Supporting Information

Homogeneous CO2 Reduction by Ni(cyclam) on a Glassy Carbon Electrode

Jesse D. Froehlich and Clifford P. Kubiak*

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093-0358

S1 – Synthesis

Nickel(II) chloride hexahydrate, 1,4,8,11-tetraazacyclotetradecane (cyclam), 1,8-Dimethyl-1,4,8,11-tetraazacyclotetradecane (DMC) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) were purchased from Sigma-Aldrich and used without further purification. The nickel complexes were synthesized according to an adaptation of a literature report by combining 1 eq. $NiCl_2{\cdot}(H_2O)_6$ and 1.02 eq. ligand in ethanol (concentration: 0.1 to 0.2 M).[1] The products were precipitated upon the addition of ether.
Ni(cyclam)$(Cl)_2$. Anal. Calcd. for $C_{10}H_{24}Cl_2N_4Ni$: C, 36.40; H, 7.33; N, 16.98. Found: C, 36.45; H, 7.18; N, 16.82.
Ni(DMC)$(Cl)_2$. Anal. Calcd. for $C_{12}H_{28}Cl_2N_4Ni$: C, 40.26; H, 7.88; N, 15.65. Found: C, 40.31; H, 7.88; N, 15.69.
Ni(TMC)$(Cl)_2$. Anal. Calcd. for $C_{14}H_{32}Cl_2N_4Ni$: C, 43.56; H, 8.36;N, 14.51. Found: C, 43.81; H, 8.32; N, 14.39.

S2 – Electrochemistry

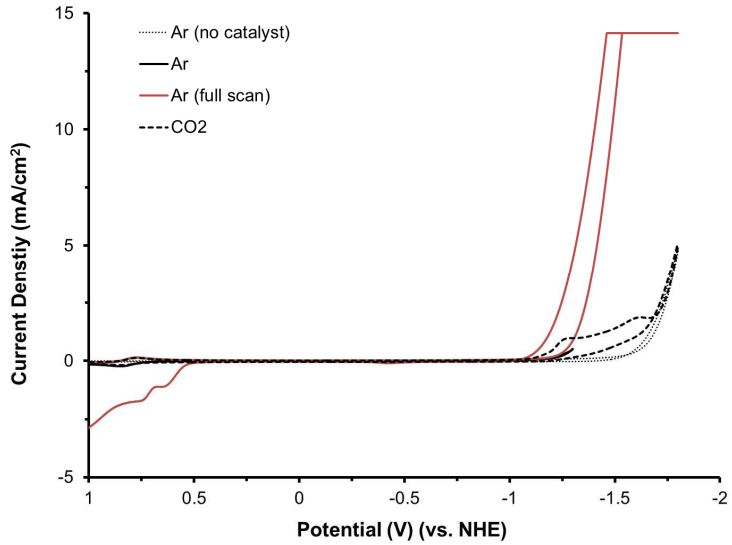


Figure S1. Same as Figure 1 with the inclusion of a full cathodic scan under argon: Cyclic voltammogram of 1 mM $Ni(cyclam)^{2+}$ in 0.1 M $KCl_{(aq)}$, GC electrode, 100 mV/s scan rate.

S2.1. Cyclic Voltammetry and Controlled Potential Electrolysis. They were performed using a BASi Epsilon potentiostat. A one compartment cell was used with a glassy carbon working electrode (3 mm in diameter from BASi), a Pt wire counter electrode, and a Ag/AgCl for aqueous solutions or a Ag/Ag^+ reference for the 1:4 water:acetonitrile solutions. All potentials are converted to NHE by the following conversion:
NHE = Ag/AgCl + 0.2 V
NHE = Ag/Ag^+ + 0.54 V

Gas analysis for controlled potential electrolysis experiments were performed using 1 mL sample taken from the headspace of the electrochemical cell and injected on a Hewlett-Packard 7890A Series gas chromatograph with a molsieve column (30 m x 0.53 mm ID x 25 μm film).

S2.2. Turnover Number (TON) Measurement. A controlled potential electrolysis experiment was run with a 25 mL solution consisting of a 1 mM Ni(cyclam) and 0.1M KCl saturated with CO_2. A carbon rod was used as the working electrode and carbon rod separated by a glass frit as the counter electrode. A total of 4 catalytic turnovers (verified by GC) were achieved after 3.5 hours of electrolysis at -1.2 V (vs. NHE).

S2.3. Turnover Frequency (TOF) Measurement.

S2.3.1. TOF – Controlled Potential Electrolysis Method. TOF was calculated using the following equation after a controlled potential electrolysis (same experiment to determine TON above):

mols CO produced/mols catalyst in bulk solution (Eq. 1)

The TOF calculated by this method was calculated to be 1.1 h^{-1} over 3.5 hours of electrolysis.

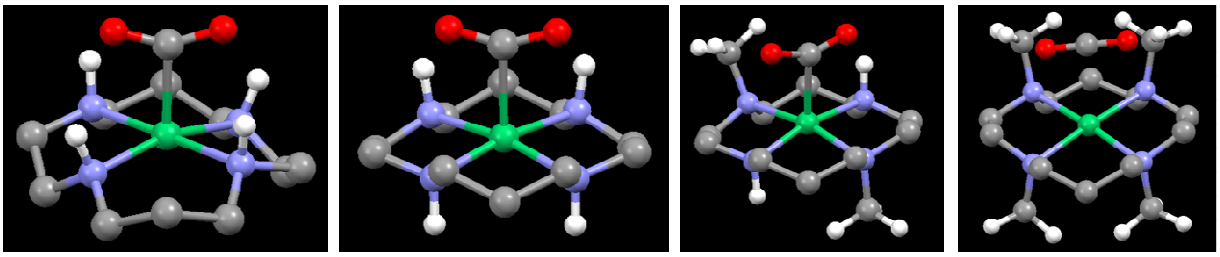
S2.3.2. TOF - Savéant Method. The TOF for Ni(cyclam) in water was determined using the electrochemical method described by Savéant.[2] A limiting current was found using a 11 μm diameter glassy carbon ultra-micro electrode, 1mM Ni(cyclam), 0.1M KCl and a scan rate of 10 mV/s. The catalytic current was then found and the following equation was used to find the rate constant for catalysis:

$$i_c = nFA[\text{cat}](Dk[CO_2])^{1/2} \qquad \text{(Eq. 2)}$$

In the equation above, i_c is the catalytic current (limiting current under CO_2 subtracted by the limiting current under Ar; used limiting current from Ni(II/III) couple since Ni(I/II) is covered by solvent window under Ar), n is the number of electrons (2 for this reaction reflecting the reduction of CO_2 to CO), F is Faraday's constant, A is the area of the electrode surface, [cat] the catalyst concentration (mols/cm^3 in Eq. 2) , D is the diffusion coefficient of the catalyst which was previously reported[3] as 5.6 x 10^{-6} cm^2s^{-1}, k is the rate constant (the variable of interest in this case), [CO_2] is the concentration of dissolved CO_2 which was assumed to be 36 mM[4] (mols/cm^3 in Eq. 2). A second order rate constant of 2.4 x 10^3 M^{-1} s^{-1} is obtained using this equation. Multiplying by the concentration of CO_2 (0.036 M) yields a TOF of 90 s^{-1}. Since the Savéant method is based on catalytic limiting current density for a given catalyst concentration it therefore represents a more accurate assessment of the initial rate for the catalysis at the electrode surface.

S3 - DFT Calculations

S3.1. Computational Details. Density Functional Theory calculations were performed with the Amsterdam Density Functional (ADF) program suite,[5,6] version 2007.01.[7] For all atoms, the triple-ζ Slater-type orbital TZ2P ADF basis set was utilized without frozen cores. Relativistic effects were included by use of the zeroth-order regular approximation (ZORA).[8,9] The functional used was BP86: The local density approximation (LDA) of Vosko, Wilk and Nusair,[10] (VWN) was coupled with the generalized gradient approximation (GGA) corrections described by Becke[11] and Perdew[12,13] for electron exchange and correlation, respectively. Single point frequency calculations were performed to verify that the geometries were at their minima. The trend in ΔE_{CO2} was also confirmed with the alternative functional BLYP.



[Ni(cyclam)–CO_2] *trans I* [Ni(cyclam) –CO_2]$^-$ *trans III* [Ni(DMC) –CO_2]$^-$ *trans III* [Ni(DMC) –CO_2] *trans III*

Figure S2. Geometry Optimized DFT Structures. Only amine and methyl protons are shown for clarity.

Table S1. Characterization of Geometry Optimized DFT Structures

Structure	TBE (kJ/mol)[a]	ΔE_{CO2} (kJ/mol)[b]	Average Ni–N distance (Å)	Ni–C Distance (Å)[c]
CO_2	-2216.9	–	–	–
Ni(cyclam)$^+$ *trans I*	-20050.1	–	2.087	–
Ni(cyclam)$^+$ *trans III*	-20081.1	–	2.034	–
Ni(DMC)$^+$ *trans III*	-23162.0	–	2.102	–
Ni(TMC)$^+$ *trans III*	-26230.6	–	2.147	–
Ni(cyclam)$(CO_2)^+$ *trans I*	-22285.2	-18.2	2.112	2.123
Ni(cyclam)$(CO_2)^+$ *trans III*	-22295.1	2.9	2.099	2.183
Ni(DMC)$(CO_2)^+$ *trans III*	-25364.7	14.2	2.127	2.173
Ni(TMC)$(CO_2)^+$ *trans III*[d]	–	–	–	–

[a]TBE = total bonding energy. [b]$\Delta E_{CO2} = TBE_{LNi(I)-CO2} - (TBE_{LNi(I)} + TBE_{CO2})$. [c]Carbon from CO_2. [d]Geometry optimization did not converge.

S3.2. Example Input File for DFT Geometry Optimization Calculations (Ni(cyclam)$^+$ *trans I*).

```
$ADFBIN/adf -n8 \
 <<< "
TITLE Nickel 1 cyclam transI

MAXMEMORYUSAGE 11000

RELATIVISTIC ZORA

UNRESTRICTED

CHARGE 1 1

SCF
DIIS
END

XC
 LDA VWN
 GGA Becke Perdew
END

SYMMETRY NOSYM
ATOMS
Ni      6.514636  -2.422812   3.314640
N       7.298424  -2.784832   5.107134
N       8.087466  -1.245249   3.121890
H       7.883570  -0.436169   3.726813
N       5.567170  -1.823667   1.668672
H       4.987479  -1.082107   2.084194
N       4.970893  -3.643598   3.472773
C       6.972148  -4.046363   5.851418
```

```
H       7.317567   -3.924777    6.889239
H       7.553964   -4.860193    5.398239
C       5.484718   -4.367433    5.824571
H       4.890245   -3.524903    6.216001
H       5.303953   -5.200769    6.517292
C       4.995865   -4.784616    4.443393
H       5.647376   -5.561827    4.022212
H       3.978986   -5.199788    4.504973
C       4.708203   -4.111355    2.075975
H       5.548224   -4.756379    1.789834
H       3.789360   -4.713849    2.033846
C       4.617952   -2.893194    1.168101
H       3.600712   -2.480816    1.138033
H       4.894350   -3.163717    0.143499
C       6.309758   -1.160346    0.545801
H       5.566836   -0.716793   -0.134265
H       6.844622   -1.943595   -0.007966
C       7.276564   -0.094213    1.039783
H       7.656324    0.453006    0.166086
H       6.756080    0.658425    1.655556
C       8.467083   -0.681377    1.786403
H       8.925607   -1.491873    1.204290
H       9.236277    0.087886    1.949941
C       9.214311   -2.013983    3.737538
H       9.418886   -2.866682    3.078096
H      10.124009   -1.398229    3.786568
C       8.782649   -2.481299    5.120598
H       9.329065   -3.388084    5.400732
H       8.984260   -1.723289    5.889009
H       4.187908   -3.038755    3.760735
H       6.835454   -2.032169    5.634214
END

GEOMETRY
 GO
END

BASIS
 type TZ2P
END

END INPUT
```

S3.3. Input Coordinates for DFT Geometry Optimization Calculations (xyz).

CO_2

```
ATOMS
C     -0.659700    0.173600    0.000000
O      0.713000   -0.227000    0.000000
O     -2.032500    0.574200    0.000000
```

Ni(cyclam)$^+$ ***trans I***

```
ATOMS
Ni      6.514636   -2.422812    3.314640
N       7.298424   -2.784832    5.107134
N       8.087466   -1.245249    3.121890
H       7.883570   -0.436169    3.726813
N       5.567170   -1.823667    1.668672
H       4.987479   -1.082107    2.084194
N       4.970893   -3.643598    3.472773
C       6.972148   -4.046363    5.851418
H       7.317567   -3.924777    6.889239
H       7.553964   -4.860193    5.398239
C       5.484718   -4.367433    5.824571
H       4.890245   -3.524903    6.216001
H       5.303953   -5.200769    6.517292
C       4.995865   -4.784616    4.443393
H       5.647376   -5.561827    4.022212
```

H	3.978986	-5.199788	4.504973
C	4.708203	-4.111355	2.075975
H	5.548224	-4.756379	1.789834
H	3.789360	-4.713849	2.033846
C	4.617952	-2.893194	1.168101
H	3.600712	-2.480816	1.138033
H	4.894350	-3.163717	0.143499
C	6.309758	-1.160346	0.545801
H	5.566836	-0.716793	-0.134265
H	6.844622	-1.943595	-0.007966
C	7.276564	-0.094213	1.039783
H	7.656324	0.453006	0.166086
H	6.756080	0.658425	1.655556
C	8.467083	-0.681377	1.786403
H	8.925607	-1.491873	1.204290
H	9.236277	0.087886	1.949941
C	9.214311	-2.013983	3.737538
H	9.418886	-2.866682	3.078096
H	10.124009	-1.398229	3.786568
C	8.782649	-2.481299	5.120598
H	9.329065	-3.388084	5.400732
H	8.984260	-1.723289	5.889009
H	4.187908	-3.038755	3.760735
H	6.835454	-2.032169	5.634214

Ni(cyclam)$^+$ *trans III*

ATOMS

Ni	6.419635	-2.281644	3.615359
N	7.420484	-2.935093	5.138695
H	7.777702	-3.730482	4.878656
N	7.908807	-1.092027	3.290604
H	7.684346	-0.306664	3.692668
N	5.411291	-1.667433	2.086460
H	4.989400	-0.907608	2.355870
N	4.940451	-3.475813	3.963542
H	5.198692	-4.292482	3.656064
C	6.716952	-3.202719	6.402870
H	6.347396	-2.373449	6.742560
H	7.352428	-3.535956	7.055895
C	5.617225	-4.197263	6.238882
H	5.265877	-4.426552	7.114463
H	5.978654	-5.006103	5.843552
C	4.497691	-3.688127	5.379406
H	3.766372	-4.326501	5.394048
H	4.170535	-2.850223	5.741060
C	3.796215	-3.067798	3.124565
H	3.179280	-3.809061	3.011823
H	3.319671	-2.331030	3.538929
C	4.339281	-2.655001	1.821443
H	3.641957	-2.255860	1.276767
H	4.698661	-3.421401	1.348512
C	6.122398	-1.317554	0.846297
H	5.482182	-1.010819	0.183023
H	6.563108	-2.106219	0.493429
C	7.149549	-0.234068	1.089352
H	7.475143	0.093084	0.235733
H	6.727106	0.506937	1.550569
C	8.312387	-0.726425	1.906366
H	8.701200	-1.501981	1.472968
H	8.990893	-0.034164	1.944434
C	9.078961	-1.611973	4.060178
H	9.482503	-2.361580	3.596032
H	9.747159	-0.917863	4.168528
C	8.562075	-2.041863	5.382335
H	9.253744	-2.508822	5.877229
H	8.280069	-1.271717	5.899191

Ni(DMC)$^+$ *trans III*

ATOMS

Ni	6.419100	-2.285000	3.618800

N	7.528200	-2.967100	5.249100
H	7.920000	-3.864600	4.934600
N	8.037000	-1.008600	3.288100
N	5.306200	-1.629100	1.986100
H	4.842500	-0.774200	2.312100
N	4.810900	-3.564400	3.969800
C	6.746400	-3.227200	6.486600
H	6.344200	-2.260900	6.827600
H	7.404300	-3.611000	7.286400
C	5.600600	-4.219900	6.260900
H	5.193200	-4.480500	7.248300
H	5.999400	-5.162700	5.847200
C	4.430700	-3.731600	5.398100
H	3.590500	-4.440900	5.494700
H	4.078900	-2.754100	5.760200
C	3.695300	-3.111200	3.099600
H	2.938800	-3.897100	2.946300
H	3.201400	-2.270200	3.605700
C	4.257000	-2.652600	1.752700
H	3.440800	-2.276800	1.113300
H	4.725900	-3.497300	1.230600
C	6.090900	-1.278200	0.772700
H	5.423100	-0.904900	-0.023700
H	6.558400	-2.201900	0.404100
C	7.167800	-0.225700	1.064700
H	7.542900	0.142000	0.099000
H	6.710400	0.648900	1.557900
C	8.378100	-0.707800	1.873600
H	8.781600	-1.629000	1.428900
H	9.174800	0.056700	1.824300
C	9.169000	-1.554400	4.076700
H	9.583000	-2.404500	3.515000
H	9.979500	-0.819000	4.210900
C	8.658700	-2.023100	5.438500
H	9.482400	-2.467500	6.019200
H	8.278300	-1.163700	6.011400
C	7.617900	0.249800	3.921800
H	8.383900	0.985900	3.794100
H	6.712900	0.594300	3.466500
H	7.451700	0.085400	4.965900
C	5.261400	-4.873200	3.474800
H	4.495500	-5.601200	3.643400
H	5.465900	-4.807000	2.426600
H	6.150600	-5.164100	3.994000

Ni(TMC)$^{+}$ *trans III*

ATOMS

Ni	6.422200	-2.287900	3.617600
N	7.454500	-2.937700	5.180500
N	7.952300	-1.072600	3.283700
N	5.382200	-1.659300	2.055000
N	4.894600	-3.500700	3.973600
C	6.720900	-3.221700	6.457900
H	6.328900	-2.265600	6.831200
H	7.448100	-3.594100	7.195100
C	5.599800	-4.232900	6.268700
H	5.185500	-4.471500	7.258100
H	5.995100	-5.185100	5.876900
C	4.465500	-3.720100	5.393900
H	3.631700	-4.438400	5.393100
H	4.079700	-2.763400	5.771900
C	3.736400	-3.085600	3.114700
H	3.015400	-3.908000	3.010800
H	3.228100	-2.254200	3.622200
C	4.293100	-2.652400	1.780300
H	3.516900	-2.210100	1.139300
H	4.739000	-3.496500	1.237000
C	6.110300	-1.278800	0.801500
H	5.370200	-0.917900	0.071300
H	6.563100	-2.193000	0.392500

C	7.167700	-0.214100	1.053800
H	7.554100	0.125300	0.082900
H	6.716200	0.678700	1.520100
C	8.342000	-0.719900	1.878800
H	8.778900	-1.619300	1.423400
H	9.130600	0.046000	1.927600
C	9.129000	-1.577100	4.064500
H	9.563500	-2.417300	3.506500
H	9.898400	-0.797900	4.155600
C	8.616300	-2.017000	5.414900
H	9.395800	-2.518300	6.004300
H	8.250100	-1.161900	5.999300
C	4.731200	-0.438100	2.550700
H	5.477300	0.260100	2.868200
H	4.145600	-0.003100	1.767900
H	4.096800	-0.682400	3.377000
C	7.519200	0.176400	3.926700
H	8.377200	0.722700	4.258700
H	6.970000	0.767500	3.223900
H	6.895300	-0.051900	4.765400
C	8.008600	-4.216700	4.713400
H	8.604600	-4.651400	5.488500
H	7.208600	-4.881700	4.463100
H	8.615800	-4.047800	3.848800
C	5.363100	-4.797700	3.464500
H	5.817800	-5.350000	4.260100
H	4.532600	-5.349600	3.076400
H	6.079800	-4.637600	2.686300

Ni(cyclam)(CO2)$^{+}$ *trans I*

ATOMS

Ni	6.482200	-2.376800	3.346900
N	7.347300	-2.796500	5.196600
N	8.173100	-1.174100	3.138000
H	8.013500	-0.330400	3.703200
N	5.511500	-1.801300	1.585400
H	4.964800	-1.032800	1.988900
N	4.868600	-3.691000	3.469300
C	7.032900	-4.097400	5.846800
H	7.358800	-4.087900	6.901300
H	7.611800	-4.877800	5.331700
C	5.537800	-4.429100	5.781000
H	4.947600	-3.583400	6.173400
H	5.352000	-5.262200	6.474000
C	5.010400	-4.842000	4.402600
H	5.706500	-5.555400	3.938600
H	4.044000	-5.362200	4.515900
C	4.645600	-4.101500	2.061200
H	5.509900	-4.714900	1.772600
H	3.739500	-4.719400	1.942200
C	4.549800	-2.862500	1.155800
H	3.525200	-2.462700	1.163300
H	4.766900	-3.160300	0.121900
C	6.318600	-1.209300	0.484300
H	5.658200	-0.744900	-0.268300
H	6.857700	-2.028500	-0.013600
C	7.316800	-0.165500	0.996900
H	7.699300	0.384500	0.125200
H	6.792800	0.585900	1.612000
C	8.521100	-0.723800	1.762700
H	8.930000	-1.592700	1.227300
H	9.320400	0.036000	1.801800
C	9.244000	-1.975400	3.781100
H	9.415500	-2.845900	3.133500
H	10.194600	-1.420900	3.858800
C	8.798400	-2.436000	5.179600
H	9.398000	-3.306800	5.473900
H	8.995600	-1.648300	5.921100
H	4.056300	-3.143900	3.781800
H	6.855400	-2.076300	5.736200

C	5.505200	-0.985200	4.238700
O	4.213200	-1.077600	4.363500
O	6.137300	0.047100	4.716300

Ni(cyclam)$(CO2)^+$ ***trans III***

ATOMS

Ni	6.419100	-2.285000	3.618800
N	7.528200	-2.967100	5.249100
H	7.920000	-3.864600	4.934600
N	8.037000	-1.008600	3.288100
H	7.744100	-0.129200	3.730900
N	5.306200	-1.629100	1.986100
H	4.842500	-0.774200	2.312100
N	4.810900	-3.564400	3.969800
H	5.125600	-4.478700	3.624000
C	6.746400	-3.227200	6.486600
H	6.344200	-2.260900	6.827600
H	7.404300	-3.611000	7.286400
C	5.600600	-4.219900	6.260900
H	5.193200	-4.480500	7.248300
H	5.999400	-5.162700	5.847200
C	4.430700	-3.731600	5.398100
H	3.590500	-4.440900	5.494700
H	4.078900	-2.754100	5.760200
C	3.695300	-3.111200	3.099600
H	2.938800	-3.897100	2.946300
H	3.201400	-2.270200	3.605700
C	4.257000	-2.652600	1.752700
H	3.440800	-2.276800	1.113300
H	4.725900	-3.497300	1.230600
C	6.090900	-1.278200	0.772700
H	5.423100	-0.904900	-0.023700
H	6.558400	-2.201900	0.404100
C	7.167800	-0.225700	1.064700
H	7.542900	0.142000	0.099000
H	6.710400	0.648900	1.557900
C	8.378100	-0.707800	1.873600
H	8.781600	-1.629000	1.428900
H	9.174800	0.056700	1.824300
C	9.169000	-1.554400	4.076700
H	9.583000	-2.404500	3.515000
H	9.979500	-0.819000	4.210900
C	8.658700	-2.023100	5.438500
H	9.482400	-2.467500	6.019200
H	8.278300	-1.163700	6.011400
C	5.598900	-0.934200	4.709300
O	6.312900	-0.282100	5.580100
O	4.331000	-0.674000	4.575000

Ni(DMC)$(CO2)^+$ ***trans III***

ATOMS

Ni	6.309700	-2.025000	3.829900
N	7.415400	-2.943200	5.069700
N	7.891500	-1.055400	3.372800
H	7.728200	-0.130300	3.715500
N	5.354700	-1.656500	2.193200
N	5.068700	-3.483500	3.909200
H	5.509700	-4.285000	3.505200
C	6.770900	-3.314300	6.334800
H	6.344600	-2.440800	6.782100
H	7.514500	-3.727800	6.983700
C	5.695800	-4.359800	6.133200
H	5.285300	-4.622100	7.085900
H	6.122900	-5.227200	5.674900
C	4.588000	-3.818800	5.255500
H	3.838900	-4.577700	5.166500
H	4.167000	-2.944300	5.706000
C	3.889700	-3.124100	3.149900
H	3.206900	-3.943900	3.068900
H	3.370100	-2.297100	3.587100

C	4.473600	-2.757600	1.867800
H	3.746200	-2.469300	1.137900
H	5.026800	-3.591300	1.488700
C	6.130800	-1.467300	0.961100
H	5.440500	-1.171200	0.199100
H	6.599000	-2.392200	0.695800
C	7.219900	-0.422200	1.063500
H	7.639500	-0.275500	0.090200
H	6.837700	0.509100	1.426300
C	8.299300	-0.970200	1.971300
H	8.561800	-1.944800	1.616100
H	9.150000	-0.322700	1.928000
C	9.022400	-1.686800	4.045200
H	9.304100	-2.589400	3.544400
H	9.866700	-1.030100	4.072900
C	8.510200	-2.038300	5.391700
H	9.250600	-2.518300	5.996900
H	8.166200	-1.166900	5.908600
C	5.500500	-0.681400	4.937300
O	6.300800	0.060800	5.861200
O	4.097600	-0.422900	4.838200
C	4.598400	-0.430700	2.487000
H	3.971800	-0.593800	3.338800
H	5.279800	0.368100	2.693100
H	3.993000	-0.174200	1.642800
C	7.928700	-4.158500	4.421300
H	8.445300	-3.892300	3.522800
H	8.602200	-4.659500	5.084900
H	7.112300	-4.808200	4.184100

Ni(TMC)(CO2)$^{+}$ ***trans III***

ATOMS

Ni	6.422200	-2.287900	3.617600
N	7.454500	-2.937700	5.180500
N	7.952300	-1.072600	3.283700
N	5.382200	-1.659300	2.055000
N	4.894600	-3.500700	3.973600
C	6.720900	-3.221700	6.457900
H	6.328900	-2.265600	6.831200
H	7.448100	-3.594100	7.195100
C	5.599800	-4.232900	6.268700
H	5.185500	-4.471500	7.258100
H	5.995100	-5.185100	5.876900
C	4.465500	-3.720100	5.393900
H	3.631700	-4.438400	5.393100
H	4.079700	-2.763400	5.771900
C	3.736400	-3.085600	3.114700
H	3.015400	-3.908000	3.010800
H	3.228100	-2.254200	3.622200
C	4.293100	-2.652400	1.780300
H	3.516900	-2.210100	1.139300
H	4.739000	-3.496500	1.237000
C	6.110300	-1.278800	0.801500
H	5.370200	-0.917900	0.071300
H	6.563100	-2.193000	0.392500
C	7.167700	-0.214100	1.053800
H	7.554100	0.125300	0.082900
H	6.716200	0.678700	1.520100
C	8.342000	-0.719900	1.878800
H	8.778900	-1.619300	1.423400
H	9.130600	0.046000	1.927600
C	9.129000	-1.577100	4.064500
H	9.563500	-2.417300	3.506500
H	9.898400	-0.797900	4.155600
C	8.616300	-2.017000	5.414900
H	9.395800	-2.518300	6.004300
H	8.250100	-1.161900	5.999300
C	4.731200	-0.438100	2.550700
H	5.477300	0.260100	2.868200
H	4.145600	-0.003100	1.767900

H	4.096800	-0.682400	3.377000
C	7.519200	0.176400	3.926700
H	8.377200	0.722700	4.258700
H	6.970000	0.767500	3.223900
H	6.895300	-0.051900	4.765400
C	8.008600	-4.216700	4.713400
H	8.604600	-4.651400	5.488500
H	7.208600	-4.881700	4.463100
H	8.615800	-4.047800	3.848800
C	5.363100	-4.797700	3.464500
H	5.817800	-5.350000	4.260100
H	4.532600	-5.349600	3.076400
H	6.079800	-4.637600	2.686300
C	5.605000	-0.926700	4.697300
O	6.254700	-0.421700	5.705400
O	4.403400	-0.512300	4.418600

References

[1] Bosnich, B.; Tobe, M. L.; Webb, G. A. *Inorg. Chem.* **1965**, *4*, 1109.
[2] Savéant, J.-M. *Chem. Rev*. **2008**, *108*, 2348.
[3] Pierce, D. T.; Hatfield, T. L.; Billo, E. J.; Ping, Y. *Inorg. Chem.* **1997**, *36*, 2950.
[4] Wilhelm, E.; Battino, R.; Wilcock, R. J. *Chem. Rev.* **1977**, *77*, 219.
[5] te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.
[6] Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391.
[7] *ADF2007.01*, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.
[8] van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.
[9] van Lenthe, E.; Snijders, J. G.; Baerends, E. J. *J. Chem. Phys.* **1996**, *105*, 6505.
[10] Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
[11] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
[12] Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
[13] Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406. (*Erratum).*