172	0.89326
H	4.11037	-2.31771	1.46981
C	3.59390	0.00455	-0.01161
H	4.38580	0.00545	0.73194
H	4.03818	0.00528	-1.00508
N	2.80607	1.21063	0.15371
N	1.30672	2.68990	-0.13458
N	-1.27320	1.33186	-0.27789
N	-1.26980	-1.33501	-0.27817
N	1.31365	-2.68664	-0.13555
N	2.80912	-1.20354	0.15330
Ni	0.26965	0.00025	-0.71212

^{3}3-Ni + 2e^{-}

Energy = -2570.600861
Enthalpy 0K = -2570.270664
Enthalpy 298K = -2570.250440
Free Energy 298K = -2570.318964
Nimag = 1 (35.6837 cm-1)

C	-1.63141	1.43008	0.48985
C	-3.19536	2.30939	-0.89460
H	-4.10280	2.32734	-1.47233
C	-2.24204	3.24671	-0.71195
H	-2.15051	4.24496	-1.10270
C	-0.10070	3.33175	0.62142

H	-0.13732	3.33636	1.71216
H	-0.10845	4.36480	0.28380
C	1.18765	2.66602	0.18456
C	2.23291	3.46499	-0.22077
H	2.10698	4.53637	-0.28903
C	3.46606	2.84951	-0.52418
H	4.31783	3.44925	-0.81889
C	3.57096	1.49232	-0.45547
H	4.50955	1.01604	-0.69902
C	2.44714	0.70915	-0.08157
C	2.44559	-0.71442	-0.08169
C	3.56766	-1.49997	-0.45580
H	4.50721	-1.02568	-0.69952
C	3.45985	-2.85693	-0.52449
H	4.31029	-3.45849	-0.81934
C	2.22542	-3.46978	-0.22096
H	2.09720	-4.54089	-0.28918
C	1.18189	-2.66858	0.18441
C	-0.10790	-3.33154	0.62129
H	-0.11793	-4.36455	0.28360
H	-0.14447	-3.33614	1.71203
C	-1.63423	-1.42635	0.48934
C	-2.24963	-3.24219	-0.71117
H	-2.16057	-4.24084	-1.10145
C	-3.20086	-2.30275	-0.89386
H	-4.10859	-2.31890	-1.47118
C	-3.59349	0.00396	0.00903
H	-4.38376	0.00474	-0.73629
H	-4.03999	0.00439	1.00147
N	-2.80556	1.21025	-0.15448
N	-1.30725	2.68985	0.13628
N	1.27185	1.33095	0.27850
N	1.26897	-1.33369	0.27835
N	-1.31309	-2.68701	0.13623
N	-2.80820	-1.20413	-0.15447
Ni	-0.26852	0.00034	0.71152