Ligand Protonation Triggers H₂ Release from a Dinickel Dihydride Complex to Give a Doubly “T”-Shaped Dinickel(I) Metallodiradical

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1. General Considerations and Materials

All manipulations were performed under an anaerobic and anhydrous atmosphere of dry argon by using standard Schlenk techniques, or in a glove box (O₂ < 0.5 ppm, H₂O < 0.5 ppm). Chemicals used were either present in the working group or were purchased from commercial sources, or their synthesis is described below. Glassware was dried at 120°C prior to use. THF, diethyl ether, pentane and hexane were dried over sodium in the presence of benzophenone; all solvents were distilled prior to use. THF-d₈ was also dried over sodium in the presence of benzophenone and distilled, then stored in the presence of 3 Å molecular sieves. Complexes LNi₂Br, 1K and 1' were prepared as reported previously.¹

UV–Vis spectra were recorded on an Agilent Cary 60 equipped with an Unisoku Cryostat (CoolSpek) and magnetic stirrer using quartz cuvettes with an attached tube and a screw cap with a septum. All UV–vis samples were prepared in a glovebox and transferred out of the glovebox prior to the measurement.

IR measurements were performed with a Cary 630 FTIR spectrometer with Dial Path Technology with solid samples and analyzed by FTIR MicroLab software.

2. Syntheses

Synthesis of [KLNi₂]²⁺ (2K): KC₈ (20 mg, 0.5 mmol, 2 equiv) was added to a brown slurry of LNi₂Br (200 mg, 0.25 mmol, 1 equiv) in THF. The reaction mixture became dark red within 30 min and was stirred for 2 hours at room temperature to yield a deep red solution. The solvent was removed under vacuum. The residue was then dissolved in THF, and the KBr and graphite removed by filtration through Celite. After layering with hexane, the product was obtained as red block crystals after one week (yield: 35%).

ATR-IR (ν/cm⁻¹) = 3056 (w), 2955 (m), 2923 (m), 2863 (m), 1552 (m), 1521 (m), 1458 (m), 1432 (s), 1397 (s), 1319 (m), 1270 (m), 1253 (m), 1231 (m), 1192 (m), 1090 (w), 1056 (m), 1019 (m), 935 (w), 848 (m), 795 (m), 756 (s), 735 (w), 645 (w), 631 (w), 545 (w), 520 (w).

UV-vis (THF): λmax = 270, 370 and 384 nm.

Synthesis of [NaLNi₂]²⁺ (2Na): A solution of sodium naphthalide (1 M) in THF (0.5 mL, 0.5 mmol, 2 equiv) was added to a brown slurry of LNi₂Br (200 mg, 0.25 mmol, 1 equiv) in THF. The reaction mixture became dark red immediately and was stirred for 2 hours at room
temperature to yield a deep red solution. The reaction mixture was filtered through Celite. After layering with hexane, the product was obtained as red block crystals after one week (Yield: 40%).

**UV-vis** (THF): $\lambda_{\text{max}} = 269, 365$ and $380$ nm.

**Synthesis of [K(DB18C6)]LNiI$_2$ (2'):** Method A. Dibenzo(18-crown-6) (17.3 mg, 0.048 mmol, 1.2 equiv) was added into a solution of 2K (30 mg, 0.04 mmol, 1 equiv) in THF at room temperature. After stirring the red solution for 2 h, all volatiles were removed in vacuo. The red residue was washed twice with hexane (10 mL) and the product obtained as red block crystals by layering hexane/Et$_2$O onto a solution of the crude product in THF for two days.

**Method B.** A sample of [K(DB18C6)][L(NiH)$_2$] (1'), prepared as described in ref. 1, has been thoroughly dried under vacuum for one day. Dissolving it in THF, layering with hexane/Et$_2$O and slow diffusion of the solvents at -30°C yielded the product as red crystals suitable for X-ray diffraction (yield: 40%).

**ATR-IR** ($\tilde{\nu}$/cm$^{-1}$) = 3054 (w), 2953 (m), 2924 (m), 2964 (m), 1595 (m), 1549 (w), 1503 (s), 1453 (m), 1435 (m), 1399 (m), 1358 (w), 1321 (m), 1297 (w), 1248 (s), 1230 (m), 1209 (m), 1123 (vs), 1086 (m), 1052 (s), 1026 (w), 995 (m), 956 (w), 934 (m), 901 (m), 851 (w), 810 (w), 778 (w), 738 (vs), 646 (w), 595 (m), 557 (w), 524 (w).

**UV-vis** (THF): $\lambda_{\text{max}} = 270, 330, 370$ and $384$ nm.

**Synthesis of [LH$_2$Ni]BArF$_4$ (3):** 1K (30 mg, 0.04 mmol, 1 equiv) was dissolved in THF (2 mL) to give a clear, orange solution. To this solution [H(Et$_2$O)$_2$]BArF$_4$ (89.1 mg, 0.088 mmol, 2.2 equiv) was quickly added, resulting in an brown-red clear solution which was cooled (-30°C) and layered with hexanes. Slow diffusion of the solvents at -30°C yielded the product as yellow, block-shaped crystals suitable for X-ray diffraction (yield: 40%). Often the crystals were accompanied by inorganic salts (presumably KBrF$_4$) and manual separation was necessary to collect pure product. However, because of remaining trace impurities and its high sensitivity no reliable SQUID data of complex 3 could be obtained.

**ATR-IR** ($\tilde{\nu}$/cm$^{-1}$) = 2960 (m), 2926 (m), 2873 (m), 2861 (m), 1670 (C=N) (m), 1610 (m), 1464 (m), 1442 (m), 1387 (m), 1357 (m), 1271 (m), 1113 (m), 957 (m), 936 (m), 887 (m), 841 (m), 803 (m), 791 (m), 770 (m), 758 (m), 744 (m), 711 (m), 682 (m), 670 (m).

**UV-vis** (THF): $\lambda_{\text{max}} = 270, 322$ and $385$ nm.
3. IR and UV-Vis Spectra

**Figure S1**: ATR-IR spectrum of solid $2^K$.

**Figure S2**: UV-vis spectrum of $2^K$ in THF at different temperatures.
Figure S3: ATR-IR spectrum of solid 2'.

Figure S4: UV-vis spectrum of 2' in THF at different temperatures.
Figure S5: ATR-IR spectrum of solid 3.

Figure S6: UV-Vis spectrum of $1^k$ (black line) and after addition of [H(Et$_2$O)$_2$]BAR$_4$ to give 3 (blue line); at rt in THF under Ar.
Figure S7: UV-Vis spectrum of 3 (blue line) and after addition of KHMDS giving $2^k$ (green line); at rt in THF under Ar.
4. Magnetic Measurements

Temperature-dependent magnetic susceptibility measurements for $2^K$ and $2^Na$ were carried out with a Quantum-Design MPMS-XL-5 SQUID magnetometer equipped with a 5 Tesla magnet at a magnetic field of 0.5 T. The powdered samples were contained in a Teflon bucket and fixed in a non-magnetic sample holder. Each raw data file for the measured magnetic moment was corrected for the diamagnetic contribution of the Teflon bucket according to $M_{\text{dia}(\text{bucket})} = \chi g m H$, with an experimentally obtained gram susceptibility of the Teflon bucket. The molar susceptibility data were corrected for the diamagnetic contribution according to $\chi_{\text{M dia}(\text{sample})} = -0.5 M \cdot 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$. Experimental data were modelled with the julX program using a fitting procedure to the Heisenberg-Dirac-van-Vleck (HDvV) spin Hamiltonian for isotropic exchange coupling and Zeeman splitting, equation (1).

$$\hat{H} = -2J \hat{S}_1 \cdot \hat{S}_2 + g \mu_B (\hat{S}_1 + \hat{S}_2) B$$  \hspace{1cm} (1)

Temperature-independent paramagnetism (TIP) and a Curie-behaved paramagnetic impurity (PI) with spin $S = 1$ were included according to $\chi_{\text{calc}} = (1 - \text{PI}) \cdot \chi + \text{PI} \cdot \chi_{\text{mono}} + \text{TIP}$. TIP = 1.4%, TIP = 340 $\cdot 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ for $2^K$ and TIP = 1.3%, TIP = 200 $\cdot 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ for $2^Na$.

Figure S8: $\chi M T$ vs. T plot for $2^Na$; the solid red line represents the calculated curve fit ($\hat{H} = -2J \hat{S}_1 \hat{S}_2$ with $J = -83 \text{ cm}^{-1}$ and $g = 2.14$).
5. X-Ray Crystallography

Crystal data and details of the data collections are given in Table S1, selected bond lengths and angles in Table S2, molecular structures are shown in Figures S9 – S11. X-ray data were collected on a STOE IPDS II or a BRUKER D8-QUEST diffractometer (monochromated Mo-Kα radiation, λ = 0.71073 Å) by use of ω or ω and φ scans at −140 °C or −173 °C. The structures were solved with SHELXT and refined on \( F^2 \) using all reflections with SHELXL-17/18. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 1.5/1.2 \( U_{eq}(C) \).

One \(^{1}\)Pr-group (occupancy factors: 0.837(4) / 0.163(4) (C37, C38, C39A/B)) and a thf solvent molecules (occupancy factors: 0.679(9) / 0.321(9) (only C46A/B)) were found to be disordered in 2Na (ras27). SADI restraints \( (d_{C46A/B-C45/47}) \) and EADP constraints (for \(^{1}\)Pr carbon atoms) were applied to model the disordered parts. In case of 3 (pd275b) one \(^{1}\)Pr-group was found to be disordered about two positions (occupancy factors: 0.602(5) / 0.398(5)). SAME, SADI & RIGU restraints and EADP constraints were applied to model the disorder. Two CF\(_3\)-groups of the counter-ion (occupancy factors: 0.305(4) / 0.695(4) and 0.552(19) / 0.448(19)) and three out of four thf molecules (occupancy factors: 0.226(15) / 0.774(15), 0.569(7) / 0.431(7) and 0.497(8) / 0.503(8)) are disordered as well. SADI, RIGU & ISOR restraints and EADP constraints in case of the CF\(_3\)-groups and DFIX \( (d_{C-O} = 1.44 \, \text{Å}, d_{C-C} = 1.54 \, \text{Å}) \), SAME, SIMU, DELU & ISOR restraints in case of the thf molecules and a BUMP restraint have been used. Face-indexed absorption corrections were performed numerically with the program X-RED\(^4\) or by the multi-scan method with SADABS\(^5\).
| Compound | $2^\alpha$ (ras27) | $2^\beta$ (ras33) | 3 (pd275b) |
|----------|--------------------|--------------------|-------------|
| **Empirical formula** | $C_{47}H_{69}NaNaNi_2O_2$ | $C_{55}H_{55}KN_6Ni_2O_4$ | $C_{39}H_{35}NaNi_2^+ \cdot C_{32}H_{12}BF_{24}^- \cdot 4(CdH_8O)$ |
| **Moiety formula** | $C_{47}H_{69}NaNaNi_2O_2$ | $C_{55}H_{55}KN_6Ni_2O_4$ | $C_{39}H_{35}NaNi_2^+ \cdot C_{32}H_{12}BF_{24}^- \cdot 4(CdH_8O)$ |
| **Formula weight** | 890.49 | 1050.80 | 1876.95 |
| **Crystal size [mm$^3$]** | 0.352 x 0.263 x 0.176 | 0.500 x 0.490 x 0.360 | 0.500 x 0.490 x 0.480 |
| **Crystal system** | monoclinic | monoclinic | triclinic |
| **T [K]** | 100(2) | 133(2) | 133(2) |
| **Formula** | $C_{47}H_{69}NaNaNi_2O_2$ | $C_{55}H_{55}KN_6Ni_2O_4$ | $C_{39}H_{35}NaNi_2^+ \cdot C_{32}H_{12}BF_{24}^- \cdot 4(CdH_8O)$ |
| **Crystal system** | monoclinic | monoclinic | triclinic |
| **Space group** | $P_{2_1}/n$ (No. 14) | $P_2_1$ (No. 4) | $P$–1 (No. 2) |
| **a [Å]** | 18.6514(7) | 13.8033(4) | 12.7703(4) |
| **b [Å]** | 13.9305(5) | 14.7683(3) | 18.0462(5) |
| **c [Å]** | 18.7394(7) | 14.2159(4) | 20.8906(6) |
| **α [°]** | 90 | 90 | 72.510(2) |
| **β [°]** | 108.870(1) | 106.622(2) | 74.014(2) |
| **γ [°]** | 90 | 90 | 80.426(2) |
| **V [Å$^3$]** | 4607.3(3) | 2776.83(13) | 4395.8(2) |
| **Z** | 4 | 2 | 2 |
| **ρ [g cm$^{-3}$]** | 1.284 | 1.257 | 1.418 |
| **F(000)** | 1904 | 1128 | 1944 |
| **µ [mm$^{-1}$]** | 0.870 | 0.801 | 0.532 |
| **T$\min$ / T$\max$** | 0.67 / 0.75$^5$ | 0.4327 / 0.9060$^*$ | 0.6054 / 0.7674$^*$ |
| **θ-range [°]** | 2.297 - 28.293 | 1.495 - 25.649 | 1.359 - 26.968 |
| **hkl-range** | -24 to 23, ±18, ±24 | ±16, ±17, ±17 | -16 to 14, ±22, ±26 |
| **Measured refl.** | 128356 | 32019 | 59769 |
| **Unique refl. [Rint]** | 11438 [0.0821] | 10195 [0.0437] | 18539 [0.0198] |
| **Observed refl. (I > 2σ(I))** | 8904 | 9605 | 15534 |
| **Data / restr. / param.** | 11438 / 6 / 557 | 10195 / 1 / 625 | 18539 / 724 / 1335 |
| **Goodness-of-fit (F$^2$)** | 1.062 | 1.053 | 1.025 |
| **R1, wR2 (I > 2σ(I))** | 0.0372 / 0.0776 | 0.0302 / 0.0749 | 0.0399 / 0.1001 |
| **R1, wR2 (all data)** | 0.0592 / 0.0903 | 0.0344 / 0.0785 | 0.0504 / 0.1076 |
| **Res. el. dens. [e·Å$^{-3}$]** | -0.994 / 0.961 | -0.197 / 0.481 | -0.503 / 0.636 |

$^5$ SADABS, $^*$X-RED
Table S2. Selected distances [Å] and angles [°].

|                  | $^2$Na                      | $^2$K                      | 3                     |
|------------------|-----------------------------|----------------------------|-----------------------|
| Ni–N$_{pz}$      | 1.8944(17) / 1.9118(17)     | 1.890(3) / 1.892(3)        | 1.8785(16) / 1.8807(16)|
| Ni–N$_{NaNa}$    | 1.8624(18) - 1.9212(17)     | 1.857(3) - 1.917(3)        | 1.8860(16) - 1.9513(16)|
| Ni–C             | -                           | -                          | -                     |
| Ni···Na          | 3.0507(10) / 3.3477(10)     | 3.8554(9) / 3.9661(9)      | 4.1032(5)             |
| Ni···K           | 4.1899(4)                   | 4.1243(7)                 | 4.057(5)              |
| Na–N             | 2.4466(19) / 2.5314(19)     | 2.954(3) / 3.039(3)        | -                     |
| K–N              | 2.7523(14)                  | -                          | -                     |
| Na–C (< 3.2 Å)   | 3.101(2) / 3.195(3)         | 3.226(3) - 3.498(4)        | -                     |
| K–C (< 3.5 Å)    | 2.7523(14)                  | 3.057(7)                  | -                     |
| Na–C$_{pz}^a$    | 175.59(7) / 176.50(7)       | 176.21(12) / 176.76(13)    | 177.91(7) / 178.04(7)  |
| K–C$_{pz}^a$     | 84.34(7) - 98.36(8)         | 84.43(12) - 99.22(12)      | 84.62(7) - 96.99(7)    |

$^a$) C$_{pz}^a$ is defined as the centroid of the five pyrazolate ring atoms.
Figure S9. Plot (30% probability thermal ellipsoids) of the molecular structure of $2^{Na}$ (most hydrogen atoms omitted for clarity). Sodium carbon contacts < 3.2 Å are shown as dashed lines. Cg$^{pz}$ is defined as the centroid of the five pyrazolate ring atoms. Selected bond lengths [Å] and angles [°]: Ni1–N1 1.9118(17), Ni2–N2 1.8944(17), Ni1–N3 1.9212(17), Ni1–N4 1.8794(17), Ni2–N5 1.9140(17), Ni2–N6 1.8624(18), Na1–O1 2.248(2), Na1–O2 2.269(2), Na1–N1 2.5314(19), Na1–N2 2.4466(19), Na1–C2 3.195(3), Na1–C3 3.101(2), Na1–Cg$^{pz}$ 2.7523(14), Ni1···Na1 3.3477(10), Ni2···Na1 3.0507(10), Ni1···Ni2 4.1899(4); N4–Ni1–N1 175.59(7), N4–Ni1–N3 98.17(7), N1–Ni1–N3 84.34(7), N6–Ni2–N2 176.50(7), N6–Ni2–N5 98.36(8), N2–Ni2–N5 85.04(7).
Figure S10. Plot (30% probability thermal ellipsoids) of the molecular structure of the $2^k$ (most hydrogen atoms omitted for clarity). Potassium carbon contacts < 3.5 Å are shown as dashed lines. Cg$_{pz}$ is defined as the centroid of the five pyrazolate ring atoms. Selected bond lengths [Å] and angles [°]: Ni1–N1 1.890(3), Ni2–N2 1.892(3), Ni1–N3 1.917(3), Ni1–N4 1.858(3), Ni2–N5 1.917(3), Ni2–N6 1.857(3), K1–O1 2.760(3), K1–O2 2.776(3), K1–O3 2.718(3), K1–O4 2.798(3), K1–N1 3.039(3), K1–N2 2.954(3), K1–C1 3.498(4), K1–C2 3.371(3), K1–C3 3.226(3), K1–Cg$_{pz}$ 3.0057(7), Ni1···K1 3.8554(9), Ni2···K1 3.9661(9), Ni1···Ni2 4.1243(7); N4–Ni1–N1 176.76(13), N4–Ni1–N3 98.75(13), N1–Ni1–N3 84.43(12), N6–Ni2–N2 176.21(12), N6–Ni2–N5 99.22(12), N2–Ni2–N5 84.49(12).
Figure S11. Plot (30% probability thermal ellipsoids) of the molecular structure of the cationic part of 3 (most hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni1–N1 1.8807(16), Ni2–N2 1.8785(16), Ni1–N3 1.9513(16), Ni1–N4 1.8881(16), Ni2–N5 1.9476(15), Ni2–N6 1.8860(16), Ni1⋯Ni2 4.1032(5); N1–Ni1–N4 177.91(7), N1–Ni1–N3 84.73(7), N4–Ni1–N3 96.99(7), N2–Ni2–N6 178.04(7), N2–Ni2–N5 84.62(7), N6–Ni2–N5 96.52(7).
6. X-Ray Spectroscopy

X-ray absorption was measured for powder sample. Each sample was ground together with boron nitride to give ~1% Ni by weight, so that self-absorption would be avoided. Samples were packed into 1 mm Al spacers and sealed with Kapton tape. Samples were handled anaerobically in a glove box and immediately frozen in liquid N₂ following preparation. XAS measurements were performed at beamline 9-3 at the Stanford Synchrotron Radiation Laboratory (SSRL) operating at 3 GeV with a 500 mA ring current. During measurements the samples were cooled to 10 K using a continuous flow liquid He cryostat from Oxford Instrument. The X-ray energy was selected with a liquid nitrogen cooled Si(220) double crystal monochromator. To reduce higher harmonics, a harmonic rejection mirror set to a 13 eV cutoff was combined with 10% detuning of the monochromator. The energy was calibrated by setting the first inflection point of Ni metal foil to 8331.7 eV which was collected in transmission mode placed in the beam path after the sample. The XAS spectra were measured by monitoring the total fluorescence yield using a 100-element Ge Detector, windowed to the Ni Kα emission. Multiple layers of aluminum foils as needed were employed to attenuate the incident beam to minimize photodamage.
7. DFT Calculations

A) (geometry optimization, IR, UV-vis, magnetic properties & orbitals, spin density)

Computational Details. The ORCA program package (version 4.2.1) was employed for all calculations. Geometry optimization and frequency calculation was performed starting from the crystallographic data of $2^K$ with [K(THF)$_4$]$^+$ removed and the cationic $3$ (BP86 functional, def2-TZVP basis set, RI approximation using the auxiliary def2/J basis set, Grimme’s D3 dispersion correction with Becke-Johnson damping, tight convergence and optimization criteria). All other calculations were performed on the optimized coordinates or coordinates from crystallographic data with the B3LYP functional and the RIJCOSX approximation with the same basis sets and dispersion correction as stated above. TD-DFT calculations were carried out at the B3LYP/def2-TZVP level of theory (80 states included).

Molecular structures have been optimized using the conductor-like polarizable continuum mode (CPCM) with default settings for THF. $J$ has been calculated from $-(\langle E[\text{high-spin}] - E[\text{broken symmetry}]\rangle - \langle S^2 \rangle[\text{high-spin}] - \langle S^2 \rangle[\text{broken symmetry}]$).

Table S3. Comparison of experimental and DFT calculated metric parameters of [LNi$_2$]$^-$; selected distances [Å] and angles [°].

|                  | [LNi$_2$]$^-$ (exp: $2^K$) | [LNi$_2$]$^-$ ($S = 1$) | [LNi$_2$]$^-$ ($S = 0$) |
|------------------|----------------------------|-------------------------|-------------------------|
| Ni–N$_{pz}$      | 1.890(3) / 1.892(3)        | 1.89603 / 1.89637        | 1.88855 / 1.88864       |
| Ni–N$_{NacNac}$  | 1.857(3) - 1.917(3)        | 1.85804 - 1.91244        | 1.85812 - 1.91444       |
| Ni⋯Ni            | 4.1243(7)                 | 4.12728                 | 4.08404                 |
| N–Ni–N           | 176.21(12) / 176.76(13)    | 176.405 / 176.438        | 176.840 / 176.859       |
| (opposite)       |                           |                         |                         |
| N–Ni–N ($<$ 100°)| 84.43(12) - 99.22(12)      | 85.146 - 98.169          | 85.000 - 98.156         |

Table S4. Comparison of experimental and DFT calculated metric parameters of [L$^{12}$Ni$_2$]$^+$; selected distances [Å] and angles [°].

|                  | [L$^{12}$Ni$_2$]$^+$ (exp: 3) | [L$^{12}$Ni$_2$]$^+$ ($S = 1$) | [L$^{12}$Ni$_2$]$^+$ ($S = 0$) |
|------------------|-------------------------------|-------------------------|-------------------------|
| Ni–N$_{pz}$      | 1.8785(16) / 1.8807(16)       | 1.88290 / 1.88471        | 1.87878 / 1.88042       |
| Ni–N$_{NacNac}$  | 1.8860(16) - 1.9513(16)       | 1.85551 - 1.94147        | 1.85730 - 1.94274       |
| Ni⋯Ni            | 4.1032(5)                     | 4.07989                 | 4.05164                 |
| N–Ni–N           | 177.91(7) / 178.04(7)         | 177.339 / 177.485        | 177.198 / 177.407       |
| (opposite)       |                               |                         |                         |
| N–Ni–N ($<$ 100°)| 84.62(7) - 96.99(7)          | 84.997 - 97.251          | 84.849 - 97.180         |
Table S5. Comparison of relative energies (kcal/mol) and \( J \) (cm\(^{-1}\)).

|                | \( \Delta E \) | \( J \)  |
|----------------|----------------|---------|
| \([\text{LNi}_2]\) (\(S = 1\)) | 0              | -       |
| \([\text{LNi}_2]\) (\(S = 0\))   | +0.19          | -56.44  |
| anion of \(2^k\) (single point, \(S = 1\)) * | +0.29          | -       |
| anion of \(2^k\) (single point, \(S = 0\)) * | 0              | -100.04 |
| \([\text{L}^{\text{H}_2}\text{Ni}_2]\) (\(S = 1\)) | +0.17          | -       |
| \([\text{L}^{\text{H}_2}\text{Ni}_2]\) (\(S = 0\)) | 0              | -51.79  |
| cation of \(3\) (single point, \(S = 1\)) * | +0.31          | -       |
| cation of \(3\) (single point, \(S = 0\)) * | 0              | -107.98 |

*) coordinates from crystallographic data, not DFT optimized, \([\text{K(THF)}_4]^+\) part removed in case of \(2^k\), anionic part removed in case of 3

Figure S12. DFT optimized molecular structure of \([\text{LNi}_2]^-(S = 1)\) (Ni = red, N = blue, C = grey).
Figure S13. DFT optimized molecular structure of $[L^\text{H}_2\text{Ni}_2]^+$ ($S = 1$) (Ni = red, N = blue, C = grey).

Figure S14. Calculated IR spectrum of $[\text{LNi}_2]^-$ ($S = 1$). The spectrum was convoluted using a Gaussian line shape function with a half-width of 20 cm$^{-1}$. 
**Figure S15.** Calculated IR spectrum of $[\text{LNi}_2^-] \ (S = 0)$. The spectrum was convoluted using a Gaussian line shape function with a half-width of 20 cm$^{-1}$.

**Figure S16.** Calculated IR spectrum of $[\text{L}^{\text{H}_2}\text{Ni}_2]^+ \ (S = 1)$. The spectrum was convoluted using a Gaussian line shape function with a half-width of 20 cm$^{-1}$.
**Figure S17.** Calculated absorption spectrum of $[\text{LNi}_2]^-$ ($S = 0$) in THF. The spectrum was convoluted using a Gaussian line shape function with a half-width of 20 nm.

**Figure S18.** Calculated absorption spectrum of $[\text{L}{^{14}\text{Ni}}_2]^+$ ($S = 0$) in THF. The spectrum was convoluted using a Gaussian line shape function with a half-width of 20 nm.
Figure S19. Spin density plot of $[\text{LNi}_2^-]$ ($S = 1$). Loewdin spin population: Ni1 = 0.87, Ni2 = 0.87. (isosurface value: 0.04).

Figure S20. Spin density plot of $[\text{L}^\text{H}_2\text{Ni}_2^+]$ ($S = 1$). Loewdin spin population: Ni1 = 0.87, Ni2 = 0.87. (isosurface value: 0.04).
**Figure S21.** Combined corresponding orbitals\textsuperscript{10} representing the magnetic orbitals for the broken symmetry state of $[\text{LNi}_2]^-$ (isosurface value: 0.08).

**Figure S22.** Combined corresponding orbitals\textsuperscript{10} representing the magnetic orbitals for the broken symmetry state of $[\text{L}^\text{H}_2\text{Ni}_2]^+$. (isosurface value: 0.08).
Figure S23. Corresponding orbitals\textsuperscript{10} (\(\alpha\) left, \(\beta\) right) representing the magnetic orbitals for the broken symmetry state of \([LNi\textsubscript{2}]^–\). (isosurface value: 0.08).

Figure S24. Corresponding orbitals\textsuperscript{10} (\(\alpha\) left, \(\beta\) right) representing the magnetic orbitals for the broken symmetry state of \([L\textsuperscript{H2}Ni\textsubscript{2}]^+\). (isosurface value: 0.08).

Table S6. Selected states, energies (cm\(^{-1}\)), wavelengths (nm), oscillator strengths, and compositions (according to Lowedin reduced orbital populations per MO) of electronic transitions of \([LNi\textsubscript{2}]^–\) (\(S = 0\)) from TD-DFT calculation (\(H\) = HOMO, \(L\) = LUMO).

| state | energy | wavelength | osc. strength | selected large contributions |
|-------|--------|------------|---------------|-----------------------------|
| 3     | 10420.0| 959.7      | 0.000612546   | H-2 (a) (91% Ni) \(\rightarrow\) L+2 (a) (16% Ni) (d-d), H-2 (a) (91% Ni) \(\rightarrow\) L+6 (a) (33% Ni) (d-d) |
| 6     | 11826.8| 845.5      | 0.000907444   | H-4 (b) (61% Ni) \(\rightarrow\) L+2 (b) (16% Ni) (d-d), H-3 (b) (61% Ni) \(\rightarrow\) L+6 (b) (33% Ni) (d-d) |
| 7     | 13747.4| 727.4      | 0.001711298   | H-7 (a) (67% Ni) \(\rightarrow\) L+2 (a) (16% Ni) (d-d), H-7 (a) (67% Ni) \(\rightarrow\) L+6 (a) (33% Ni) (d-d) |
| 12    | 19060.9| 524.6      | 0.006385497   | H-1 (a) (56% Ni) \(\rightarrow\) L+1 (a) (7% Ni) (MLCT), H-1 (a) (56% Ni) \(\rightarrow\) L(a) (8% Ni) (MLCT) |
| 15    | 21572.8| 463.5      | 0.017377888   | H-6 (a) (70% Ni) \(\rightarrow\) L+1 (a) (7% Ni) (MLCT), H-4 (a) (63% Ni) \(\rightarrow\) L(a) (8% Ni) (MLCT) |
| 18    | 23010.8| 434.6      | 0.026032864   | H-3 (a) (60% Ni) \(\rightarrow\) L+1 (a) (7% Ni) (MLCT), H (a) (63% Ni) \(\rightarrow\) L+1 (a) (7% Ni) (MLCT) |
| 26    | 24673.9| 405.3      | 0.029405567   | H-1 (b) (56% Ni) \(\rightarrow\) L+6 (b) (3% Ni) (MLCT), H-1 (a) (56% Ni) \(\rightarrow\) L+6 (a) (3% Ni) (MLCT) |
| 57    | 27951.4| 357.8      | 0.014417610   | H-2 (b) (91% Ni) \(\rightarrow\) L+4 (b) (2% Ni) (MLCT) |
| 64    | 29464.3| 339.4      | 0.014884541   | H-3 (a) (60% Ni) \(\rightarrow\) L+3 (a) (5% Ni) (MLCT) |
| 71    | 29992.8| 333.4      | 0.048750075   | H-2 (a) (91% Ni) \(\rightarrow\) L+5 (a) (3% Ni) (MLCT) |
Table S7. Selected states, energies (cm\(^{-1}\)), wavelengths (nm), oscillator strengths, and compositions (according to Lowedin reduced orbital populations per MO) of electronic transitions of [L\(^{\text{H2}}\)Ni\(_2\)]\(^+\) (S = 0) from TD-DFT calculation (H = HOMO, L = LUMO).

| state | energy | wavelength | osc. strength | selected large contributions |
|-------|--------|------------|---------------|-----------------------------|
| 2     | 10467.2 | 955.4      | 0.001019499   | H-1 (a) (91% Ni) → L+4 (a) (33% Ni) (d-d) |
| 6     | 12033.4 | 831.0      | 0.000648272   | H-3 (a) (87% Ni) → L+4 (a) (33% Ni) (d-d) |
| 7     | 14045.3 | 712.0      | 0.001166516   | H-7 (b) (87% Ni) → L+4 (b) (34% Ni) (d-d) |
| 13    | 20155.9 | 496.1      | 0.012365618   | H-2 (b) (55% Ni) → L+1 (b) (6% Ni) (MLCT), H-2 (b) (55% Ni) → L (b) (6% Ni) (MLCT) |
| 24    | 24605.7 | 406.4      | 0.016499617   | H-3 (b) (87% Ni) → L+3 (b) (10% Ni) (MLCT) |
| 32    | 25303.1 | 395.2      | 0.011178716   | H (a) (55% Ni) → L+4 (a) (33% Ni) (d-d) |
| 36    | 27239.6 | 367.1      | 0.034795307   | H-4 (a) (64% Ni) → L+1 (a) (6% Ni) (MLCT) |
| 45    | 28376.4 | 352.4      | 0.031564584   | H-4 (b) (64% Ni) → L+2 (b) (6% Ni) (MLCT) |
| 56    | 29578.0 | 338.1      | 0.040157944   | H-4 (a) (64% Ni) → L (a) (6% Ni) (MLCT) |

Figure S25. Orbitals with large contributions to state 3 in [LNi\(_2\)]\(^-\) (S = 0); H-2 (a) (91% Ni) → L+2 (a) (16% Ni). (isosurface value: 0.08).

Figure S26. Orbitals with large contributions to state 6 in [LNi\(_2\)]\(^-\) (S = 0); H-4 (b) (61% Ni) → L+2 (b) (16% Ni). (isosurface value: 0.08).
Figure S27. Orbitals with large contributions to state 7 in [LNi₂]⁻ (S = 0); H-7 (a) (67% Ni) → L+6 (a) (33% Ni). (isosurface value: 0.08).

Figure S28. Orbitals with large contributions to state 12 in [LNi₂]⁻ (S = 0); H-1 (a) (56% Ni) → L+1 (a) (7% Ni). (isosurface value: 0.08).

Figure S29. Orbitals with large contributions to state 26 in [LNi₂]⁻ (S = 0); H-1 (b) (56% Ni) → L+6 (b) (3% Ni). (isosurface value: 0.08).
Figure S30. Orbitals with large contributions to state 64 in [LNi₂]⁻ (S = 0); H-3 (a) (87% Ni) → L+4 (a) (33% Ni). (isosurface value: 0.08).

Figure S31. Orbitals with large contributions to state 2 in [LH₂Ni₂]⁺ (S = 0); H-1 (a) (91% Ni) → L+4 (a) (33% Ni). (isosurface value: 0.08).

Figure S32. Orbitals with large contributions to state 6 in [LH₂Ni₂]⁺ (S = 0); H-3 (a) (87% Ni) → L+4 (a) (33% Ni). (isosurface value: 0.08).
Figure S33. Orbitals with large contributions to state 7 in $[\text{L}^{\text{H2Ni}}]^{+}$ ($S = 0$); H-7 (b) (87% Ni) $\rightarrow$ L+4 (b) (34% Ni). (isosurface value: 0.08).

Figure S34. Orbitals with large contributions to state 13 in $[\text{L}^{\text{H2Ni}}]^{+}$ ($S = 0$); H-2 (b) (55% Ni) $\rightarrow$ L+1 (b) (6% Ni). (isosurface value: 0.08).

Figure S35. Orbitals with large contributions to state 24 in $[\text{L}^{\text{H2Ni}}]^{+}$ ($S = 0$); H-3 (b) (87% Ni) $\rightarrow$ L+3 (b) (10% Ni). (isosurface value: 0.08).
Figure S36. Orbitals with large contributions to state 32 in \([L^1H_2Ni_2]^+\) \((S = 0)\); \(H\)-3 (b) (87% Ni) \(\rightarrow\) L+3 (b) (10% Ni). (isosurface value: 0.08).

Figure S37. Orbitals with large contributions to state 36 in \([L^1H_2Ni_2]^+\) \((S = 0)\); \(H\)-4 (a) (64% Ni) \(\rightarrow\) L+1 (a) (6% Ni). (isosurface value: 0.08).

Figure S38. Orbitals with large contributions to state 45 in \([L^1H_2Ni_2]^+\) \((S = 0)\); \(H\)-4 (b) (64% Ni) \(\rightarrow\) L+2 (b) (6% Ni). (isosurface value: 0.08).
Figure S39. Orbitals with large contributions to state 56 in \([\text{L}^{\text{H}}\text{Ni}_2]^+\) (S = 0); H-4 (a) (64% Ni) → L (a) (6% Ni). (isosurface value: 0.08).

Coordinates for DFT calculations, \([\text{LNi}_2]^−\) (S = 1):

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Ni   | -2.04825740448843 | 1.05520925956665 | -0.23339917927300 |
| Ni   | 2.05420827357330  | 1.02348807804217 | 0.21737348728861 |
| N    | -0.65936441726771  | 2.33940415550780  | -0.10403213576772  |
| N    | -3.18718511816098  | 2.55764937227795  | -0.55398425512728  |
| N    | -3.32823243095713  | -0.28339654587603  | -0.38443937610033  |
| N    | 0.68365612179456  | 2.32878837587716  | 0.09902295224143  |
| N    | 3.2152675244815   | 2.50740932480347  | 0.54500971558717  |
| N    | 3.31553638662333  | -0.33362262237313  | 0.35741203223072  |
| C    | -1.07282130359413  | 3.63030586213649  | -0.17644972706950  |
| C    | -2.53119651223460  | 3.85852062152485  | -0.43957758799912  |
| C    | -4.46366120245776  | 2.46021688307365  | -0.89911281830711  |
| C    | -4.60099653124125  | -0.06746822556585  | -0.75452821030755  |
| C    | -2.92186697018423  | -1.55258291394088  | 0.09476531699988  |
| C    | -0.37472630682318  | -1.09771205955263  | -1.96771546991134  |
| C    | 1.1164162390013   | 3.61307812157119  | 0.17672043246121  |
| C    | 0.02830176738460  | 4.48261970261745  | 0.00186496220296  |
| C    | -5.1227640081871  | 1.21131507812510  | -1.01782974381061  |
| C    | -5.26704796496765  | 3.71149506640399  | -1.18453963468036  |
| C    | -5.52453171189536  | -1.25760777434631  | -0.90559166900309  |
| C    | -3.28149659599798  | -1.95139781996235  | 1.41107624013758  |
| C    | -2.11750969057102  | -2.39074124252634  | -0.71706358015641  |
| C    | -1.67351360518199  | -1.91253260553753  | -2.08735426142389  |
| C    | 2.57804492823431  | 3.81830196024540  | 0.44022609385586  |
| C    | -2.85003301097697  | -3.19753524355544  | 1.87526567957528  |
| C    | -4.03900692971743  | -0.98695907084520  | 2.31128014061673  |
| C    | -1.70913450487135  | -3.62728515929687  | -0.2080304712829  |
| C    | -1.50108490946886  | -3.04711029567063  | -3.10376018391224  |
| C    | 4.49114635161722  | 2.38980615812894  | 0.8859842027730  |
| C    | 4.59200898511581  | -0.1384756955046  | 0.72648202245515  |
| C    | 2.88970543605902  | -1.59356416729270  | -0.12921984479737  |
| C       | H       |
|---------|---------|
| 0.34499025400574 | -1.12134150417307 | 1.9400919204483 |
| -2.07497134258952 | -4.03876851576089 | 1.0740604248873 |
| -3.05818397606365 | -0.00548002461512 | 2.97391236410717 |
| -4.91528660785807 | -1.68217068732971 | 3.35840767372569 |
| 5.13268325391884 | 1.13108312463461 | 0.99610935329909 |
| 5.31325498502872 | 3.62795653342006 | 1.1753107729605 |
| 5.49849636786838 | -1.34270716875875 | 0.86840661146726 |
| 2.07232606622350 | -2.42373744418112 | 0.67745557454549 |
| 3.24233029088290 | -1.98998136313636 | -1.4481241598408 |
| 1.6373111719732 | -1.94748428418372 | 2.05150742838495 |
| 1.64373391821716 | -3.65024313438937 | 0.1610864691088 |
| 2.79028129039581 | -3.22586918891444 | -1.92007584176047 |
| 4.01648787569050 | -1.03261746103154 | -2.34208316413430 |
| 1.45996460481540 | -3.08495909338996 | 3.06386838680775 |
| 2.00195238518050 | -4.05943927400364 | -1.12382535393891 |
| 3.05274214560696 | -0.02995361155376 | -2.98032231502626 |
| 4.88042485987522 | -1.73578933272163 | -3.39415559986569 |
| -6.16011001043380 | 1.24520486527913 | -1.3491682098532 |
| 6.17115178239734 | 1.14870492379587 | 1.32516752936182 |
| -0.52389030186807 | -0.20810872397827 | -1.32577095542212 |
| -0.04891151772792 | -0.73374198330911 | -2.95238311882919 |
| 0.43117771220563 | -1.70346109223384 | -1.53435918224530 |
| -2.98341936250404 | 4.45632318798473 | 0.37794904079205 |
| -2.65940696415625 | 4.45707922979042 | -1.36318683930497 |
| 0.49655430502475 | -0.23396908209617 | 1.29587268746534 |
| 0.02922421567454 | -0.75346422141848 | 2.92661696674165 |
| -0.46910006991843 | -1.72121118171687 | 1.5138352756553 |
| 0.03646756808664 | 5.56939776529320 | 0.00392444291470 |
| -6.29923254363902 | 3.46139433227149 | -1.45898032538921 |
| -4.82098373852796 | 4.29364865549299 | -2.00893069153632 |
| -5.29387409621854 | 4.37625230500671 | -0.305384338370 |
| -6.48334727867571 | -0.95001762601471 | -1.34074268262104 |
| -5.7511248109801 | -1.74159943092951 | 0.06335241128776 |
| -5.07180549147774 | -2.02812897372726 | -1.54831038628750 |
| -2.45624929627098 | -1.22927016650051 | -2.45371057746267 |
| 3.03826480183397 | 4.41533732050312 | -0.37330991038784 |
| 2.71552574538233 | 4.40853949376746 | 1.36797916126731 |
| -3.11222793790000 | -3.51628039334173 | 2.88517647598977 |
| -4.70140657326104 | -0.38428579983071 | 1.67239282474080 |
| -1.08664343568986 | -4.27587729306936 | -0.82375358302792 |
| -1.3100505429383 | -2.6279366315881 | -4.10355301165999 |
| -2.39760785818057 | -3.68392532880705 | -3.16004407738889 |
| -0.64039271919541 | -3.68504930259682 | -2.85264910699774 |
| -1.74809717450739 | -5.00841035856824 | 1.45358408350119 |
Coordinates for DFT calculations, $[\text{LNi}_2^–]$ ($S = 0$):

\[
\begin{align*}
\text{Ni} & \quad -2.02020341320738 & \quad 1.05186009484380 & \quad -0.28664066094488 \\
\text{Ni} & \quad 2.0261903508893 & \quad 1.02066716840199 & \quad 0.2670104204576 \\
\text{N} & \quad -0.65235395215928 & \quad 2.34511376131768 & \quad -0.13461140191254 \\
\text{N} & \quad -3.16284048393109 & \quad 2.54576990946655 & \quad -0.64326982544436 \\
\text{N} & \quad -3.29606818549210 & \quad -0.29274650114719 & \quad -0.4162943564591 \\
\text{N} & \quad 0.67723225332505 & \quad 2.334679664641982 & \quad 0.12170923629463 \\
\text{N} & \quad 3.19036527491853 & \quad 2.49595516140451 & \quad 0.63157252142317 \\
\text{N} & \quad 3.28245835105097 & \quad -0.34282316003649 & \quad 0.39001177545781 \\
\text{C} & \quad -1.06539016064009 & \quad 3.63498445906018 & \quad -0.22300454991423 \\
\text{C} & \quad -2.51650625007447 & \quad 3.85237636483460 & \quad -0.53318759020401 \\
\text{C} & \quad -4.43708784053476 & \quad 2.43713711970640 & \quad -0.99268496790412 \\
\text{C} & \quad -4.57004968173694 & \quad -0.08662395884227 & \quad -0.78703121536067 \\
\text{C} & \quad -2.837878656745058 & \quad -1.54752041617029 & \quad 0.10435008356691 \\
\text{C} & \quad -0.41426978845629 & \quad -1.18022024739775 & \quad -2.03561731837092 \\
\text{C} & \quad 1.10923401301160 & \quad 3.61789001284705 & \quad 0.21629267528085 \\
\text{C} & \quad 0.02827465038345 & \quad 4.48788165658033 & \quad -0.00128558013033 \\
\end{align*}
\]

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| C   | -5.09232924352715 | 1.18413550208005 | -1.08644618161893  |
| C   | -5.24319561410780 | 3.67979125194220 | -1.30690632341450  |
| C   | -5.49413336366188 | -1.28103268405627 | -0.89288583543243  |
| C   | -3.23562823643687 | -1.89001695151422 | 1.44055294997219    |
| C   | -2.11980849468156 | -2.42957547759690 | -0.69006703886464  |
| C   | -1.70395357086595 | -2.01590139357449 | -2.0905510639095    |
| C   | 2.56329819654479  | 3.81243375459635 | 0.52771952000938    |
| C   | 2.81492554702539  | -3.12371286898764 | 1.94555954071117    |
| C   | -3.96674647669579 | -0.8812520071017 | 2.3133150046551     |
| C   | -1.72236820797533 | -3.65265270514577 | -0.14084193047332   |
| C   | -1.5295156301284  | -3.19897136267733 | -3.0500819246174    |
| C   | 4.46279081174644  | 2.36707540332617 | 0.98071224910073    |
| C   | 4.55910712996430  | -0.15718715451733 | 0.76244317822665    |
| C   | 2.86291924097426  | -1.58876522848042 | -0.13813001053926   |
| C   | 0.39002042836910  | -1.19874435023059 | 2.00382336564922    |
| C   | -2.06910456595303 | -4.00779582545679 | 1.16328646006432    |
| C   | -2.95931649959372 | 0.10894915691836 | 2.92423355385233    |
| C   | -4.83748042916146 | -1.52137701761920 | 3.39971930270543    |
| C   | 5.09968116552289  | 1.10423921274265 | 1.0682468259950     |
| C   | 5.28697139500109  | 3.59626336720692 | 1.30091507473250    |
| C   | 5.46572908113172  | -1.36542809493698 | 0.86222745330690    |
| C   | 2.07724196425371  | -2.46508562844973 | 0.65115490423722    |
| C   | 3.19996656140637  | -1.92758956885912 | -1.47644008539795   |
| C   | 1.66710125141606 | -2.05383748957186 | 2.05403115586698    |
| C   | 1.66343195896806  | -3.67940251198898 | 0.09458588504256    |
| C   | 2.76235684527985  | -3.15227689132380 | -1.9889691738676    |
| C   | 3.94512380453432  | -0.9236709843504  | -2.34299486365134   |
| C   | 1.47418097238882  | -3.2397590610061  | 3.00635503089156    |
| C   | 2.00490843237463  | -4.0310245398123  | -1.2118837533986    |
| C   | 2.952079815556780 | 0.08434877807542  | -2.9483236888122    |
| C   | 4.80740554171504  | -1.5692463943709  | -3.43287830784856   |
| H   | -6.13218206634215 | 1.20916335269398  | -1.41218145168945   |
| H   | 6.13961144700274  | 1.11254243496149  | 1.39496164602032    |
| H   | -0.56766491779059 | -0.25455980957281 | -1.44802059513393   |
| H   | -0.10212560368008 | -0.87635968377118 | -3.0456287989725    |
| H   | 0.40332026678712  | -1.74895133506646 | -1.5741386537950    |
| H   | -2.99379091799332 | 4.46156024926956 | 0.26053681953254    |
| H   | -2.62082289852876 | 4.43439564439256 | -1.47065876210972   |
| H   | 0.55536162094587  | -0.27467710901349 | 1.41707318503134    |
| H   | 0.08538956266804  | -0.8916995036428  | 3.01517302896239    |
| H   | -0.43714278914997 | -1.75495139577377 | 1.54419252120096    |
| H   | 0.03628648661034  | 5.57403687106105 | 0.00132757550729    |
| H   | -6.27503400770770 | 3.42139601360448 | -1.57557487145983    |
| H   | -4.79839726769622 | 4.2436159923732 | -2.14333081881264   |
Coordinates for DFT calculations, \([\text{L}^\text{H}_2\text{Ni}_2]^+ (S = 1)\):

|  |  |  |
|---|---|---|
| Ni | -2.02997164288090 | 0.97407626184308 | -0.19846877678201 |
| Ni | 2.00434682739460 | 0.95013753332475 | 0.4091339539136 |
N -0.68048534481077  2.26595490183964  0.0365567098454
N -3.18808704304459  2.49092685368449 -0.55263603612538
N -3.31554456633022 -0.35079093007004 -0.38545400260837
N  0.54879486496963  2.25507021304341  0.30059707711921
N  3.15654744696793  2.43264310994407  0.90302021751041
N  3.30618582203252 -0.3756227088557  0.44752161213808
C -1.09886451877303  3.55548579700428  0.00100913674376
C -2.54183769900177  3.79443195746084 -0.30211527202481
C -4.39942819388748  2.43636555998009 -0.99020489746852
C -4.52855597257277 -0.2117609754815 0.82772279082077
C -2.86817250693930 -1.62865247210589  0.10241837548613
C  1.06587270695513  3.53778003933393  0.44429600015431
C -0.01684396684544  4.40743451257608  0.25901548678658
C  0.72797238439351  1.11796515099994  0.27987916243745
C -5.22322161185111  3.6635231737825  0.92765758566568
C -5.49910874503939 -1.35175593835119  0.82772279082077
C -3.18925656362774 -1.99836655927297  1.4283610485157
C -2.09678896039392 -2.44827108756278 -0.74807965727073
C  2.51242366140145  3.75230620293944  0.76275932445338
C -2.75097299366625 -3.2509086994472  1.8731439377755
C -3.91593757699536 -1.03258389723848  2.35181554088586
C -1.69065875206688 -3.69249770301511 -0.25390719695260
C -1.68849496421855 -1.9633248443127  2.1286356451245
C  4.37173259210981  2.34352375914925  1.32367223927928
C  4.51484415844131 -0.27453613677549  0.91110689618624
C  2.88484631881315 -1.58595403184162 -0.20677754219320
C -2.02167296559998 -4.09736958785154  1.03850475582388
C -2.91551516134425 -0.01662310837772  2.93171698369813
C -4.70580084712379 -1.72152754832316  3.4608645122455
C -0.43834876298381 -1.07319428064478 -2.0180320850476
C -1.44839987625944 -3.0978306604841  3.13039166435624
C  5.04068132767425  1.00355884066233  1.51124980332827
C  5.20229533442137  3.54345427880292  1.6915188233728
C  5.49619133959860 -1.40877470070004  0.8899346723450
C  2.12329193325604 -2.52755934502713  0.51658208442426
C  3.2190148168652 -1.7650048504986  -1.5684034616522
C  1.73051199532638 -3.69222865014421 -0.15170953698157
C  1.71216785726302 -2.2561629531640  1.95450986651258
C  2.79381159435936 -2.94473163535793  2.1888451109660
C  3.95508176508653 -0.68123214067165 -2.340982505519
C  2.06592890918149 -3.90536257827285 -1.48773713017402
C  0.48465609091637 -1.3285369359528  1.98465998645215
C  1.43326460530085 -3.52808419931671  2.7609690561810
C  2.95841965925011  0.38984055468786 -2.8193696901216
Coordinates for DFT calculations, $[\text{L}^2\text{Ni}_2]^+$ ($S = 0$):

\[
\begin{array}{cccc}
\text{H} & -0.35296406390424 & -1.76740070220941 & 1.42714579825390 \\
\text{H} & 0.71301316337155 & -0.33992191709982 & 1.53373587929520 \\
\text{H} & 1.26000878728774 & -3.27164001298839 & 3.81514116853427 \\
\text{H} & 2.27332516204866 & -4.23568967176397 & 2.71279002072797 \\
\text{H} & 0.52987480442842 & -4.03793977619875 & 2.39754430330384 \\
\text{H} & 3.48141617240017 & -3.33735879295200 & 3.32965130983636 \\
\text{H} & 2.39701092992709 & -1.96873249953831 & 0.81705045222211 \\
\text{H} & 2.23131402295751 & -3.52023395420643 & -0.04578050016400 \\
\text{H} & 5.38987080865982 & -4.31432038894405 & -1.61385169203545 \\
\text{H} & 4.15504853969525 & -3.94236558527607 & -2.01639152765593 \\
\text{H} & 5.47242918897224 & -3.18902378572160 & 3.45325300346036
\end{array}
\]

\[
\begin{array}{cccc}
\text{Ni} & -0.01032162569621 & 0.97901584073507 & 0.22108789782962 \\
\text{Ni} & 1.99059698605607 & 0.95444261222493 & 0.41753176432869 \\
\text{N} & -0.67359977578193 & 2.27749537697236 & 0.017528178553 \\
\text{N} & -3.17404111040676 & 2.49139709114752 & -0.58539045545210 \\
\text{N} & -3.29549195059829 & -0.35032493671187 & -0.39649662268522 \\
\text{N} & 0.64830643181801 & 2.26612133117452 & 0.30031675881061 \\
\text{N} & 3.14506015357389 & 2.43165442116527 & 0.92870290613641 \\
\text{N} & 3.28985113897415 & -0.37499510911068 & 0.45325300346036 \\
\text{C} & -1.09363967108015 & 3.56621563404877 & -0.0208242648638 \\
\text{C} & -2.53712539596476 & 3.79924622378596 & -0.3414005392536 \\
\text{C} & -4.38520150161396 & 2.43074395209643 & -1.02265990191869 \\
\text{C} & -4.50926395312161 & -0.21573877371800 & -0.83805492476073 \\
\text{C} & -2.84996317932510 & -1.62478752885290 & 0.1026054337251 \\
\text{C} & 1.06518047245255 & 3.54775330635316 & 0.45269521987791 \\
\text{C} & -0.01520183289200 & 4.41792255093854 & 0.25432652689661 \\
\text{C} & -5.05391292848454 & 1.10834419251385 & -1.30619844189193 \\
\text{C} & -5.21334732815872 & 3.65289884704777 & -1.31469019762191 \\
\text{C} & -5.48078139041881 & -1.35612110858254 & -0.92125005387790 \\
\text{C} & -3.16011921868776 & -1.97862564922142 & 1.43595024531395 \\
\text{C} & -2.09707958933994 & -2.46171419209701 & -0.74763636975372 \\
\text{C} & 2.50843345714751 & 3.75524474139288 & 0.79013400610459 \\
\text{C} & -2.72534977447499 & -3.22580037959075 & 1.89170995258054 \\
\text{C} & -3.87269198643300 & -0.99528915079499 & 2.35430843392834 \\
\text{C} & -1.69137241396016 & -3.70141822924633 & -0.24119356646250 \\
\text{C} & -1.71616332179079 & -2.00374770604964 & -2.14576652359796 \\
\text{C} & 4.35331849328183 & 2.33405485767923 & 1.36666270642547 \\
\text{C} & 4.49646233482740 & -0.27863689672058 & 0.92303537313738 \\
\text{C} & 2.86768743224678 & -1.57942858047562 & -0.2116197577357 \\
\text{C} & -2.00916782633120 & -4.08669797390663 & 1.06038496459197 \\
\text{C} & -2.85925722524278 & 0.01546233538393 & 2.92026330593787
\end{array}
\]
B) (calculation of XAS spectra)

The pre-edges of the XAS spectra were calculated using time-dependent density functional theory (TDDFT) using previously established protocol (Figure S12).\(^\text{11}\) For DFT calculations, complexes \(1^K\) and \(2'\) were optimized using the BP86\(^\text{12}\) functional in combination with the def2-TZVP basic set. The D3 method of Grimme was used to model dispersion forces.\(^\text{13}\) X-ray absorption spectra were calculated within the Tamm-Dancoff approximation to TDDFT where only the 1s donor orbitals of Ni were included in the donor space when solving the response equations. The B3LYP functional was used for TDDFT calculation.\(^\text{14}\) The calculated X-ray energies were shifted by +180 eV to align the theory with experiment. The X-ray intensities where computed as the sum of electric dipole, magnetic dipole and electric quadrupole contributions to the oscillator strength.
Figure S40: Comparison of experimental (solid) and calculated (dashed) Ni K-edge pre-edge XAS of complexes $1^K$ and $2'$. The structural models show representative difference densities for transitions contributing to the pre-edge features. The sticks show the individual transitions.

C) (reaction pathway calculations)

The initial structures for optimization were derived from extensive constrained scans (on the singlet, broken-symmetry and triplet PES) of the complexes $1'$ and $3'$ using the same functional as in all other optimisations (BP86) but a smaller basis set (def2-SVP). The scans followed the decrease of the distance between the two leaving hydrogen atoms, as an approximation to the reaction coordinate. The final energies and structures for the minima (MIN1, MIN2) were obtained via optimisations at the BP86-D3/def2-SVP(CPCM(THF)) level of theory. The final energies and structures for the first transition state (TS1) were obtained by employing the nudged elastic band method integrated in ORCA (using the keyword NEB-TS). The final energies and structures for the second transition state (TS2*) is an approximation, obtained by fixing the distance between the leaving hydrogen to the equilibrium distance of free hydrogen at this level of theory (0.767 Å). Scans at smaller H-H distances confirm an earlier crossover to the broken-symmetry state of $3'$ (before MIN2), comparing to $1'$ ($r$(H-H) > 1.2 Å).
### Coordinates for DFT calculations, 1'(MIN1):

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| Ni   | -0.69621238202907 | 17.16010453535381 | 18.89397449819229 |
| Ni   | -1.42169206562480 | 15.5837444937835 | 15.31783284361861 |
| C    | -3.09269974375762 | 18.11900895871219 | 17.97378024564606 |
| C    | -3.94926769436863 | 18.2532263133880 | 16.8594577844568 |
| H    | -4.87078320166480 | 18.84183747690109 | 16.7839922456768 |
| C    | -3.35062443359426 | 17.44816868982311 | 15.8632119226326 |
| C    | -3.66235443439431 | 17.10956341968354 | 14.43930327872207 |
| H    | -4.69294028759002 | 16.68952940829010 | 14.3507872370629 |
| H    | -3.6689665436790 | 18.03650501270912 | 13.81617770608684 |
| C    | -2.69361878366846 | 15.70137022572623 | 12.71817086148050 |
| C    | -3.7489922375187 | 16.2152066204904 | 11.76053345899838 |
| H    | -4.77163367303046 | 15.94887040936036 | 12.1307588299614 |
| H    | -3.63755284690189 | 15.76461016017633 | 10.75708409112695 |
| C    | -0.97905814268659 | 14.73151876215628 | 12.2443909176524 |
| C    | -1.85733742767170 | 14.44420257153841 | 11.18715455896800 |
| H    | -2.87466374822321 | 14.05262957084779 | 13.0026729683813 |
| C    | 0.03372116305799 | 12.95825126420683 | 12.30377060902596 |
| H    | 1.12167324285006 | 13.16884937699263 | 12.42876127490919 |
| H    | -0.2014869131254 | 12.94807313878503 | 11.2235732668753 |
| H    | -0.15823803818401 | 11.98128495211252 | 12.7386629443804 |
| C    | 0.35065818028804 | 13.43549102806618 | 15.01177086172289 |
| C    | -0.13256011632266 | 12.20803299588973 | 15.54736168603370 |
| C    | 0.76081778239077 | 11.37960568285710 | 16.25291735719109 |
| H    | 0.39719791737585 | 10.43273016910066 | 16.67971849841841 |
| C    | 0.21019553243920 | 11.75352219966998 | 16.43836010295744 |
| H    | 2.78472143123094 | 11.1010031196561 | 17.0040553896023 |
| C    | 2.56307750387128 | 12.9668802972870 | 15.9068728969770 |
| C    | 3.60981116467496 | 13.26428600361713 | 16.06651622152352 |
| C    | 1.71063952449590 | 13.81436244942137 | 15.17389926924204 |
| C    | 2.20681154100389 | 15.13950345147229 | 14.61059102379217 |
| H    | 1.55704673942023 | 15.3757044982407 | 13.74076346877796 |
| C    | 3.66039186682960 | 15.08763320496991 | 14.11659788201184 |
| H    | 3.93344515993778 | 16.04437961071741 | 13.62383642493356 |
| H    | 3.82276956783042 | 14.26512789678747 | 13.38831284988689 |
| H    | 4.37170421206661 | 14.94252798575036 | 14.95667986756778 |
| C    | 2.00767352394671 | 16.25624279881886 | 15.6519736781430 |
| H    | 2.63678141534931 | 16.08175506259075 | 16.5407364533162 |
| H    | 0.95099808109841 | 16.28015989086065 | 15.99165112078921 |
| C    | 2.77119047329995 | 17.24772966678667 | 15.22763560057276 |
| C    | -1.61379339346826 | 11.86516014688986 | 15.43376259772322 |
H  -1.98400794972582  12.33157968526627  14.49742359735415
C  -2.37968741925479  12.5351856589656  16.59115297962873
H  -3.47795693692970  12.42162028161188  16.46597099827665
H  -2.1283208483640  13.62017304191580  16.62572607833564
H  -2.08744562892234  12.08496087475174  17.56249355263631
C  -1.90471453258104  10.36049813417155  15.35418676046912
H  -1.33178711369510  9.87405311934090  14.53732162614863
H  -2.98450361946665  10.18801400512119  15.16465227556124
H  -1.65397356369878  9.83700565455839  16.30100067426347
C  -3.08258402527355  18.6406743510121  19.37790048429661
H  -3.11259702230891  19.75998450743526  19.38245031404871
H  -4.0031761101744  18.32299709311098  19.91473273726464
C  -1.64081142695339  18.44027396729831  21.31727067420814
C  -2.65029477576875  19.25369623981533  22.10154915532292
H  -2.80588668142880  20.25217332937482  21.6391638478050
H  -2.32216487819038  19.40593407491294  23.14618940264420
H  -3.6455612330994  18.7593409969763  22.11416928628222
C  -0.45449981601385  18.0214902907843  21.97966012451202
H  -0.36319270444695  18.28471018447971  23.04014351274171
C  0.64979309407123  17.35666182359384  21.39689227654477
C  1.85681693373333  17.09306086505294  22.27739231534446
H  2.13478614450141  16.01905789296039  22.26580457257902
H  1.66095070022593  17.4004650880321  23.3215330658072
H  2.74835362949974  17.64213771937935  21.90952740712262
C  1.92959743322589  16.45991271911845  19.59008672064824
C  2.17693424630295  15.06021748621373  19.56152476634178
C  3.39271221655914  14.60304069015361  19.01771430320284
H  3.58673672398160  13.5210427690172  18.96854258597686
C  4.36024169332307  15.50076568506224  18.5417941626930
H  5.30697884951047  15.12292065438922  18.12455276047627
C  4.11302897308521  16.88135875137652  18.59567585463174
H  4.87139716472344  17.5830522026584  18.21604751324179
C  2.90297973592309  17.38226718401998  19.1130187220128
C  2.58859111088846  18.8745047057897  19.0950282185682
H  1.89493013461933  19.06966514403547  19.93973292224725
C  1.81875729196888  19.22470945214491  17.80561213275926
H  2.45724768049548  19.05801159285318  16.91247294458054
H  1.48968239831604  20.28531177308119  17.81163324069653
H  0.92248358623496  18.5703860895848  17.71682167143437
C  3.8183821097484  19.77259042689641  19.28156251885004
H  4.3924519015843  19.50036677601860  20.19273556829564
H  3.50898483033444  20.83413489022549  19.3766382947068
C  4.51159794166896  19.71311349797553  18.41512003137534
C  1.11847221085617  14.09023571243368  20.06969275627358
Coordinates for DFT calculations, 1'(TS1):

Ni  -0.90795931242336  1.44785178229359  1.69125607287037
Ni  -1.47646332842390  0.09294579748850  -1.8933233218668
C  -3.28897293457901  2.53276018858770  0.77198528185814
C  -4.13900354601120  2.67352809150835  -0.34977592164934
H  -5.06048523017849  3.26227685407573  -0.4263670606298
C  -3.53400588991306  1.87623142563406  -1.34878330376821
C  -3.82772859722161  1.52339123779044  -2.78064945076782
H  -4.84477273250014  1.07184561765682  -2.87212836801412
H  -3.85668588735640  2.44458082503858  -3.41114925045122
C  -2.80636976089653  0.12667569857815  -4.49329261779426
C  -3.87595281986731  0.59846507619379  -5.45756276934788
H  -4.89130733647207  0.33852564201250  -5.08714795959728
H  -3.74820518065658  0.14487714598666  -6.4575186229128
H  -3.86018948166360  1.70397455334887  -5.5710754623442
C  -1.85174740825967  -0.82065339811650  -4.95846659631967
H  -1.94652061486184  -1.12849932125921  -6.00990759943151
C  -0.83940325021411  -1.46582719375429  -4.20776896732004
C  -0.04535487003560  -2.56236054691067  -4.8930838412915
H  1.04744543463982  -2.40570714752913  -4.77843227906975
H  -0.28980144593298  -2.61552583691872  -5.9704788999812
H  -0.26247249433489  -3.55198376788289  -4.4374119349924
C  0.32641754138975  -2.04598195215022  -2.19971235525690
C  -0.19505250457495  -3.23146021763828  -1.60895706970800
C  0.67601578641609  -4.06324407412199  -0.88048958509196
H  0.28238545725682  -4.97679158029499  -0.40886297024642
C  2.03185122379770  -3.73488433257199  -0.7306342504577
H  2.69839071545909  -4.38845033947854  -0.1460926628436
C  2.53387531027102  -2.56681578440747  1.32438997007469
H  3.59597829217002  -0.30535685703668  -3.6693097884275
C  3.73081988245200  -0.52882351326272  -3.09702867667498
H  4.03506059903559  0.37152656871852  -3.67093483077789
C  3.95809874285102  -1.42375133471305  -3.71386760800729
H  4.37172189871045  -0.56838583758350  -2.1921948815982
C  1.9611133515305  0.77569053224404  -1.83604809815740
H  2.50030866450165  0.69561189204780  -0.87231130513234
H  0.8729850525940  0.83380056619003  -1.5935467324744
C  2.27827075669503  1.71456967774396  -2.33910318223622
C  -1.68824262022058  -3.52965044282607  -1.69495965176666
H  -2.06999112276674  -3.00258955644617  -2.59325886213497
C  -2.4135313100777  -2.91349035070452  -0.48146564716928
C  -3.5162197766747  -2.98748361386414  -0.59597173219220
H  -2.1359402067871  -1.84091568052558  -0.37723817587552
H  -2.12286273631556  -3.43648978549049  0.45278928961855
C  -2.01359413975961  -5.02192121954621  -1.85297752058897
H  -1.47720023832297  -5.46782899212535  -2.71694177425567
C  -3.10240103440546  -5.16349591175689  -2.01634581293303
H  -1.74175253448461  -5.6071354313919  -0.94903657701322
C  -3.25764759646356  3.05560018838803  2.18137402184968
C  -3.27626050250198  4.17183880964701  2.18674017363734
H  -4.17732337430550  2.74325579920429  2.73335180395495
C  -1.77964142110729  2.84024789540727  4.1034166801257
C  -2.75739808890919  3.68166121616014  4.89944929269695
H  -2.9069095550843  4.67672203369560  4.42795324145912
H  -2.40482989542229  3.84063925594520  5.93506522609141
H  -3.75995465278653  3.2039034702901  4.93931683923220
C  -0.58973626101911  2.40144185748642  4.74824070290510
H  -0.47162512759253  2.69291986923664  5.80158634588854
C  0.49143063061540  1.69092116122339  4.17399964498600
C  1.72232832066467  1.47018092171081  5.03379480665952
C  2.02111856729612  0.40199751261992  5.04699085076575
H  1.54690037850357  1.80576236675882  6.07287053435961
H  2.59424825979460  2.02546348287969  4.62867139956983
C  1.72651147835324  0.72078131897852  2.36778208705591
C  2.00398637741312  -0.67408316639533  2.38940241419978
C  3.20213943111661  -1.12888194792787  1.80692392496472
H  3.41971852224853  -2.20692321800223  1.79574669309332
Coordinates for DFT calculations, 1'(MIN2):

Ni  -0.7804050288936  17.05104742333115  18.89831740125684
NI  -1.31878356425322  15.72416056534131  15.31499560676285
C   -3.18441268918856  18.0896977867493  17.9971490468256
C   -4.04703435495690  18.2085572954349  16.8812895792627
H   -4.98817923530322  18.76547870985753  16.81519483181395
C   -3.42130139983205  17.43803023429364  15.8735213500059
C   -3.71172925383116  17.07309118399843  14.4497225119860
H   -4.71761070488832  16.59594589338328  14.35973707869923
H   -3.76610693449759  17.9899069329616  13.80954134437125
C -2.66622656698524  15.69411322789496  12.73554097834418
C -3.7484825423363  16.14042839552278  11.77299449728420
H -4.75268575261759  15.86039065764337  12.14668938678773
H -3.61400662536523  15.68620508810111  10.7739865658004
H -3.75652639557767  17.24567211295138  11.65592666721019
C -1.69820802960574  14.75972935015577  12.27357717047711
H -1.79229970961958  14.43852849483691  11.22606668016818
C -0.67912367270582  14.13560513502664  13.03189150408596
C 0.10958327217899  13.021030866766  12.37021249898140
H 0.13025829548220  12.290124989094  11.25797783311191
C 0.47112133781432  13.59466588257797  15.0569087009027
C 0.77806588383607  11.59008053551734  16.40583637966465
H 0.36669049868112  10.69093686036218  16.8901343964177
C 2.14174188027351  11.88999099018535  16.54657304690964
H 2.79528037500695  11.22938659001833  17.13780413519504
H 2.66875016142013  13.03690529233615  15.93306492708607
C 3.73744771778929  12.26691891358875  16.0486942869122
C 1.85742877249519  13.89420076583800  15.1668820315642
C 2.42335472754721  15.12869276712749  14.47379503075637
H 1.87340511715248  15.22618466325670  13.5116680125644
C 3.92010749710121  15.02179472778078  14.15172651484764
C 4.2435292055770  15.89006109792791  13.54075245785786
C 4.16091410469215  14.0956458680903  13.5884862971300
C 4.53403993633732  15.02726953307803  15.07652034343026
C 2.12775113556882  16.39531525829429  15.29604249829368
H 2.65019750225909  16.35980280913350  16.27137184336955
H 1.04135741823783  16.4696524329578  15.51310192512013
H 2.4574858841020  17.30686972122732  14.75232499855918
C -1.57586259103208  12.1656642386016  15.58221287292420
H -1.93712960909244  12.66546839440532  14.66033565023021
C -2.29837529066128  12.84680405970411  16.7618888265377
H -3.40059799552996  12.81022428890194  16.62839728462296
H -1.98692022142298  13.91289837064800  16.83623215315219
H -2.04420033625272  12.3414932592013  17.71758291559398
C -1.93853184786212  10.67762694336128  15.48061280697553
H -1.40844675798356  10.18394701433100  14.63955640890324
H -3.02971695447757  10.55813043251772  15.3159893655401
H -1.68893804004083  10.12230353304277  16.40944995190127
C -3.15559312456219  18.5995487096000  19.41092966067381
H -3.20324593265754  19.71480421128631  19.42837931772965
H -4.06147171671139  18.25739682479560  19.96789628109596
|   |   |   |   |
|---|---|---|---|
| C | -1.65407046912281 | 18.41070631282528 | 21.31734141215704 |
| C | -2.64258288131046 | 19.22827652731186 | 22.12500396530968 |
| H | -2.81905614125967 | 20.22104177761259 | 21.65805294966461 |
| H | -2.28300514755967 | 19.39230565549987 | 23.15743630858882 |
| H | -3.63374248915436 | 18.72825114565522 | 22.17399893715507 |
| C | -0.45005618914744 | 17.99519846209199 | 21.9499142835009 |
| H | -0.3261465219343 | 18.28875716892530 | 23.00192389971497 |

|   |   |   |   |
|---|---|---|---|
| C | 0.63481103774317 | 17.30028860066647 | 21.36422946010101 |
| C | 1.87697196379898 | 17.09189713367412 | 22.21068311687979 |
| H | 2.18238326614148 | 16.02553177315153 | 22.22636095651524 |
| H | 1.71172652971996 | 17.43188109170008 | 23.24995926359265 |
| H | 2.74116989645521 | 17.64983016223151 | 21.79254179059638 |
| C | 1.85106497346313 | 16.32733840252476 | 19.54737193386110 |
| C | 2.12937191217694 | 14.93277010988302 | 19.59049572705186 |
| C | 3.32349662891555 | 14.46834770136974 | 19.0083500049920 |
| C | 3.54256964530681 | 13.39077554337887 | 19.0158600174154 |
| H | 2.42320531681581 | 15.35391244344956 | 18.42711459374795 |
| H | 5.17292303596325 | 14.96949847901276 | 17.9792042338395 |
| C | 3.97209337778693 | 16.73048209312459 | 18.41851197682290 |
| H | 4.69548370214803 | 17.42322556125118 | 17.96145614730344 |
| C | 2.78207699273542 | 17.23888517160721 | 18.97270439901584 |
| C | 2.43952311480775 | 18.72307487216256 | 18.89751367267241 |
| H | 1.74576551105292 | 18.93506288048978 | 19.73719691595265 |
| C | 1.65911486368369 | 19.01601530676969 | 17.60018627568526 |
| H | 2.30735455592374 | 18.87087895087880 | 16.71145325066333 |
| H | 1.27828921577151 | 20.05917945877317 | 17.59158136124347 |
| H | 0.79338071373293 | 18.32124027584811 | 17.51573481151979 |
| C | 3.65465850796634 | 19.64756729734654 | 19.0478370202228 |
| H | 4.22907363193135 | 19.42180980867030 | 19.97135069073838 |
| C | 3.32976106848678 | 20.70780236693150 | 19.09753061089000 |
| H | 4.3511181372891 | 19.56182047977801 | 18.1865417198113 |
| C | 1.1290838953414 | 13.97865548490313 | 20.23279103160496 |
| H | 0.69280008135035 | 14.51611180377863 | 21.10308703528381 |
| C | -0.02086102436201 | 13.67889394969535 | 19.25602974812253 |
| H | -0.48232792654371 | 14.62522130549280 | 18.90496381584687 |
| H | -0.79841424485765 | 13.04661583718967 | 19.73567013044405 |
| H | 0.36062143073249 | 13.1544952113405 | 18.35941862509524 |
| C | 1.76093933280821 | 12.67793157556664 | 20.74899707293514 |
| H | 1.01011137982064 | 12.08661039206692 | 21.3135519026038 |
| H | 2.62541099186862 | 12.87086211338905 | 21.41823607439958 |
| H | 2.11284737386632 | 12.04145832387389 | 19.90964864268771 |
| N | -2.12525850613826 | 17.70122644199698 | 17.65994014928235 |
| N | -2.26936292706666 | 16.90399695334898 | 16.36958346719058 |
| N | -2.65041827169602 | 16.16175687710646 | 13.98602460790212 |
Coordinates for DFT calculations, 1'(TS2):

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| Ni      | -0.7805149532896 | 16.99493032299730 | 18.91350279738419 |
| Ni      | -1.27567844633600 | 15.74189573008856 | 15.30659282351530 |
| C       | -3.16841675562565  | 18.05312194550365 | 18.00931133306070 |
| C       | -4.01153869570598  | 18.20630150807895 | 16.88131604477917 |
| H       | -4.94997507769614  | 18.76885521714115 | 16.81309911844594 |
| C       | -3.36987011872246  | 17.45967569222006 | 15.86341912585720 |
| C       | -3.63215915426830  | 17.12607945224629 | 14.42218296821200 |
| H       | -4.64275016037691  | 16.66518687478595 | 14.30419605760280 |
| C       | -3.65910985920564  | 18.05482107293268 | 13.80177556004624 |
| C       | -2.58338600495927  | 15.74039362544203 | 12.87208237639032 |
| H       | -3.64589257768607  | 16.20667358758832 | 11.74516099416458 |
| H       | -4.66439260056512  | 15.94145509172047 | 12.10339709022720 |
| H       | -3.50478979192007  | 15.75289152884436 | 10.74668196459007 |
| H       | -3.63539381460050  | 17.31226623235280 | 11.63103573984197 |
| C       | -1.62985168716460  | 14.78619925478787 | 12.27053781624288 |
| H       | -1.71735017151141  | 14.46541024210551 | 11.2222387541368 |
| C       | -0.63678480227370  | 14.14091113672665 | 13.04926379911997 |
| C       | 0.13659270124086   | 13.00382649645854 | 12.40285045169120 |
| H       | 1.23152317653422   | 13.12435661525573 | 12.54068479036726 |
| H       | -0.08482644875238  | 12.93202029815095 | 11.32281360044090 |
| H       | -0.12594148974736  | 12.0382865481806 | 12.87666857120785 |
| C       | 0.46979942252546   | 13.60775412070800 | 15.09791230059775 |
| C       | -0.09800219993186  | 12.44753498800497 | 15.70444285478923 |
| C       | 0.74095508887969   | 11.59289780131843 | 16.44183726788566 |
| H       | 0.31707991602804   | 10.69486361060133 | 16.91722314355430 |
| C       | 2.10910920483616   | 11.87217332569202 | 16.58933874364602 |
| H       | 2.75181019690400   | 11.19511807943270 | 17.17386521851822 |
| C       | 2.65486758841939   | 13.01703410688816 | 15.98724252571115 |
| H       | 3.72574270146040   | 13.23044767863203 | 16.10981600334864 |
| C       | 1.86106155310618   | 13.8895569585418  | 15.22105841681980 |
| C       | 2.44760376037107   | 15.11538649120899 | 14.52824454639358 |
| H       | 1.96678669130221   | 15.16972855200067 | 15.32572779727535 |
| C       | 3.96631749515417   | 15.04201303409575 | 14.32186331279891 |
| H       | 4.31135689523913   | 15.90270102749916 | 13.71206395800554 |
| H       | 4.27533856146711   | 14.10914018732969 | 13.80552088698237 |
| C       | 4.50415675075198   | 15.09050291704822 | 15.29142031336969 |
| C       | 2.06662237109782   | 16.40021128853354 | 15.28356953116001 |
| H   | 2.49297009534144 | 16.39206265797779 | 16.30418864851504 |
| H   | 0.96158066470208 | 16.47218023814970 | 15.39004526942309 |
| H   | 2.44006474320146 | 17.30199004075050 | 14.75159052850016 |
| C   | -1.60050762148821 | 12.2055068009846 | 15.60297492060050 |
| C   | -1.93203674217360 | 12.46313458110015 | 14.63881515163396 |
| C   | -2.33649527403003 | 12.98156410616424 | 16.71382142104200 |
| C   | -3.43574258966959 | 12.95565990425689 | 15.55732410270790 |
| C   | -2.01081897362727 | 14.04763001879651 | 16.71742905390850 |
| C   | -2.11205123061094 | 12.54692964712337 | 17.70900091253923 |
| C   | -1.99363794887945 | 10.72258762360011 | 15.60399473037975 |
| C   | -1.45233523011848 | 10.15371556357482 | 14.81985098561581 |
| H   | -3.08245051066140 | 10.61325761733657 | 15.41797070429846 |
| C   | -1.78195293957470 | 10.23801516185277 | 15.58078265478483 |
| C   | -3.15236493445903 | 18.52628989531552 | 14.93511161627932 |
| C   | -3.21079457802343 | 19.64037218820405 | 19.48063124530487 |
| C   | -4.05809866310086 | 18.16222162560099 | 19.97910064322020 |
| C   | -1.64312627940408 | 18.32628321613855 | 21.33560282616447 |
| C   | -2.63918524135753 | 19.12831659153754 | 22.15438248098208 |
| C   | -2.82429803802719 | 20.12512546132742 | 21.69243851281800 |
| C   | -2.27832647877307 | 19.28395224775250 | 23.18782578268688 |
| C   | -3.62677418296906 | 18.62083199361484 | 22.20034173989249 |
| C   | -0.43408298008429 | 17.92080767590130 | 21.95816050549649 |
| C   | -0.30482312491688 | 18.20992412296182 | 23.01083131306259 |
| C   | 0.65428875673070 | 17.24694137287523 | 21.3554082299137 |
| C   | 1.91612332053143 | 17.05781652828238 | 22.17611773101393 |
| C   | 2.24070749376701 | 15.99679729602786 | 22.18095761306163 |
| C   | 1.76660199315872 | 17.39080726634324 | 23.22010379197047 |
| C   | 2.76200875362254 | 17.63300244162116 | 21.74313245949538 |
| C   | 1.83831593233985 | 16.30702520645201 | 19.49796329513612 |
| C   | 1.24517477913520 | 14.91607554411948 | 19.53307592302612 |
| C   | 3.34415764740763 | 14.47914773685209 | 18.94155674524860 |
| C   | 3.58971676157007 | 13.40760666297085 | 18.94896756342641 |
| C   | 2.41342658071056 | 15.38621774510116 | 18.35535590125042 |
| C   | 5.17923600371797 | 15.02285865061280 | 17.90715910545983 |
| C   | 3.93912174818118 | 16.75739863817995 | 18.34735315135000 |
| C   | 4.64456394195862 | 17.46462234571545 | 17.88471812112993 |
| C   | 2.74481410933486 | 17.24031952304363 | 18.91284759445534 |
| C   | 2.36716813472536 | 18.7175562664355 | 18.85455698324748 |
| C   | 1.72089773145732 | 18.91717940257033 | 19.73476892143978 |
| C   | 1.50266419268359 | 18.99739078527250 | 17.60823404375268 |
| C   | 2.09523123355613 | 18.86437859109872 | 16.67976755821543 |
| C   | 1.10272614682618 | 20.0330492825621 | 17.62600367526777 |
| C   | 0.64034260601471 | 18.29127046728055 | 17.5764467623455 |
| C   | 3.56887869877856 | 19.66811896118855 | 18.93092324946576 |
H 4.19982098673480 19.4568498511449 19.81997241571059
H 3.2248084368756 20.7213726248623 18.99675939487554
H 4.21523930029427 19.59399303314267 18.03050077690567
C 1.17209728924849 13.94803341738952 20.1965198776553
H 0.7917796929835 14.45858373155854 21.1090845992736
C -0.03737112232797 13.69190356753851 19.2810147276678
C -0.52020672318694 14.65307836893222 19.00402678920302
H -0.78762011446322 13.04379387797906 19.78318909363789
H 0.28273791428715 13.20378856508977 18.3425634774242
C 1.81722701085930 12.62508611383691 20.63159021673016
H 1.08790950036972 12.0396143482009 21.20305154634599
H 2.70920333001737 12.7883960945898 21.2718708265423
H 2.13251039573510 12.0238076896569 19.75292186437537
N -2.10975829974832 17.27009867801267 17.6691451204902
N -2.23416633347679 16.91007708249324 16.36553375977779
N -2.57415033879149 16.20844985422402 13.97130546526669
N -0.37306791230629 14.45903158639527 13.302948264017
N -1.91593541036278 18.03108799734676 20.0614033634913
N 0.63557248647426 16.7910637910058 20.0845760217535
H -0.2116190037491 16.06419762205336 17.5149796597045
H -0.33826562351828 15.76405256142818 16.8206840358646

Coordinates for DFT calculations, 3'(MIN1):
N -2.21208605727093 16.86930992425225 16.36746904513794
C -3.32643555351699 17.45895073832162 15.85377178396065
C -3.89173247798888 18.31440778272957 16.82243726164024
C -3.03451926532766 18.18606426124338 17.9352186847016
N -2.03478736165218 17.3116234387431 17.63572720195192
C -2.9894850314548 18.76899894373416 19.31473176085923
N -1.84748964825738 18.15329282472072 20.0255334776102
C -1.71111115692353 18.3365734660637 21.3019958067304
C -0.57564291022259 17.69327427713019 22.05472992439126
C 0.65489950454242 17.16993856531107 21.36370107037004
N 0.67282899951239 16.86342503142632 20.09234837301300
C 1.91855499028629 16.42789705260240 19.50185394668484
C 2.25668767538356 15.04930503087343 19.5168696848020
C 3.46804198932610 14.67263718693186 18.9065159210992
C 4.32177454185705 15.62555423765786 18.33047436533871
C 3.97162012514130 16.9826250226710 18.34842772348717
C 2.76356675829398 17.41256406302806 18.93210358430861
C -3.66696837952801 17.07827010879111 14.4463898202455
N -2.61887826699893 16.15718629420281 13.961482973247
C -2.59664745861838 15.80864901776911 12.71237539894930
C -1.53415431653274 14.88527680033314 12.18044770828772
### Coordinates for DFT calculations, 3'(TS1):

| H     | Coordinate                                                                 |
|-------|---------------------------------------------------------------------------|
| 0.92289554537859 | 16.3209841580249 | 15.57036915732399 |
| 2.34564453585319 | 17.15591903596426 | 14.82664669575252 |
| -2.08279397974769 | 12.51692747147126 | 14.70678464750920 |
| -3.52762463259459 | 12.73219330873304 | 16.7005945226021 |
| -2.12374889839185 | 13.8591107131372 | 16.8286349102001 |
| -2.14109147598309 | 12.3384692013338 | 17.7809203858036 |
| -1.57437650319371 | 10.03425611194387 | 14.87997588951452 |
| -3.19368660137665 | 10.46235057719744 | 15.43730397970004 |
| -1.86834111421844 | 10.0531801743469 | 16.5593177928358 |
| -2.85773296453947 | 19.87415064411988 | 19.2899528034527 |
| -3.94217818316659 | 18.58341861603172 | 19.85930449695396 |
| -2.65076249310797 | 20.21609534483181 | 21.78403936498116 |
| -2.42975216515560 | 19.1237959380368 | 23.19403268298202 |
| -3.71635765276027 | 18.8002762917677 | 21.97611115562954 |
| -1.01495225745101 | 16.84944740272742 | 22.6369724366830 |
| 2.62461493369904 | 16.36335580790271 | 21.8373600075698 |
| 1.56321291152615 | 16.70665356634564 | 23.2626621240687 |
| 2.32993453388896 | 18.04087789914892 | 22.37367624629472 |
| 3.75795056825274 | 13.61264995878365 | 18.89540052139446 |
| 5.26866292123573 | 15.30572061593103 | 17.86972777480408 |
| 4.64591733547260 | 17.72392531720707 | 17.89520958360293 |
| 1.62189697408285 | 19.04765277596956 | 17.9115263121264 |
| 2.2475140390046 | 19.99863298118627 | 16.6848148575753 |
| 1.14836733234912 | 20.16862094556522 | 17.549113537384 |
| 0.7078140961176 | 18.42137215663862 | 17.47439486331433 |
| 4.07114706151085 | 19.65571846650460 | 19.9745000986613 |
| 3.10747129406918 | 20.90072519121591 | 19.11102248900005 |
| 4.19807474466751 | 19.82792301141471 | 18.19235172705045 |
| 0.94262143296152 | 14.49103083092182 | 21.10336017498792 |
| -0.39405927810408 | 14.67450650915439 | 18.97271743218605 |
| -0.6054629515383 | 13.06681635007879 | 19.77166580104821 |
| 0.44827277234304 | 13.24980611064311 | 18.32547134722393 |
| 1.34158821005457 | 12.07124057368357 | 21.1291774618044 |
| 2.92721422622870 | 12.91325635612582 | 21.2033619502592 |
| 2.37055857967119 | 12.15884189160723 | 19.67163523454241 |
| -0.03243965869543 | 16.26512914720308 | 17.88721812921332 |
| -0.50984597135208 | 15.36000811828458 | 16.4864077999294 |
| -2.0207250010519 | 14.18129512408097 | 11.46633274787706 |
| -0.24155017357789 | 18.40117466838243 | 22.84282287837634 |

### Coordinates for DFT calculations, 3'(MIN2):

51
| N   | -2.22422920358878 | 16.88704068839452 | 16.37546420846448 |
|-----|------------------|-------------------|-------------------|
| C   | -3.36597996866150 | 17.43036521378499 | 15.87500007577990 |
| C   | -4.01815836025646 | 18.15844069713914 | 16.9583656992604  |
| C   | -3.18107571760318 | 17.99960400994685 | 18.0239501360626  |
| N   | -2.11569590775697 | 17.22761549893305 | 17.68240549883621 |
| C   | -3.18984107769377 | 18.4698903442162  | 19.45001451326340 |
| C   | -1.9605945954196  | 17.9417263088330  | 20.10639652774714 |
| C   | -1.79730381799116 | 18.11642572899826 | 21.38035700261799 |
| C   | -0.57052621466934 | 17.5884219523279  | 22.0810900038953  |
| C   | 0.66765849620291  | 17.1493960232248  | 21.34319327233072 |
| C   | 0.64361725365428  | 16.77597130009613 | 20.08931482765301 |
| C   | 1.8678531775039   | 16.3478667917178  | 19.4545496490336  |
| C   | 2.27683423325144  | 14.99362318488438 | 19.58631570928393 |
| C   | 3.45654809288909  | 14.60499382691200 | 18.92594565300415 |
| C   | 4.21502377517546  | 15.5271359887720  | 18.18897219452370 |
| C   | 3.79658238587857  | 16.86109402353341 | 18.0923874554417  |
| C   | 2.61257667741847  | 17.2991239245542  | 18.71491708424321 |
| C   | -3.6306521994570  | 17.120115340023212| 14.4319309997229  |
| C   | -2.53000140432763 | 16.25301868736952 | 13.94521961792658 |
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| C   | 1.93920786172249  | 11.85011166555795 | 16.75882386362029 |
| C   | 2.57764729961906  | 12.85197601102099 | 16.01109637058947 |
| C   | 1.84664816768562  | 13.71795869591175 | 15.1768683454731  |
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| C   | -2.28111627038537 | 11.03704723038184 | 15.75580355177523 |
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| C   | 2.24648333795936  | 16.19601296745132 | 14.91500152653837 |
| C   | 1.44747805384157  | 14.01551226351532 | 20.4148686024096  |
| C   | 2.20868963082881  | 12.74367427679573 | 20.81132532310069 |
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| Ni  | -0.80342274910260 | 16.90850628211550 | 18.92430869679286 |
| Ni  | -1.21912131635548 | 15.7771097807280  | 15.31543533715331 |
| C   | -3.39802338569784 | 16.51331180009229 | 11.65615386588513 |
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| C   | 4.02458756976736  | 14.57527930936327 | 14.1338267182584  |
| C   | -2.32108840714981 | 13.16887652203593 | 17.15566282002727 |
| C   | -2.80347345394840 | 18.82357178764956 | 22.24716105388103 |
| H  | 0.86173823546912 | 19.84586718491402 | 17.1138239984396  |
|    | 0.5650829388237  | 18.06907681744333 | 17.120185609286   |
| H  | 3.76293476356965 | 19.67886606095442 | 16.623672738801   |
| H  | 2.77700575545997 | 20.80252941936786 | 18.6291431343203  |
| H  | 3.9492293591829  | 19.7115487776529  | 17.83917642259151  |
| H  | 1.17468722580298 | 14.54035282276358 | 21.3574662444904  |
| H  | -0.4024798920037  | 14.57632089999630 | 19.36507117735933  |
| H  | -0.5311076293088  | 13.05970149377703 | 20.3301243588031   |
| H  | 0.35779660688553  | 13.08223140298412 | 18.7678459178227   |
| H  | 1.17468722580298 | 14.54035282276358 | 21.3574662444904  |
| H  | -0.4024798920037  | 14.57632089999630 | 19.36507117735933  |
| H  | -0.5311076293088  | 13.05970149377703 | 20.3301243588031   |

Coordinates for DFT calculations, 3'(TS2):

| N  | -2.20953696769681 | 16.89446048562055 | 16.37018937590512 |
| C  | -3.35968090874806 | 17.42010796980007 | 15.8765882351788  |
| C  | -4.02125129671240 | 18.1322657499638  | 16.90336671769335  |
| C  | -3.17755681997728 | 17.97950951767779 | 18.02890530012463  |
| N  | -2.10308550302410 | 17.22786588591361 | 17.67932323360493  |
| C  | -3.18265795962823 | 18.43488945768539 | 19.45728659079655  |
| N  | -1.94768797791392 | 19.72408367097241 | 20.10143474106020  |
| C  | -1.76930599169959 | 18.10520139808615 | 21.37309713992850  |
| C  | -0.52875521508531 | 17.60048292929821 | 22.06507475250617  |
| C  | 0.70008787986685 | 17.15580128809592 | 21.31794332925988  |
| N  | 0.66318405475318 | 16.7880680699142  | 20.06265617544949  |
| C  | 1.87157931670386 | 16.35043981812912 | 19.4158367606712   |
| C  | 2.25636675070802 | 14.98654416873429 | 19.53292310738445  |
| C  | 3.44256623181326 | 14.58819870030566 | 18.89125073706833  |
| C  | 4.22896593360389 | 15.50875946705849 | 18.18166939691947  |
| C  | 3.83267663563165 | 16.85092986884878 | 18.09247624762929  |
| C  | 2.64739457591876 | 17.30183702793538 | 18.7047957129941   |
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| N  | -2.51921714256810 | 16.23578161617933 | 13.95339313616659  |
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| C  | -1.30349000004840 | 15.08160900942844 | 12.17699068560177  |
| C  | -0.5123391381651  | 14.17628863904770 | 13.0847992322236   |
| N  | -0.36072473911678 | 14.43675139019103 | 14.35772804637394  |
| C  | 0.42560137114845 | 13.55749226579585 | 15.18001682242262  |
| C  | -0.23489125570810 | 12.52173453231303 | 15.8900273608648   |
| C  | 0.55549725615554 | 11.6597895781635  | 16.67421682715132  |

54
| C       | 1.94503884764182 | 11.83014220602695 | 16.75993430903037 |
| C       | 2.57166155998688 | 12.8689521870305  | 16.0538611741007  |
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Ni  -0.78048815465443 16.91768253460514 18.9141074314977

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H   -3.68216394534268 18.03057865440703 13.81935997271856

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