Electronic Supporting Information

Remarks on Catalytic Reduction of CO_2, H^+ and H_2 by Monovalent Ni

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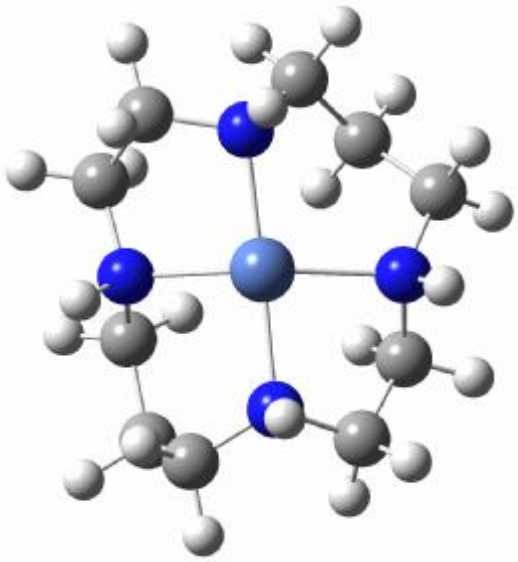
Our DFT computations (Gaussian 03 package) have been performed with the B3LYP correlation-exchange functional. We have used the Pople's basis set (6–311++G** for C, H, O and N, and 6-31G** for Ni). All minima have been tested for harmonic frequencies, while yielding no imaginary values. Since the species containing Ni(II) can exhibit spin crossover phenomenon, we have considered both singlet and triplet states in our calculations. The reaction enthalpies (calculated at T=0 K) are not corrected for zero-point vibrational energies; these corrections are typically small (up to 0.05 eV) and usually promote reaction substrates due to large zero-point energies for the H–H oscillator.

Properties of cyclam complexes of Ni are dependent on the basicity/acidity of the environment. In order to mimic the varying pH, we have studied Ni-cyclam complexes bearing various charges. For example, $Ni(I)[N_414]^{1+}$ serves as a model species in a relatively acidic environment. When a strong base, H^-, is attached to it, or when one or two protons are dissociated from the amine nitrogens, much more basic species are formed: $(Ni(I)(H^-)[N_414]^0$, $Ni(I)[N_414–H^+]^0$, $Ni(I)[N_414–2H^+]^{-1}$). It turns out that they may have different redox chemistry than the parent species, $Ni(I)[N_414]^{1+}$.

S1. Calculated molecular properties of compounds of Ni(I).



^{2}{Ni(I)[$N_4$14]}$^{+1}$

E = –2122.70791 au

μ_{dip} = 0.57 D

R(Ni–N) = 2.054, 2.056, 2.094, 2.098 Å

q(Ni) = –1.164 e

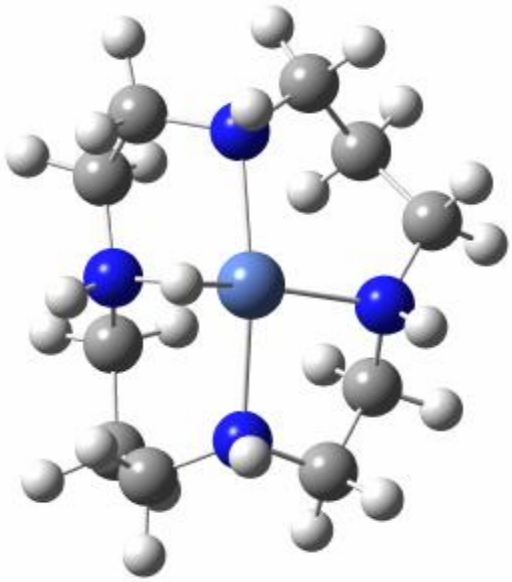
q(N) = +0.133, +0.050, –0.004, –0.021 e

$E_{SOMO,\alpha}$ = –0.276 au

$E_{SOMO-1,\alpha}$ = –0.299 au, $E_{SOMO-1,\beta}$ = –0.265 au

$E_{SOMO+1,\alpha}$ = –0.131 au, $E_{SOMO+1,\beta}$ = –0.130 au

Δ_{min} = 0.011 au



^{2}{Ni(I)(H^-)[$N_4$14]}^{0}

E = –2123.40992 au

μ_{dip} = 5.80 D

R(Ni–N) = 2.125, 2.184, 2.204, 2.459 Å

R(Ni–H) = 1.605 Å

q(Ni) = –0.310 e

$q(H_{Ni})$ = –0.409 e

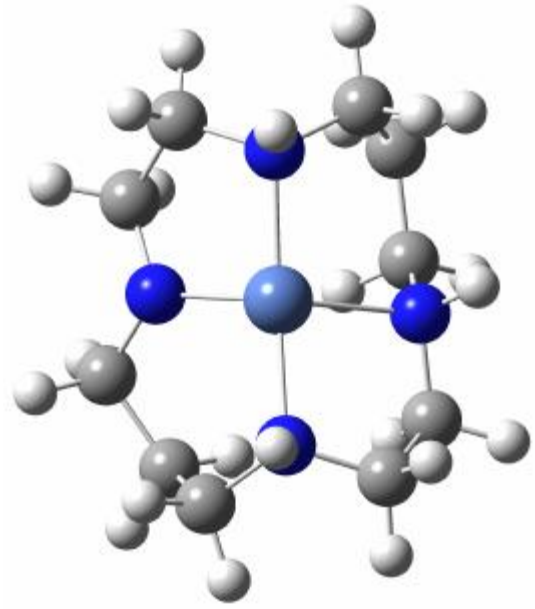
q(N) = –0.049, –0.111, –0.226, –0.247 e

$E_{SOMO,\alpha}$ = –0.100 au

$E_{SOMO-1,\alpha}$ = –0.133 au, $E_{SOMO-1,\beta}$ = –0.080 au

$E_{SOMO+1,\alpha}$ = –0.019 au, $E_{SOMO+1,\beta}$ = –0.018 au

Δ_{min} = 0.020 au



^{2}{Ni(I)[$N_4$14–1H^+]}^{0}

E = –2122.22824 au

μ_{dip} = 4.95 D

R(Ni–N) = 1.922, 2.046, 2.054, 2.115 Å

q(Ni) = –2.071 e

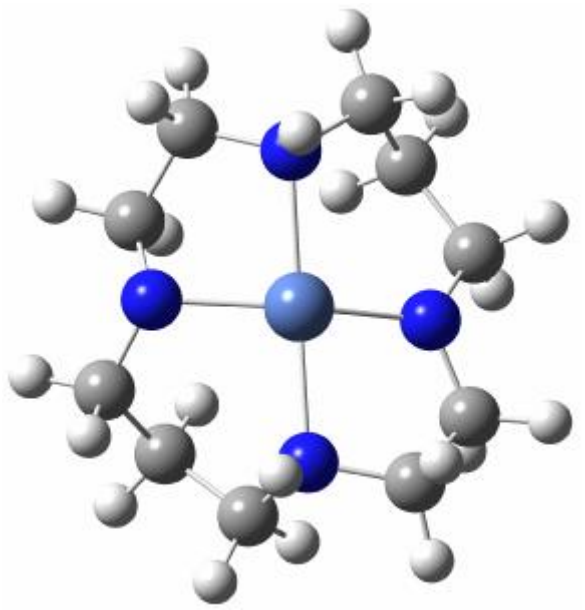
q(N) = +0.197, +0.200, +0.216, +0.280 e

$E_{SOMO,\alpha}$ = –0.111 au

$E_{SOMO-1,\alpha}$ = –0.129 au, $E_{SOMO-1,\beta}$ = –0.087 au

$E_{SOMO+1,\alpha}$ = –0.024 au, $E_{SOMO+1,\beta}$ = –0.023 au

Δ_{min} = 0.018 au



^{2}{Ni(I)[$N_4$14–2H^+]}$^{-1}$

E = –2121.64266 au

μ_{dip} = 0.53 D

R(Ni–N) = 1.943, 1.999, 2.129, 2.129 Å

q(Ni) = –1.127 e

q(N) = +0.091, +0.077, –0.042, –0.089 e

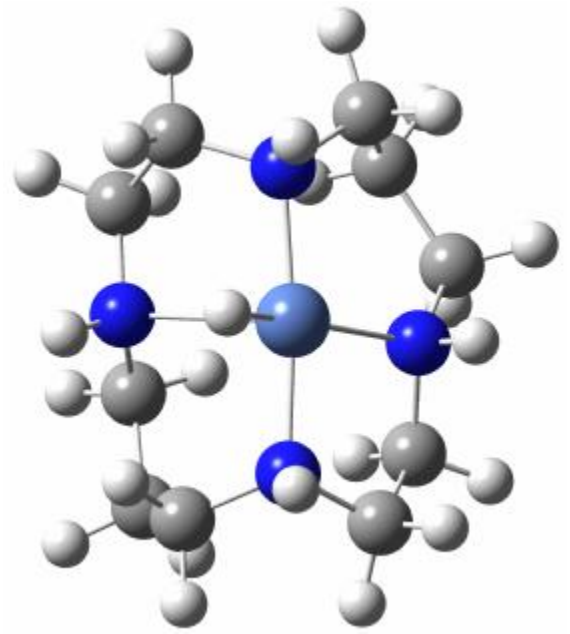
$E_{SOMO,\alpha}$ = +0.026 au (positive!)

$E_{SOMO-1,\alpha}$ = +0.016 au, $E_{SOMO-1,\beta}$ = +0.042 au

$E_{SOMO+1,\alpha}$ = +0.082 au, $E_{SOMO+1,\beta}$ = +0.083 au

Δ_{min} = 0.010 au

S2. Calculated molecular properties of compounds of Ni(II).



^{1}{Ni(II)(H^{-})[$N_4$14]}$^{+1}$

E = –2123.28086 au

μ_{dip} = 2.02 D

R(Ni–N) = 1.944, 1.945, 2.046, 2.467 Å

R(Ni–H) = 1.472 Å

q(Ni) = –0.906 e

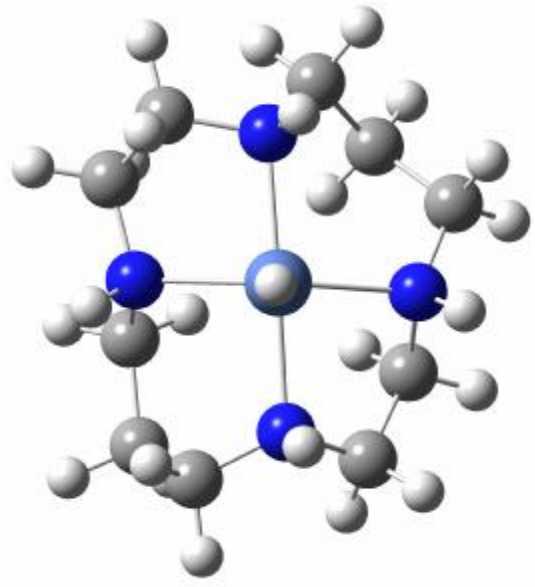
$q(H_{Ni})$ = –0.092 e

q(N) = +0.036, +0.011, –0.011, –0.134 e

E_{HOMO} = –0.293 au

E_{LUMO} = –0.147 au

Δ_{HL} = 0.146 au



^{3}{Ni(II)(H^{-})[$N_4$14]}$^{+1}$

E = –2123.28739 au

μ_{dip} = 2.50 D

R(Ni–N) = 2.119, 2.122, 2.133, 2.141 Å

R(Ni–H) = 1.574 Å

q(Ni) = –0.898 e

$q(H_{Ni})$ = –0.152 e

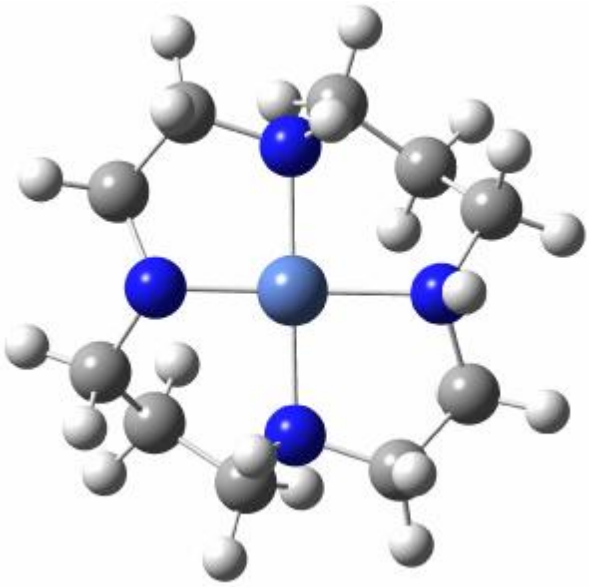
q(N) = +0.004, +0.025, +0.037, +0.040 e

$E_{SOMO,\alpha}$ = –0.303 au

$E_{SOMO-1,\alpha}$ = –0.341 au, $E_{SOMO-1,\beta}$ = –0.353 au

$E_{SOMO+1,\alpha}$ = –0.126 au, $E_{SOMO+1,\beta}$ = –0.170 au

Δ_{min} = 0.037 au



^{1}{Ni(II)[$N_4$14–H^{+}]}$^{+1}$

E = –2122.10660 au

μ_{dip} = 4.80 D

R(Ni–N) = 1.839, 1.935, 1.938, 1.997 Å

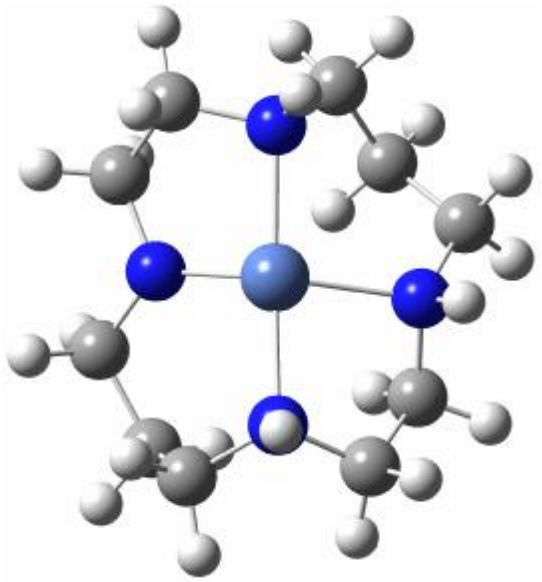
q(Ni) = –0.836 e

q(N) = +0.016, +0.008, –0.005, –0.149 e

E_{HOMO} = –0.298 au

E_{LUMO} = –0.156 au

Δ_{HL} = 0.146 au



^{3}{Ni(II)[$N_4$14–H^+]}$^{+1}$

E = –2122.10229 au

μ_{dip} = 3.89 D

R(Ni–N) = 2.085, 2.098, 2.100, 1.831 Å

q(Ni) = –0.623 e

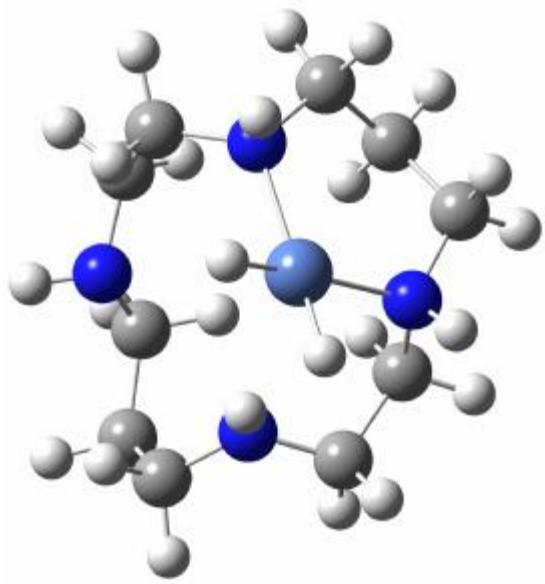
q(N) = –0.115, –0.085, –0.038, +0.051 e

$E_{SOMO,\alpha}$ = –0.318 au

$E_{SOMO-1,\alpha}$ = –0.329 au, $E_{SOMO-1,\beta}$ = –0.323 au

$E_{SOMO+1,\alpha}$ = –0.142 au, $E_{SOMO+1,\beta}$ = –0.192 au

Δ_{min} = 0.005 au



^{1}{Ni(II)(H^-)$_2$[$N_4$14]}^{0}

E = –2124.00743 au

μ_{dip} = 5.84 D

R(Ni–N) = 2.022, 2.044, (2.771, 3.655) Å

R(Ni–H) = 1.464, 1.473 Å

q(Ni) = +0.096 e

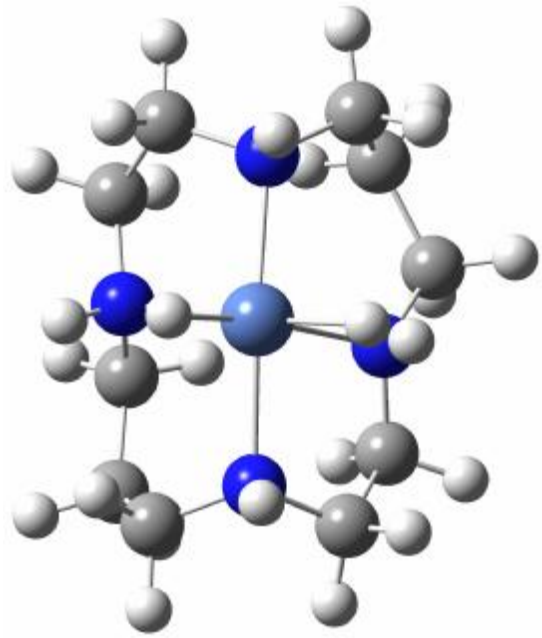
q(H_{Ni}) = –0.197, –0.204 e

q(N) = –0.009, –0.067,–0.286, –0.287 e

E_{HOMO} = –0.141 au

E_{LUMO} = –0.018 au

Δ_{HL} = 0.123 au



^{3}{Ni(II)(H^-)$_2$[$N_4$14]}^{0}

E = –2124.00328 au

μ_{dip} = 6.16 D

R(Ni–N) = 2.152, 2.171, 2.262, 2.371 Å

R(Ni–H) = 1.636, 1.674 Å

q(Ni) = –0.456 e

q(H_{Ni}) = –0.372, –0.391 e

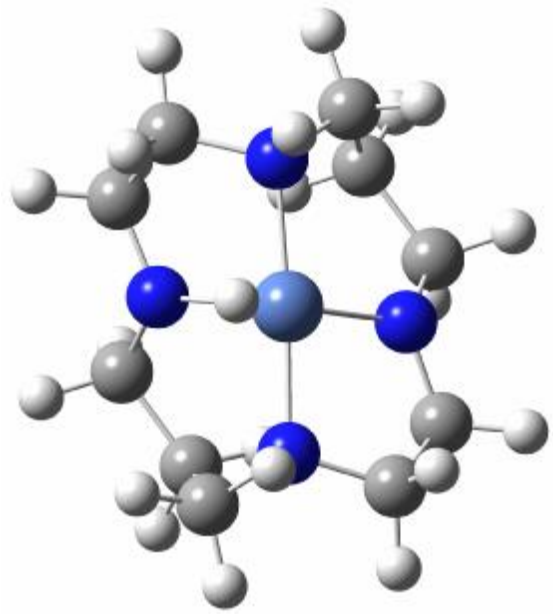
q(N) = +0.433, +0.267, +0.239, +0.221 e

$E_{SOMO,\alpha}$ = –0.119 au

$E_{SOMO-1,\alpha}$ = –0.161 au, $E_{SOMO-1,\beta}$ = –0.187 au

$E_{SOMO+1,\alpha}$ = –0.019 au, $E_{SOMO+1,\beta}$ = –0.019 au

Δ_{min} = 0.042 au



^{1}{Ni(II)(H^{-})[$N_4$14–2H^{+}]}$^{-1}$

E = –2122.21485 au

μ_{dip} = 2.23 D

R(Ni–N) = 1.935, 1.961, 1.975, 2.199 Å

R(Ni–H) = 1.539 Å

q(Ni) = –0.675 e

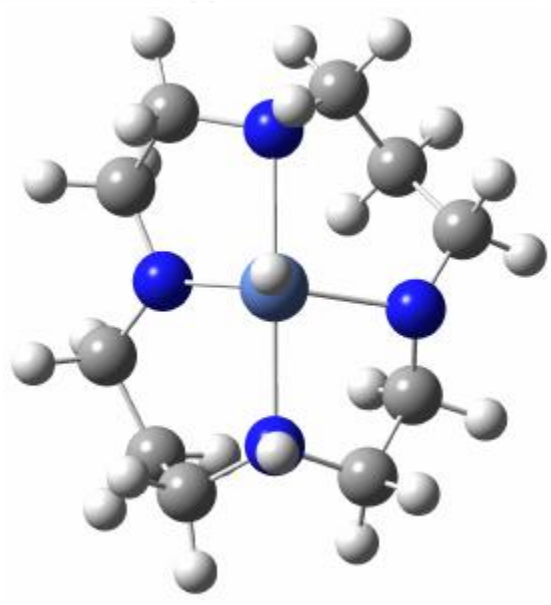
q(H_{Ni}) = –0.405 e

q(N) = –0.009, –0.030, –0.062, –0.119 e

E_{HOMO} = +0.020 au (positive!)

E_{LUMO} = +0.081 au

Δ_{HL} = 0.061 au



^{3}{Ni(II)(H^{-})[$N_4$14–2H^{+}]}$^{-1}$

E = –2122.24583 au

μ_{dip} = 2.75 D

R(Ni–N) = 1.985, 2.057, 2.187, 2.214 Å

R(Ni–H) = 1.650 Å

q(Ni) = –0.437 e

q(H_{Ni}) = –0.633 e

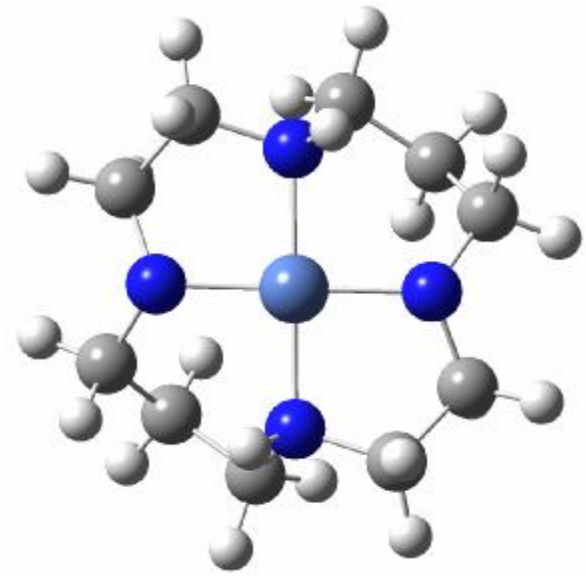
q(N) = +0.025, +0.015, +0.002, –0.005 e

$E_{SOMO,\alpha}$ = –0.006 au

$E_{SOMO-1,\alpha}$ = –0.007 au, $E_{SOMO-1,\beta}$ = –0.002 au

$E_{SOMO+1,\alpha}$ = +0.081 au, $E_{SOMO+1,\beta}$ = +0.081 au

Δ_{min} = 0.001 au



^{1}{Ni(II)[$N_4$14–2H^{+}]}^{0}

E = –2121.66280 au

μ_{dip} = 1.00 D

R(Ni–N) = 1.888, 1.890, 1.920, 1.926 Å

q(Ni) = –0.911 e

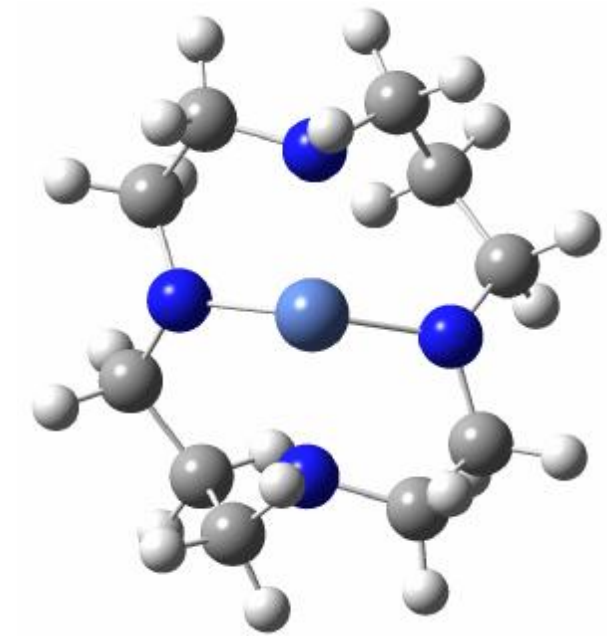
q(N) = +0.038, +0.038, –0.069, –0.072 e

$E_{SOMO,\alpha}$ = –0.138 au

$E_{SOMO-1,\alpha}$ = –0.175 au

$E_{SOMO+1,\alpha}$ = –0.012 au

Δ_{min} = 0.037 au



^{3}{Ni(II)[$N_4$14–2H^+]}^{0}

E = –2121.66120 au

μ_{dip} = 1.54 D

R(Ni–N) = 1.865, 1.865, 2.127, 2.127 Å

q(Ni) = –1.172 e

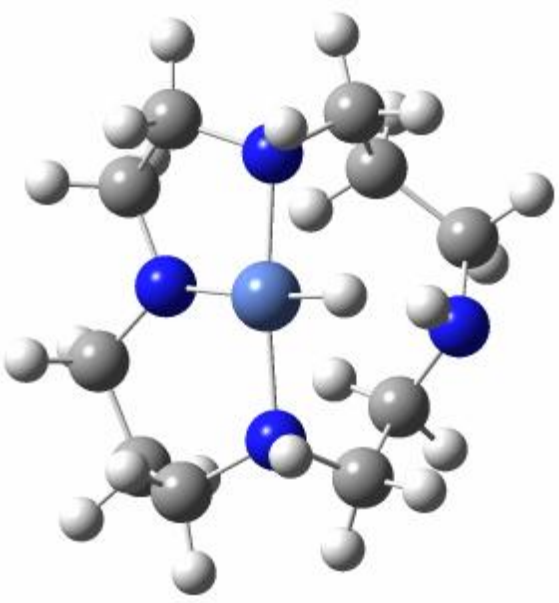
q(N) = +0.023, +0.014, +0.092, +0.093 e

$E_{SOMO,\alpha}$ = –0.152 au

$E_{SOMO-1,\alpha}$ = –0.168 au, $E_{SOMO-1,\beta}$ = –0.158 au

$E_{SOMO+1,\alpha}$ = –0.016 au, $E_{SOMO+1,\beta}$ = –0.020 au

Δ_{min} = 0.006 au



^{1}{Ni(II)(H^-)[$N_4$14–1H^+]}^{0}

E = –2122.83966 au

μ_{dip} = 0.53 D

R(Ni–N) = 1.902, 1.928, 1.942, 2.948 Å

R(Ni–H) = 1.509 Å

q(Ni) = –1.159 e

$q(H_{Ni})$ = –0.202 e

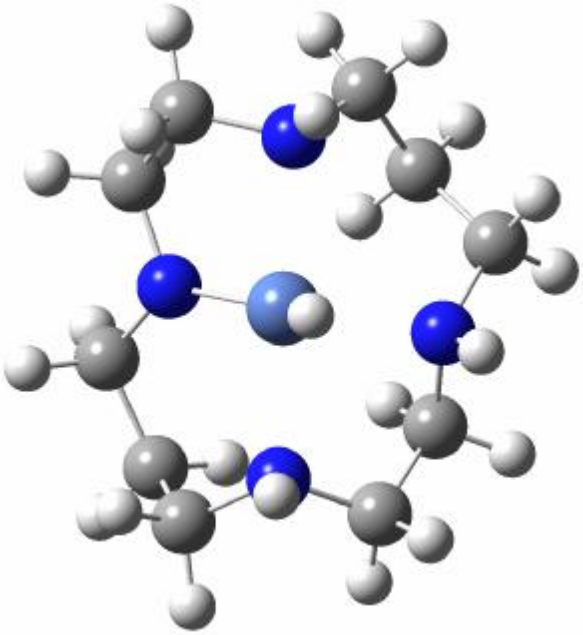
q(N) = +0.039, +0.082, +0.090, +0.113 e

$E_{SOMO,\alpha}$ = –0.146 au

$E_{SOMO-1,\alpha}$ = –0.179 au

$E_{SOMO+1,\alpha}$ = –0.018 au

Δ_{min} = 0.033 au



^{3}{Ni(II)(H^-)[$N_4$14–1H^+]}^{0}

E = –2122.84551 au

μ_{dip} = 4.39 D

R(Ni–N) = 1.921, 2.191, 2.200, 2.167 Å

R(Ni–H) = 1.625 Å

q(Ni) = –0.876 e

$q(H_{Ni})$ = –0.375 e

q(N) = +0.038, +0.057, +0.067, +0.115 e

$E_{SOMO,\alpha}$ = –0.137 au

$E_{SOMO-1,\alpha}$ = –0.168 au, $E_{SOMO-1,\beta}$ = –0.160 au

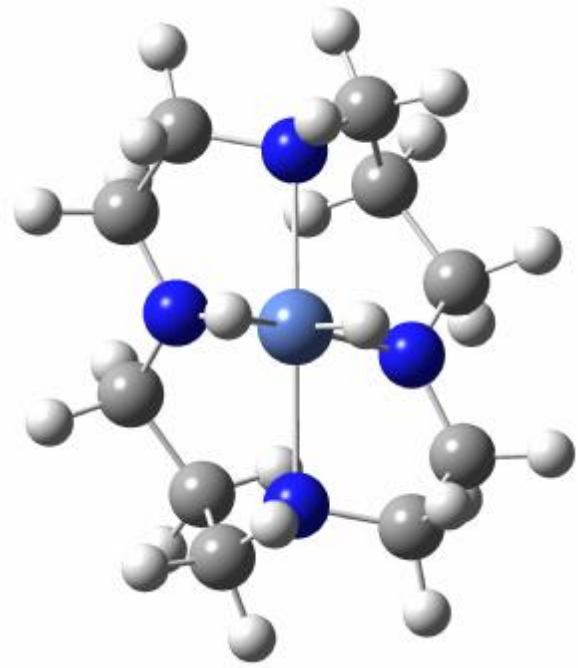
$E_{SOMO+1,\alpha}$ = –0.018 au, $E_{SOMO+1,\beta}$ = –0.018 au

Δ_{min} = 0.033 au

S3. Calculated molecular properties of compounds of Ni(III).

^{2}{Ni(III)(H^-)$_2$[$N_4$14]}$^{+1}$, ^{2}{Ni(III)(H^-)$_3$[$N_4$14]}^{0}

not computed



^{2}{Ni(III)(H^-)$_2$[$N_4$14–2H^+]}$^{-1}$

E = –2122.82121 au

μ_{dip} = 0.40 D

R(Ni–N) = 1.996, 1.997, 2.222, 2.222 Å

R(Ni–H) = 1.498, 1.498 Å

q(Ni) = –1.582 e

q(H_{Ni}) = –0.033, –0.037 e

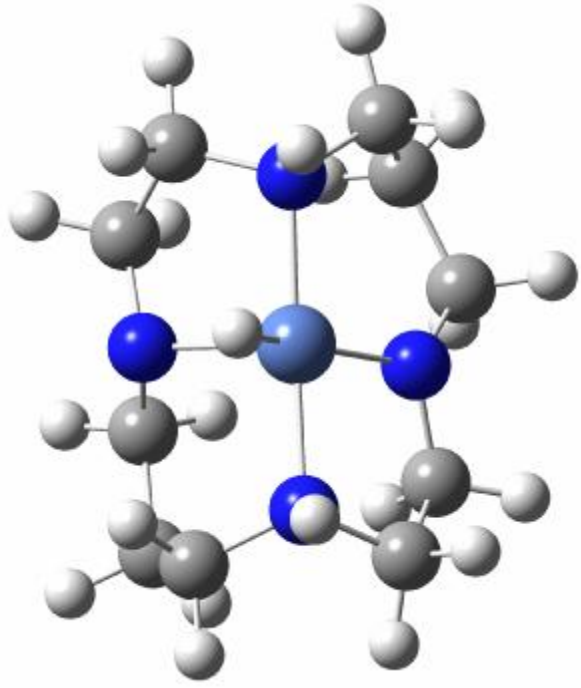
q(N) = +0.075, +0.074, +0.238, +0.240 e

$E_{SOMO,\alpha}$ = –0.004 au

$E_{SOMO-1,\alpha}$ = –0.005 au, $E_{SOMO-1,\beta}$ = –0.000 au

$E_{SOMO+1,\alpha}$ = +0.083 au, $E_{SOMO+1,\beta}$ = –0.082 au

Δ_{min} = 0.001 au



^{2}{Ni(III)(H^-)[$N_4$14–2H^+]}^{0}

E = –2122.20874 au

μ_{dip} = 2.13 D

R(Ni–N) = 1.881, 1.992, 2.002, 2.035 Å

R(Ni–H) = 1.481 Å

q(Ni) = –1.370 e

q(H_{Ni}) = –0.088 e

q(N) = +0.005, +0.086, +0.089, +0.135 e

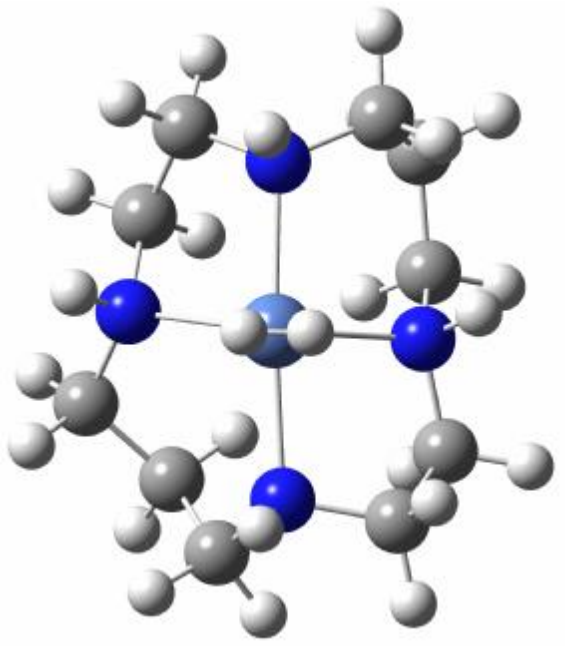
$E_{SOMO,\alpha}$ = –0.150 au

$E_{SOMO-1,\alpha}$ = –0.177 au, $E_{SOMO-1,\beta}$ = –0.154 au

$E_{SOMO+1,\alpha}$ = –0.051 au, $E_{SOMO+1,\beta}$ = –0.044 au

Δ_{min} = 0.004 au

S4. Calculated molecular properties of dihydrogen complexes.



^{2}{Ni(I)(H_2)$N_4$14]}$^{+1}$

E = –2123.88893 au

μ_{dip} = 0.35 D

R(Ni–N) = 2.137, 2.159, 2.160, 2.160 Å

R(Ni–H) = 1.645, 1.646 Å

R(H–H) = 0.841 Å

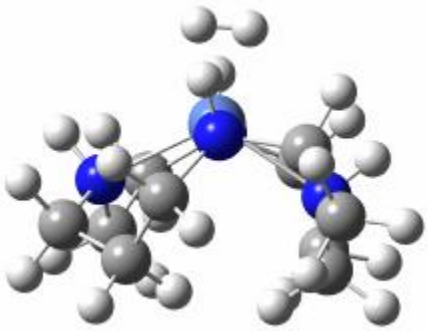
q(Ni) = –0.336 e

q(H_{Ni}) = +0.003, –0.020 e

q(N) = –0.035, –0.120, –0.169, –0.323 e

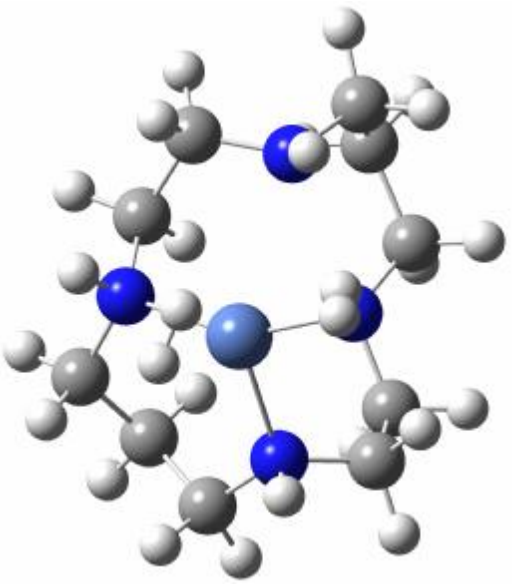
$E_{SOMO,\alpha}$ = –0.308 au

$E_{SOMO-1,\alpha}$ = –0.319 au, $E_{SOMO-1,\beta}$ = –0.292 au



$E_{SOMO+1,\alpha}$ = –0.125 au, $E_{SOMO+1,\beta}$ = –0.124 au

Δ_{min} = 0.011 au



^{2}{Ni(I)(H_2)(H^-)[$N_4$14]}^{0}

E = –2124.59224 au

μ_{dip} = 4.52 D

R(Ni–N) = 2.134, 2.144 Å

R(Ni–H) = 1.595, 1.616, 1.642 Å

R(H–H) = 0.849 Å

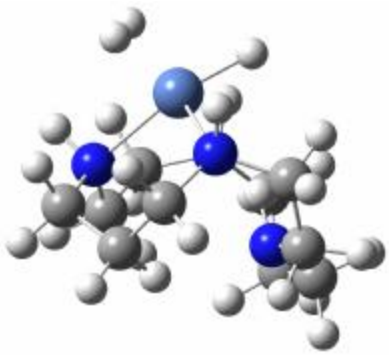
q(Ni) = –0.116 e

q(H_{Ni}) = –0.070, –0.337 e

q(N) = +0.007, –0.138, –0.231, –0.357 e

$E_{SOMO,\alpha}$ = –0.146 au

$E_{SOMO-1,\alpha}$ = –0.181 au,

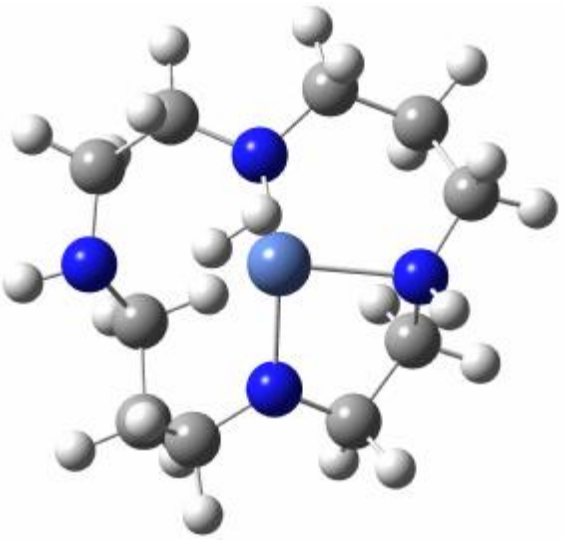


$E_{SOMO-1,\beta}$ = –0.154 au

$E_{SOMO+1,\alpha}$ = –0.017 au, $E_{SOMO+1,\beta}$ = –0.017 au

Δ_{min} = 0.008 au

^{2}{Ni(I)(H_2)[$N_4$14–2H^+]}$^{-1}$



E = –2122.82541 au

μ_{dip} = 2.73 D

R(Ni–N) = 1.940, 2.019, 2.170, (3.239) Å

R(Ni–H) = 1.567, 1.572 Å

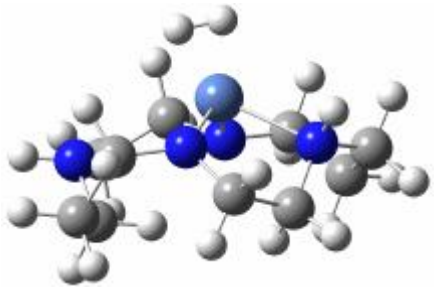
R(H–H) = 0.899 Å

q(Ni) = –0.446 e

q(H_{Ni}) = –0.093, –0.137 e

q(N) = +0.010, +0.008, –0.021, –0.174 e

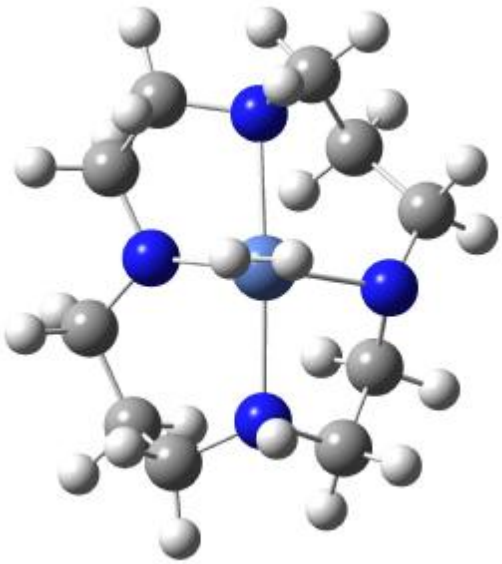
$E_{SOMO,\alpha}$ = +0.002 au



$E_{SOMO-1,\alpha}$ = –0.012 au, $E_{SOMO-1,\beta}$ = +0.001 au

$E_{SOMO+1,\alpha}$ = +0.080 au, $E_{SOMO+1,\beta}$ = +0.080 au

Δ_{min} = 0.001 au



^{2}{Ni(I)(H_2)[$N_4$14–2H^+]}$^{-1}$, high-energy isomer

E = –2122.81966 au

μ_{dip} = 0.74 D

R(Ni–N) = 2.033, 2.058, 2.210, 2.247 Å

R(Ni–H) = 1.607, 1.629 Å

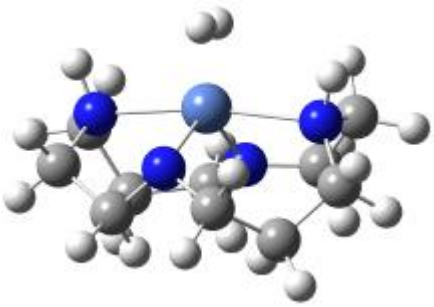
R(H–H) = 0.898 Å

q(Ni) = –0.322 e

q(H_{Ni}) = –0.096, –0.178 e

q(N) = –0.020, –0.113, –0.126, –0.150 e

$E_{SOMO,\alpha}$ = +0.006 au

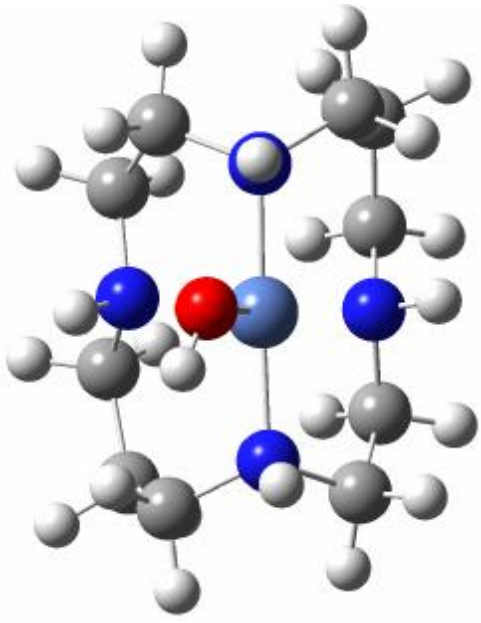


$E_{SOMO-1,\alpha}$ = +0.002 au, $E_{SOMO-1,\beta}$ = +0.021 au

$E_{SOMO+1,\alpha}$ = +0.082 au, $E_{SOMO+1,\beta}$ = +0.082 au

Δ_{min} = 0.004 au

S5. Calculated molecular properties of hydroxy complexes of Ni(III).



^{2}{Ni(III)(OH$^-$)[N$_4$14]}$^{2+}$

E = –2198.21580 au

μ_{dip} = 2.65 D

R(Ni–N) = 1.954, 1.958, 1.995, 2.080 Å

R(Ni–O) = 1.806 Å

R(O–H) = 0.965 Å

q(Ni) = –1.675 e

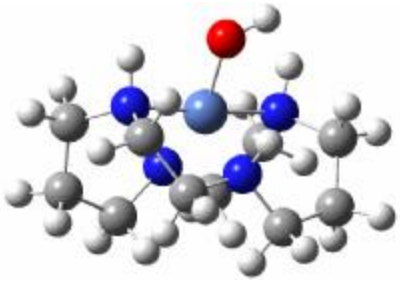
q(O) = –0.194 e

q(N) = +0.019, +0.071, +0.074, +0.206 e

$E_{SOMO,\alpha}$ = –0.531 au

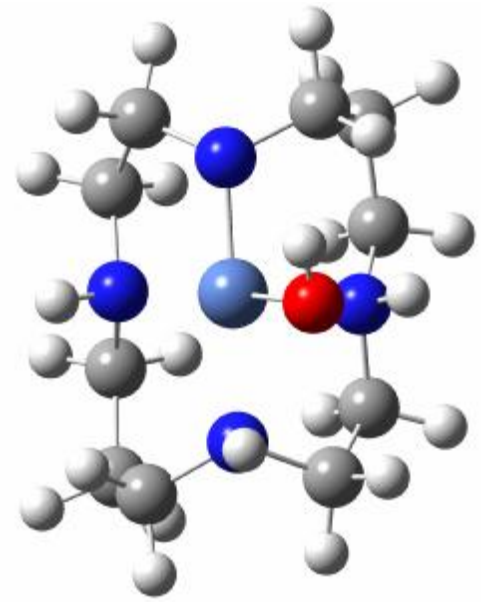
$E_{SOMO-1,\alpha}$ = –0.551 au,

$E_{SOMO-1,\beta}$ = –0.542 au



$E_{SOMO+1,\alpha}$ = –0.399 au, $E_{SOMO+1,\beta}$ = –0.392 au

Δ_{min} = 0.011 au



^{2}{Ni(III)(OH$^-$)[N$_4$14–H$^+$]}$^{1+}$

E = –2197.92938 au

μ_{dip} = 5.04 D

R(Ni–N) = 1.835, 1.999, 2.009, 2.086 Å

R(Ni–O) = 1.845 Å

R(O–H) = 0.963 Å

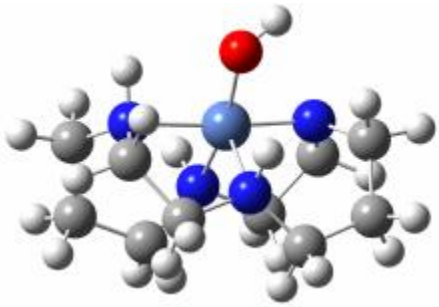
q(Ni) = –1.548 e

q(O) = –0.324 e

q(N) = +0.023, +0.055, +0.096, +0.285 e

$E_{SOMO,\alpha}$ = –0.331 au

$E_{SOMO-1,\alpha}$ = –0.366 au,



$E_{SOMO-1,\beta}$ = –0.329 au

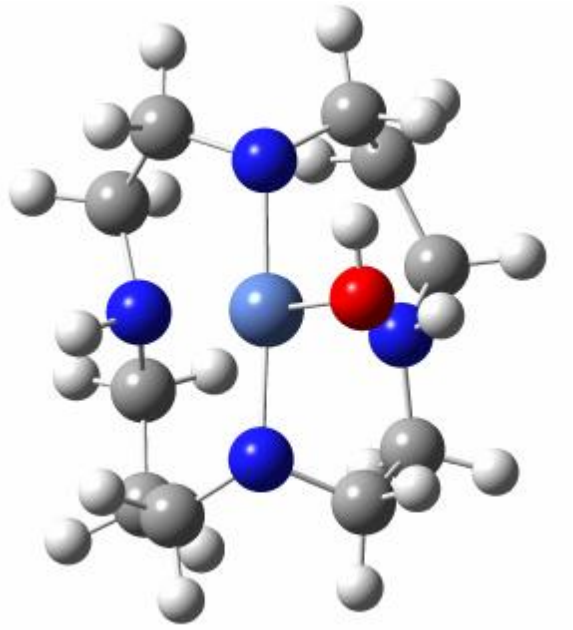
$E_{SOMO+1,\alpha}$ = –0.213 au, $E_{SOMO+1,\beta}$ = –0.224 au

Δ_{min} = 0.002 au

^{2}{Ni(III)(OH$^-$)[N$_4$14–2H$^+$]}^{0}

E = –2197.47857 au

μ_{dip} = 6.54 D



R(Ni–N) = 1.912, 1.918, 2.016, 2.093 Å

R(Ni–O) = 1.865 Å

R(O–H) = 0.964 Å

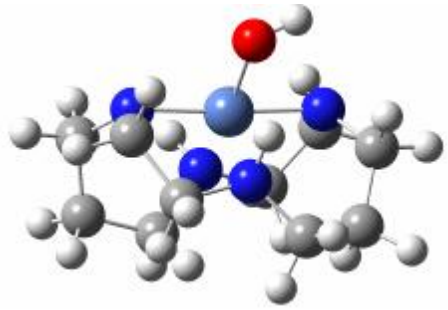
q(Ni) = –1.187 e

q(O) = –0.300 e

q(N) = –0.054, +0.056, +0.065, +0.215 e

$E_{SOMO,\alpha}$ = –0.170 au

$E_{SOMO-1,\alpha}$ = –0.186 au, $E_{SOMO-1,\beta}$ = –0.169 au



$E_{SOMO+1,\alpha}$ = –0.164 au, $E_{SOMO+1,\beta}$ = –0.072 au

Δ_{min} = 0.001 au

S6. Calculated molecular properties of OH^-, H_2O, H_3O^+, H_2 and CO_2.

$^1(OH^-)$

E = –75.82745 au

μ_{dip} = 1.74 D

R(O–H) = 0.966 Å

q(O) = –1.114 e

E_{HOMO} = +0.047 au

E_{LUMO} = +0.169 au

Δ_{HL} = 0.122 au

$^1(H_2O)$

E = –76.45853 au

μ_{dip} = 2.16 D

R(O–H) = 0.962 Å

q(O) = –0.502 e

E_{HOMO} = –0.323 au

E_{LUMO} = –0.023 au

Δ_{HL} = 0.300 au

$^1(H_3O^+)$

E = –76.73124 au

μ_{dip} = 1.43 D

R(O–H) = 0.980 Å

q(O) = –0.201e

E_{HOMO} = –0.745 au

E_{LUMO} = –0.284 au

Δ_{HL} = 0.461 au

$^1H_2$

E = –1.17957 au

R(H–H) = 0.744 Å

E_{HOMO} = –0.434 au

E_{LUMO} = +0.020 au

Δ_{HL} = 0.454 au

$^1CO_2$

E = –188.64691 au

R(C–O) = 1.161 Å

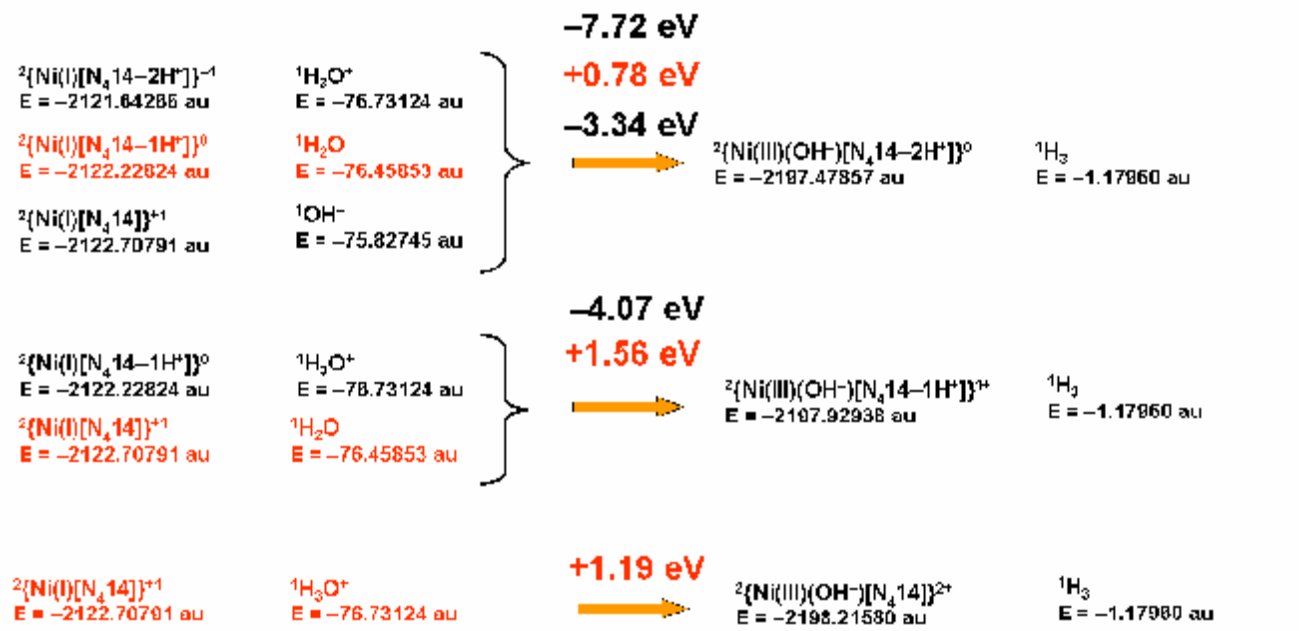
E_{HOMO} = –0.356 au

E_{LUMO} = –0.020 au

Δ_{HL} = 0.336 au

S7. Transformations of various hydroxy- complexes of Ni(I) at different deprotonation stages.

Schematic representation of H_2 elimination reactions involving tetraazamacrocyclic complexes of Ni(I) at various pH. Calculated enthalpies of reactions are shown.



Due to large differences between acidity and basicity of species considered here, the process described by Eq.(7a) in the paper is calculated to be extremely sensitive to pH. For example, the calculated enthalpies of reactions:

$2Ni(I)[N_414]^+ + H_3O^+ \rightarrow 2\ Ni(III)(OH^-)[N_414]^{2+} + H_2$, (Eq.Ss)

$2Ni(I)[N_414]^+ + H_2O \rightarrow 2\ Ni(III)(OH^-)[N_414–H^+]^+ + H_2$, (Eq.Sb)

$2Ni(I)[N_414]^+ + OH^- \rightarrow 2\ Ni(III)(OH^-)[N_414–2H^+]^0 + H_2$, (Eq.Sc)

range in an extremely broad span, from +1.19 eV via +1.56 eV to –3.34 eV, respectively.

Ni(I)-catalyzed process of H_2 evolution is calculated to be thermodynamically viable for complexes at various deprotonation stages of the amino hydrogens; among these, reaction intermediate between (Sc) and between the process:

$2Ni(I)[N_414–H^+]^0 + H_2O \rightarrow 2Ni(III)(OH^-)[N_414–2H^+]^0 + H_2$, (Eq.Sd)

seems to be the most rational choice (while analyzing graph above recollect that simultaneous presence of deprotonated complex and hydronium cations is unlikely in the same reaction medium). Such 'intermediate process' might be realized for a hydrated complex deprotonated at one amine N, which shows the (OH_2...N^-) hydrogen bond interaction.

Studies of involvement of aquacomplexes in these reaction (for example:

$2\{Ni(I)[N_414]\}^+ + 2\ H_3O^+ \rightarrow 2\{Ni(III)(OH_2)_2[N_414]\}^+ + H_2$, (Eq.Se)

and those taking into account the trans/cis isomerism of cyclam complexes are also natural extensions of present work, and they are under scrutiny in our laboratory.