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Supporting Information

Bimetallic Nickel Complexes for Selective CO_2 Carbon Capture and Sequestration

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General Procedures

All reactions were performed under dry N_2 or Ar atmosphere using standard Schlenk techniques or in a Glovebox. All solvents were dried according to standard methods. ^1H, ^{13}C NMR spectra were recorded with a Bruker DPX-200 NMR or a Bruker DPX-250 NMR spectrometer at room temperature. Peaks were referenced to residual ^1H signals from the deuterated solvent and are reported in parts per million (ppm). UV-vis spectra were recorded on a Varian Cary 100- or a Jasco V-670 UV-vis spectrophotometer at 25 °C in acetonitrile. IR spectra were measured with a Bruker Tensor 27 FT-IR spectrometer as KBr pellet and are reported in cm^{-1}. Mass spectra were measured with a Shimadzu QP-2010 instrument. Gas chromatography was conducted with a GC spectrometer from *Agilent Technologies.* Chemicals were ordered from Acros or Sigma-Aldrich and used without further purification.

X-ray Data Collection and Structure Solution Refinement. Crystals of **3**, **4**, **5**, **6**, **7**, and **$Ni(OAc)_2(H_2O)_4$** were grown by slow diffusion of diethyl ether into solutions of the compounds dissolved in acetonitrile. Single crystals suitable for X-ray analysis were coated with Paratone-N oil, mounted on a fiber loop, and placed in a cold, gaseous N_2 stream on an Oxford SuperNova or an Oxford Excalibur diffractometer performing Θ, ϕ, and ω scans at 170(2) K. Diffraction intensities were measured using graphite-monochromatic Cu (λ = 1.54184 Å) or Mo K_α radiation (λ = 0.71075 Å), respectively. Data collection, indexing, initial cell refinements, frame integration, final cell refinements, and absorption corrections were accomplished with the program CrysAlis (Agilent Technologies, Version 1.171.37.34, 2014). Space groups were assigned by analysis of the metric symmetry and systematic absences (determined by XPREP) and were further checked by PLATON[1,2] for additional symmetry. Structures were solved by direct methods and refined against all data in the reported 2θ ranges by full-matrix least squares on F^2 with the SHELXL program suite[3] using the OLEX2 interface.[4] Crystallographic data as well as refinement parameters are presented in Table S9-10.

Synthesis and Characterization

Synthesis of 1: Compound **1** was synthesized according to literature-known procedures.[5] Isophthalaldehyde (1 g; 7.5 mmol) was dissolved in 200 mL dry MeOH. *N*^{1},*N*^{1}-bis(2-aminomethyl)-ethan-1,2-diamine (0.73 g, 5.0 mmol) was suspended in 20 mL dry MeOH and added dropwise to the solution. The solution was refluxed for 3 h, cooled to RT and the solvent was reduced 20 mL. The obtained white solid was filtered off, washed with MeOH and dried in vacuum to give 36 % (1.05 g; 1.78 mmol) of hexa-imine. ^1H NMR (200 MHz, $CDCl_3$): δ 8.22 (3H, d), 8.18 (3H, d), 7.57 (3H, m), 3.57 (br s, 8H), 3.31 (6H, br s), 2.8 (18H, br s). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 160.9, 137.1, 132.5, 129.1, 127.5, 60.1, 56.2. IR (KBr, cm^{-1}): 3061, 2947, 2910, 2803, 1646. ESI-MS calculated for $C_{36}H_{42}N_8$: *m/z* = 586.35. Found: *m/z* = 587.0. Anal. Calc. for $C_{36}H_{42}N_8 \cdot H_2O$: N, 18.53; C, 71.49; H, 7.33. Found: N, 18.44; C, 71.66; H: 7.36.

The hexa-imine (500 mg; 0.85 mmol) was dissolved in 70 mL dry MeOH. KBH_4 (0.28 g; 5.12 mmol) was added at refluxing conditions in small portions over a period of 1h. The solution was refluxed for additional 3h and cooled to RT. The solvent was removed and the residue was suspended in 2M NH_4Cl-solution (20 mL), washed with $CHCl_3$ (2 x 50 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield 89 % (452 mg; 0.76 mmol) of compound **1** as white foam. ^1H NMR (200 MHz, $CDCl_3$): δ 7.19 (m, 12H, Ar-H), 3.62 (s, 12H), 3.18 (br s, 6H, NH), 2.66 (m, 12H), 2.60 (m, 12H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 140.0, 128.4, 127.4, 127.1, 54.9, 53.3, 47.6. IR (KBr, cm^{-1}): 3305 (br m, NH), 3056 (m, CH), 2956 (m, CH_2), 2835 (m, CH_2), 2812 (m, CH_2), 1454, 1266. ESI-MS calc. for $C_{36}H_{54}N_8$: *m/z* = 598.45. Found: *m/z* = 599.2. Anal. Calc. for $C_{36}H_{52}K_2N_8 \cdot 1/2\ H_2O$: N, 16.38; C, 63.22; H, 7.81. Found: N, 16.09; C, 62.75; H, 7.66.

Synthesis of 2: 5-(*Tert*-butyl)isophthalaldehyde (15.78 mmol; 3 g) was dissolved in 900 mL dry MeOH. N^1,N^1-bis(2-aminomethyl)-ethan-1,2-diamine (10.52 mmol; 1.6 mL) was suspended in 20 mL dry MeOH and added dropwise to the initial solution. The solution was refluxed for 3 d, cooled to RT and the solvent was reduced to 20 mL. The resulting white solid was filtered off, washed with little MeOH and dried in vacuum to give 48 % of the hexa-imine. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.25 (s, 8H), 7.59 (s, 6 H), 3.79 (br s, 4H), 3.29 (br s, 3 H), 2.94 (br s, 5H), 2.71 (br s, 6H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 161.1, 152.3, 136.8, 130.3, 124.6, 60.3, 56.4, 51.0, 35.3, 31.6. IR (KBr, cm^{-1}): 2960, 2906, 2814, 1643 (C=N), 1473, 1365. ESI-MS calc. for $C_{48}H_{66}N_8$: *m/z* = 754.54. Found: *m/z* = 755.3. Anal. Calc. for $C_{48}H_{66}N_8 \cdot MeOH$: N, 14.24; C, 74.77; H, 8.96. Found: N, 14.35; C, 74.01; H: 8.55.

The hexa-imine (1.98 mmol; 1.5 g) was dissolved in 100 mL dry MeOH. KBH_4 (11.93 mmol; 643 mg) was added under reflux in small portions. The solution was refluxed for additional 3h and subsequently cooled to RT. The solvent was removed under reduced pressure. The residue was suspended in 2M NH_4Cl-solution, washed with $CHCl_3$ (3 x 100 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield 98 % of compound **2** as white foam. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.20 (s, 9H), 6.90 (s, 3H), 3.59 (s, 12H), 2.66 (br d, 24 H), 1.27 (2, 27 H). ^{13}C NMR (5.3 MHz, $CDCl_3$): δ 151.8, 125.0, 54.6, 53.3, 47.7, 34.8, 31.5. IR (KBr, cm^{-1}): 3422 (br m, NH), 2959 (m, CH), 2861 (m, CH_2), 2816 (m, CH_2), 1602, 1459, 1057. ESI-MS calc. for $C_{48}H_{78}N_8$: *m/z* = 766.64. Found: *m/z* = 767.6. Anal. Calc. for. $K_3C_{48}H_{78}N_8 \cdot 2\ MeOH$: N, 11.81; C, 63.31; H, 9.41. Found: N, 11.47; C, 63.72; H, 9.42.

$[Ni_2(1)(H_2O)(Cl)(MeCN)](ClO_4)_3$, 3: Compound **1** (0.17 mmol; 100 mg) was dissolved in 10 mL dry MeCN/EtOH (4:1) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.33 mmol; 121 mg), dissolved in 4mL MeCN, was added. The blue solution was stirred for 1d under N_2-atmosphere. The solvent was removed under N_2-atmosphere and crystallized from MeCN/Et_2O to yield blue crystals of compound **3** in 56 % (0.03 mmol; 105 mg) yield. IR (KBr, cm^{-1}): 3567, 3414, 3256, 2931, 2872, 1614, 1451, 1445, 1331, 1089, 756 (ClO_4^-), 702 (ClO_4^-), 626 (ClO_4^-). ESI-MS calc. for $[C_{38}H_{59}ClN_9Ni_2O](ClO_4) + CH_3CN$: *m/z* = 947.3. Found: *m/z* = 947.0 / 949.0. Anal. Calc. for $[C_{38}H_{58}ClN_9Ni_2O](ClO_4)_3 + CH_3CN$: N, 11.78; C, 41.47; H, 5.40. Found: N, 11.34; C, 41.34; H, 5.04. UV-vis (MeCN, RT): 396 nm, 538 nm, 628 nm.

$[Ni_2(2)(H_2O)(Cl)(MeCN)](ClO_4)_3$, 4: Compound **2** (0.13 mmol; 100 mg) was dissolved in 8 mL MeCN/EtOH (4:1) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.26 mmol; 95 mg), dissolved in 2 mL MeCN, was added. The blue solution was stirred for 30 min. CO_2 was bubbled through the solution, forming a light blue solution, and stirred for additional 2 h. The formed solid was filtered off and the filtrate was crystallized from MeCN/Et_2O to give compound **4** as dark blue crystals in 52 % (0.068 mmol) yield. IR (KBr, cm^{-1}): 3561, 3256 (br), 2962, 2871, 1605, 1472, 1440, 1089, 626. ESI-MS calc. for $[C_{50}H_{83}ClN_9Ni_2O](ClO_4) + CH_3CN$: *m/z* = 1119.6. Found: *m/z* = 1119.5. Anal. Calc. for $[C_{50}H_{83}ClN_9Ni_2O](ClO_4)_3 + CH_3CN$: N, 10.62; C, 47.37; H, 6.57. Found: N, 10.76; C, 47.46; H, 6.83. UV-vis (MeCN, RT): 348 nm, 628 nm.

$[Ni_2(1)(HCO_3)(H_2O)(MeCN)](ClO_4)_2(Cl)$, 5: Compound **1** (0.17 mmol; 100 mg) was dissolved in 10 mL MeCN/EtOH (4:1) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.33 mmol; 121 mg), dissolved in 4 mL MeCN, was added. The blue solution was stirred for 30 min. CO_2 was bubbled through the solution, forming a light blue solution, and stirred for additional 2 h. The solid was separated and the filtrate was slowly evaporated to yield compound **5** as dark blue crystals in 50 % (0.084 mmol; 95 mg) yield. IR (KBr, cm^{-1}): 3397, 3258, 2926, 2868, 1673 (CO_2), 1638 (CO_2), 1451, 1371, 1090, 626. ESI-MS calc. for

$[C_{37}H_{55}N_8Ni_2O_3](ClO_4)$: *m/z* = 874.26. Found *m/z* = 874.8. Anal. Calc. for $[C_{39}H_{60}N_9Ni_2O_4](Cl)(ClO_4)_2$ + $2H_2O$: N, 11.39; C, 42.33; H, 5.83. Found: N, 11.87; C, 42.46; H, 6.00. UV-vis (MeCN, RT): 379 nm, 482 nm, 633 nm.

Likewise, this compound can be generated from a solution of compound **3** in acetonitrile either by stirring under air or bubbling CO_2 through the solution. The workup procedure subsequently applied is the same as described before.

$[Ni_2(1)(H^{13}CO_3)(H_2O)](ClO_4)Cl$, $^{13}CO_2$-5: Compound **1** (0.17 mmol; 100 mg) was dissolved in 10 mL MeCN/EtOH (4:1) and $Ni(ClO_4)_2{\cdot}6H_2O$ (0.33 mmol; 121 mg), dissolved in 4 mL MeCN, was added. The blue solution was stirred for 30 min. $^{13}CO_2$ was bubbled through the solution, forming a light blue solution, which was stirred for additional 2 h. The solid was separated and the filtrate was crystallized from MeCN/Et_2O to yield compound **5a** as blue powder in 36 % (0.06 mmol; 66 mg) yield. ESI-MS calc. for $[^{12}C_{36}{}^{13}C_1H_{55}N_8Ni_2O_3](ClO_4)$ *m/z* = 875.26. Found *m/z* = 875.3.

$[Ni_2(1)(N_3)(MeCN)](ClO_4)_3$, 6: Compound **1** (59 mg; 0.084 mmol) was dissolved in 10 mL MeCN/EtOH (1:1) and $Ni(ClO_4)_2{\cdot}6\,H_2O$ (73 mg; 0.2 mmol), dissolved in 10 mL MeCN/EtOH (1:1), was added. The blue solution was stirred for 5 min. NaN_3 (6.8 mg; 0.105 mmol) was dissolved in 5 mL EtOH/H_2O, and added to the solution. The solvent was removed after 1d and the residue crystallized from MeCN via slow evaporation of the solvent. Compound **6** was obtained in 24 % (25.3 mg; 0.024 mmol) yield. IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 3480 (br, NH), 3069 (m, CH), 2926, 2854 (m, CH_2), 2202, 2120 (s, N_3), 1443, 1147, 1115, 1086 (s, ClO_4^-), 800, 757, 701, 631 (m, ClO_4^-). MS calc. for $[C_{36}H_{54}N_{11}Ni_2](ClO_4)_2$: *m/z* = 954.23. Found: *m/z* = 954.7. Anal. Calc. for $[C_{36}H_{54}N_{11}Ni_2](ClO_4)_3{\cdot}MeCN{\cdot}2H_2O$: N, 14.83; C, 40.26; H, 5.42. Found: N, 14.84; C, 40.04; H, 5.20. UV-vis (MeCN, RT): 348 nm, 607 nm.

Likewise this compound can be generated by treatment of compound **5** or **$^{13}CO_2$-5** with NaN_3 (1 equiv.) in acetonitrile and following the work up procedure as described above.

$[Ni_2(2)(N_3)](ClO_4)_3$, 7: Compound **2** (20 mg; 0.026 mmol) was dissolved in 2 mL MeCN/EtOH (1:1) and $Ni(ClO_4)_2{\cdot}6\,H_2O$ (48 mg; 0.13 mmol), dissolved in 2 mL MeCN/EtOH (1:1), was added. The blue solution was stirred for 5 min. NaN_3 (2 mg; 0.027 mmol) was dissolved in 5 mL EtOH/H_2O, and added to the solution. The solvent was removed after 1d stirring and the residue crystallized from MeCN by slow removal of the solvent. Compound **7** was obtained in 77 % (23 mg; 0.020 mmol) yield. **IR** (KBr) $\tilde{\nu}$ [cm^{-1}] = 3406 (br, NH), 2959 (m, CH_2), 2854 (m, CH_2), 2194 (s, N_3), 1607, 1438, 136, 1086 (s, ClO_4^-), 880, 757, 701, 631 (m, ClO_4^-). MS calc. for $[C_{48}H_{78}N_{11}Ni_2](ClO_4)_2$: *m/z* = 1222.4. Found: *m/z* = 1123.8. Anal. Calc. for $[C_{48}H_{78}N_{11}Ni_2](ClO_4)_3{\cdot}MeCN\,{\cdot}H_2O$: N, 13.09; C, 46.77; H, 6.52. Found: N, 13.06; C, 46.96; H, 6.86.

Likewise this compound can be generated by treatment of compound **4** with NaN_3 (1 equiv.) in acetonitrile and following the work up procedure as described above.

$[Ni_2L^1(SCN)](ClO_4)_3$, 8: Compound **1** (100 mg; 0.17 mmol) and $Ni(ClO_4)_2{\cdot}6\,H_2O$ (121 mg; 0.33 mmol) were dissolved in 8 mL MeCN. KSCN (16 mg, 0.17 mmol) was added after 30 min. The solution was stirred for 1d. The solvent was removed and the crude material was crystallized from MeCN/Et_2O. MS Calc. for $[C_{37}H_{54}N_9Ni_2S](ClO_4)_2$: *m/z* = 970.2. Found: *m/z* = 971.8.

General irradiation procedure: Complex **6** was dissolved in acetonitrile in a quarz cuvette. Irradiation of the solution was performed with a 150 W Xe-lamp under ambient conditions. The reaction progress was monitored by ESI-MS and UV-vis spectroscopy.

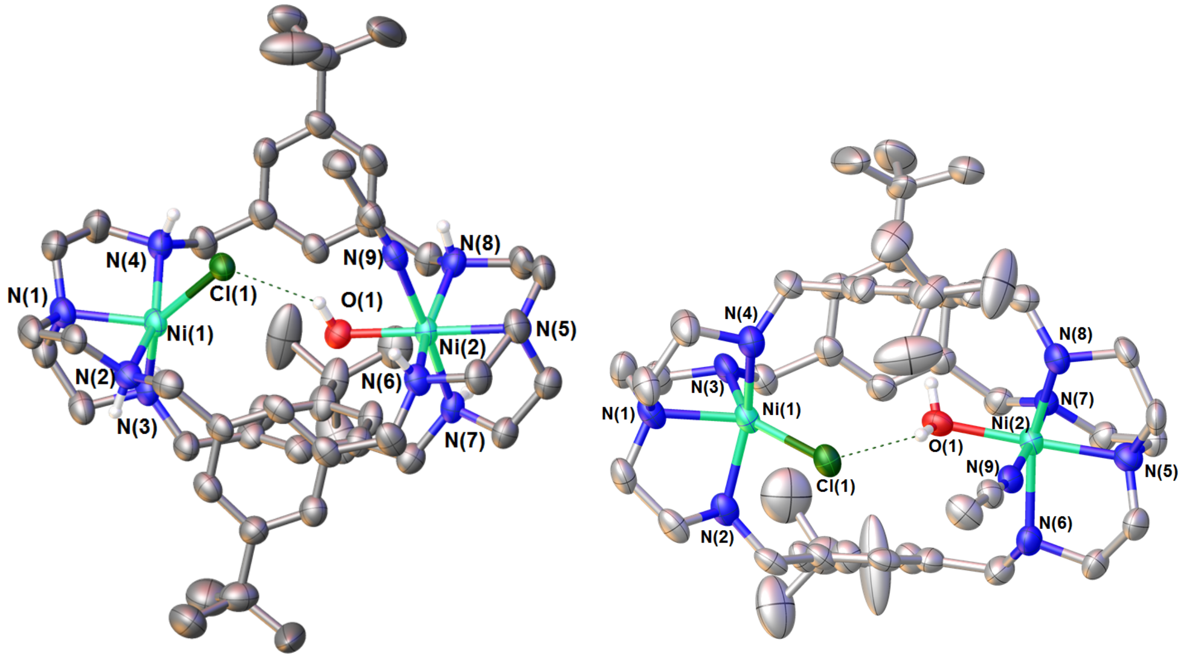

Figure S1: Molecular structure of compound **4** from side (left) and top (right) (counter ions and hydrogen atoms were omitted for clarity).

Table S1: Selected bond length [Å] and angles [°] of the dinickel complex **4**.

Ni(1)-Cl(1)	2.347(2)	Ni(2)-N(5)	2.076(6)
Ni(1)-N(1)	2.065(6)	Ni(2)-N(6)	2.209(6)
Ni(1)-N(2)	2.132(6)	Ni(2)-N(7)	2.131(6)
Ni(1)-N(3)	2.087(6)	Ni(2)-N(8)	2.170(6)
Ni(1)-N(4)	2.146(6)	Ni(2)-N(9)	2.134(7)
Ni(1)-O(1)	2.036(4)		
N(2)-Ni(1)-N(4)	157.3(2)	N(5)-Ni(2)-O(1)	177.8(2)
N(8)-Ni(2)-N(6)	159.4(2)	N(5)-Ni(2)-N(9)	98.2(2)

Table S2: Selected bond length [Å] and angles [°] of the dinickel complex **3**.

Ni(1)-N(1)	2.072(3)	Ni(2)-N(5)	2.068(3)
Ni(1)-N(2)	2.205(3)	Ni(2)-N(6)	2.131(3)
Ni(1)-N(3)	2.118(2)	Ni(2)-N(7)	2.088(3)
Ni(1)-N(4)	2.150(3)	Ni(2)-N(8)	2.142(3)
Ni(1)-N(9)	2.167(3)	Ni(2)-Cl(1)	2.3261(10)
Ni(1)-O(1)	2.043(2)		
N(2)-Ni(1)-N(4)	159.30(10)	N(6)-Ni(2)-N(8)	156.00(11)
N(1)-Ni(1)-N(9)	96.99(11)		

Table S3: Selected bond length [Å] and angles [°] of the dinickel complex **5**.

Ni(1)-N(1)	2.0912(18)	Ni(2)-N(5)	2.0916(19)
Ni(1)-N(2)	2.1879(19)	Ni(2)-N(6)	2.145(2)
Ni(1)-N(3)	2.123(2)	Ni(2)-N(7)	2.139(2)
Ni(1)-N(4)	2.1729(18)	Ni(2)-N(8)	2.125(2)
Ni(1)-O(4)	2.1773(17)	Ni(2)-O(2)	1.9913(15)
Ni(1)-O(1)	2.0186(15)	O(1)-C(1)	1.248(3)
O(3)-C(1)	1.359(3)	O(2)-C(1)	1.252(3)
N(2)-Ni(1)-N(4)	174.98(7)	O(1)-C(1)-O(2)	124.6(2)
N(8)-Ni(2)-N(6)	154.87(8)	O(2)-C(1)-O(3)	115.9(2)
		O(1)-C(1)-O(3)	119.5(2)

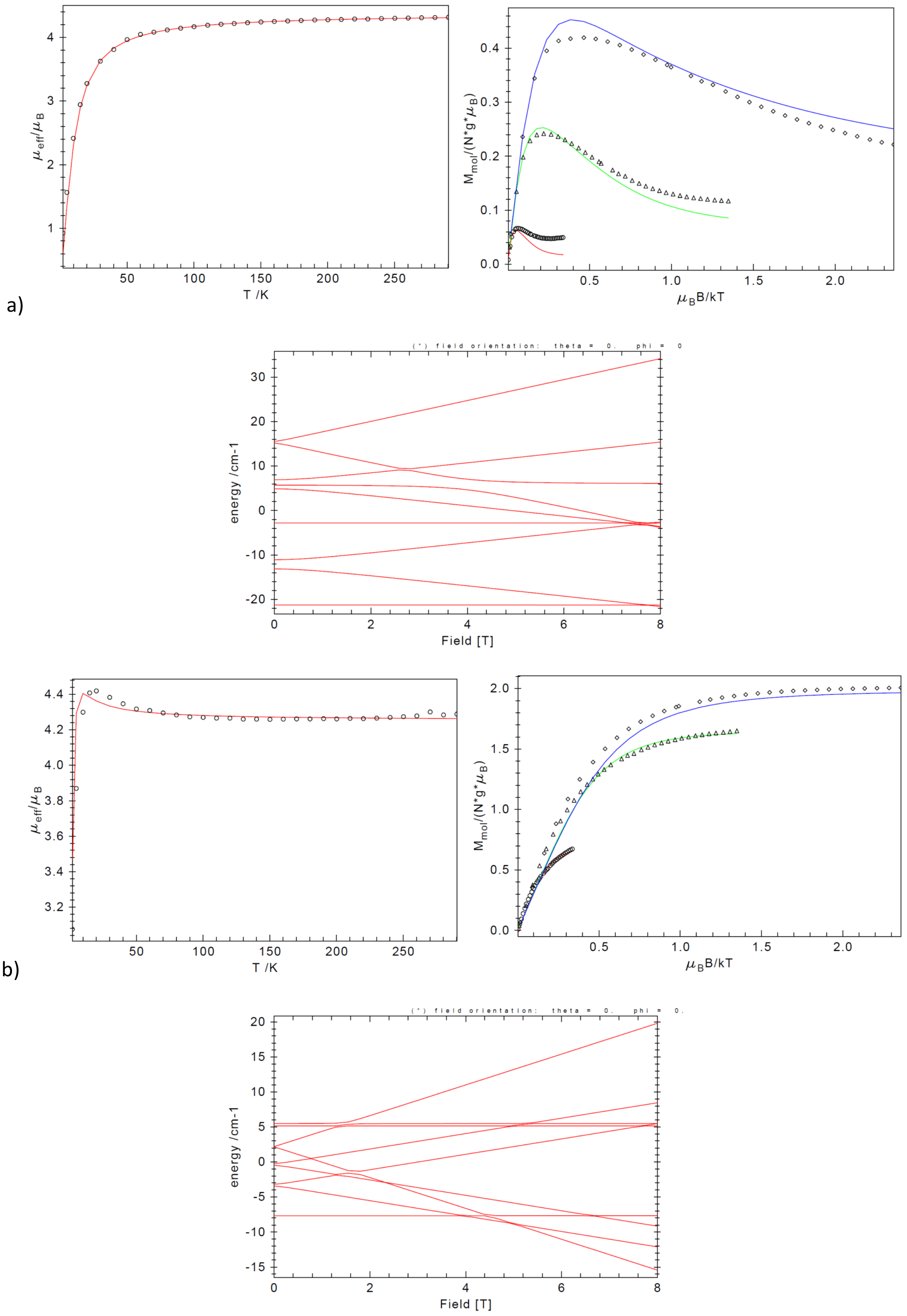

Figure S2: SQUID-data, recorded with a SQUID instrument from *Quantum Design* at 7T (2K - 310K) for compound **5** (a) and **4** (b). MultiVu was used as acquisition software. Compound **5**: S = 1.0, D = 9.30 cm^{-1} and J = -4.5 cm^{-1}**;** compound **4**: S = 1.0, D = 5.5 cm^{-1} and J = 0.74 cm^{-1}.

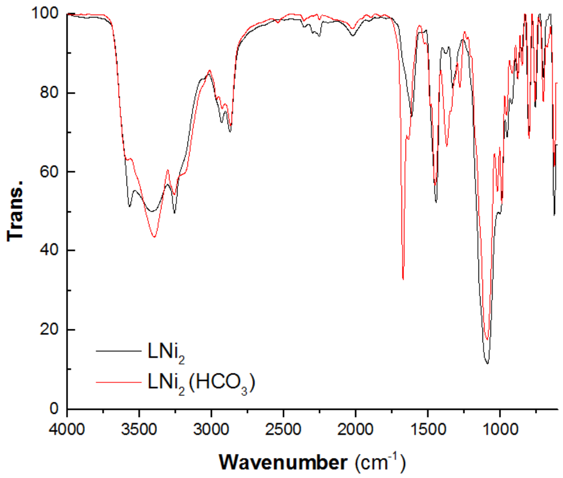

Figure S3: IR spectra of **3** and **5** measured as KBr-pellets.

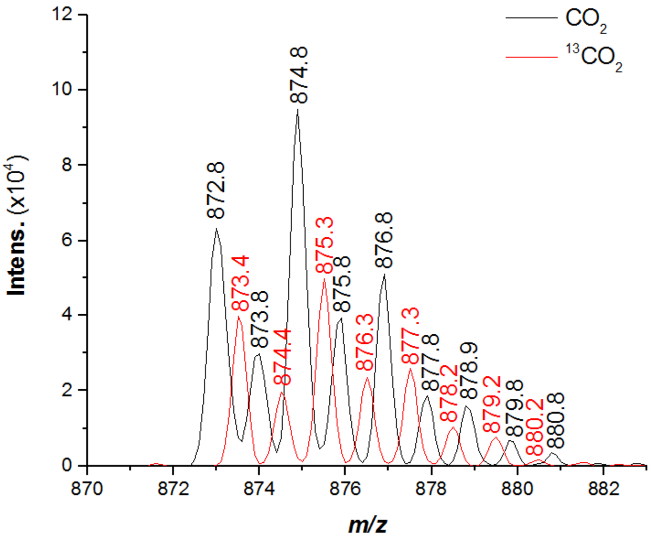

Figure S4: ESI-mass spectra of **5** with CO_2 and $^{13}CO_2$.
A full-range mass spectrum of **5** is provided in figure S13.

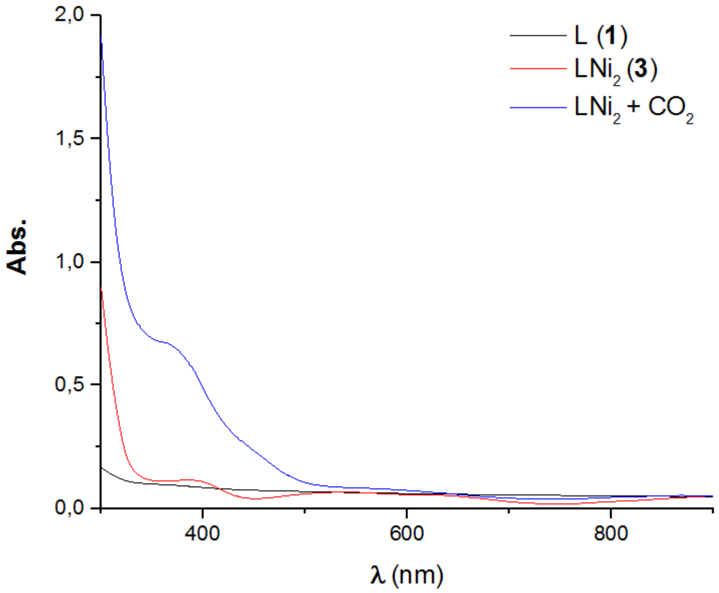

Figure S5a: UV-vis spectra, measured in acetonitrile at RT, of the fixation of CO_2 with LNi_2 **3**.

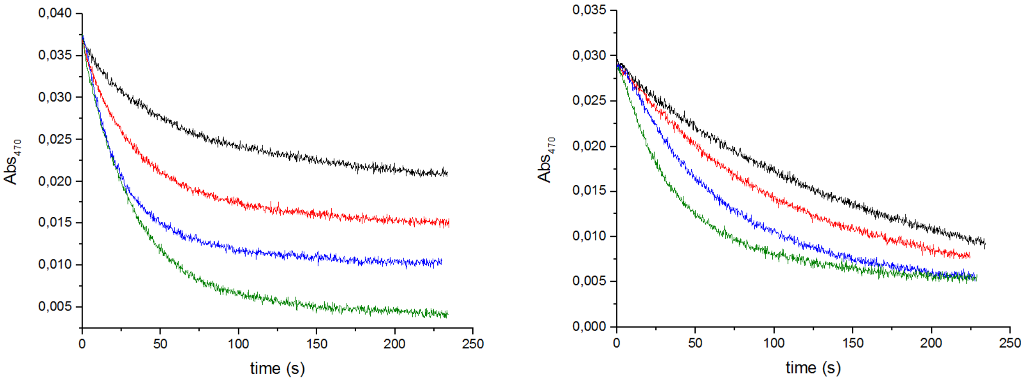

Figure S5b: Time-dependent spectrophotometry, recorded with a UV-vis spectrophotometer Specord® S600 from *Analytik Jena* and a SFA-20 Rapid Kinetics Accessory from *HI-Tech Scientific*, at various temperatures (black trace 15˚C; red trace 25˚C; blue trace 35˚C; green trace 45˚C) and CO_2 concentrations (0.28 mol/L CO_2 (left); 0.09 mol/L CO_2 (right)). For temperature control, an external thermostat and a cuvette holder with temperature unit was used. For the measurement, a 6 mM solution of LNi_2 in degassed acetonitrile was used. The solutions with different CO_2 concentrations were prepared from a CO_2 saturated acetonitrile solution (0.28 mol/L CO_2 at 25 °C) and degassed acetonitrile.[6]

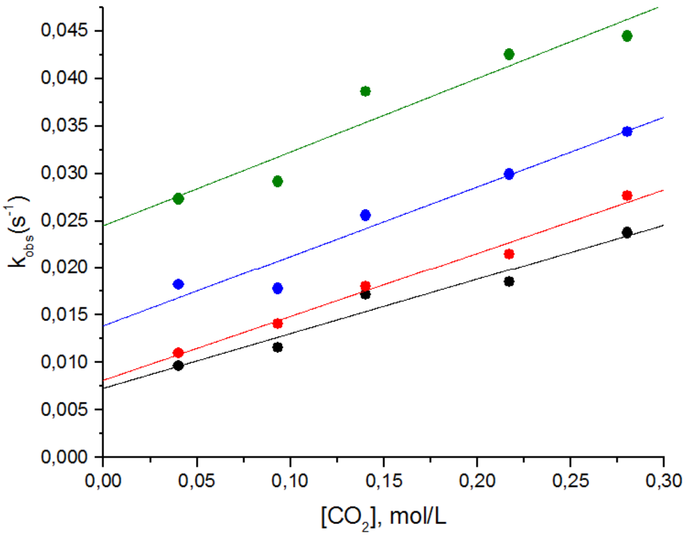

Figure S5c: Stopped-flow spectrophotometry: comparison of the different k_{obs} values at different temperatures and concentrations (black trace 15˚C; red trace 25˚C; blue trace 35˚C; green trace 45˚C). The data and fitting results are listed in table S4/S5.

Table S4: k_{obs} values (s^{-1}) of the stopped flow measurement of the CO_2 fixation of a 6 mM solution of complex **3** at different temperatures and CO_2 concentrations. Kinetic traces (Figure S5b) were fitted with the equation for first order reaction with $A = A_0 \cdot \exp(-k_{obs} \cdot t)$, with A = absorbance, A_0 = initial absorbance, t = time in s.

T [K] $[CO_2]_{acetonitrile}$	**288.15**	**298.15**	**308.15**	**318.15**
0.28 mol/L	0.02379	0.02766	0.03443	0.04449
0.217 mol/L	0.01856	0.02153	0.02996	0.04256
0.14 mol/L	0.01723	0.01809	0.02562	0.03865
0.093 mol/L	0.01162	0.01413	0.01784	0.02918
0.04 mol/L	0.00968	0.01106	0.0823	0.02736

Table S5: The k_2-values at different temperatures are obtained from the slope of the plot k_{obs} vs. $[CO_2]$ (left). Resulting activation parameters of the Eyring plot were obtained from the linear regression (Figure S6) and were calculated from the equation $\ln k = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$ (right).

T [K]	k_2 [$M^{-1}s^{-1}$]
288.15	0.057 ± 0.008
298.15	0.067 ± 0.005
308.15	0.073 ± 0.011
318.15	0.077 ± 0.014

$\Delta H^{\ddagger}$ [kJ/mol]	$\Delta S^{\ddagger}$ [J/mol·K]
7.55 ± 1.07	2.64 ± 3.55

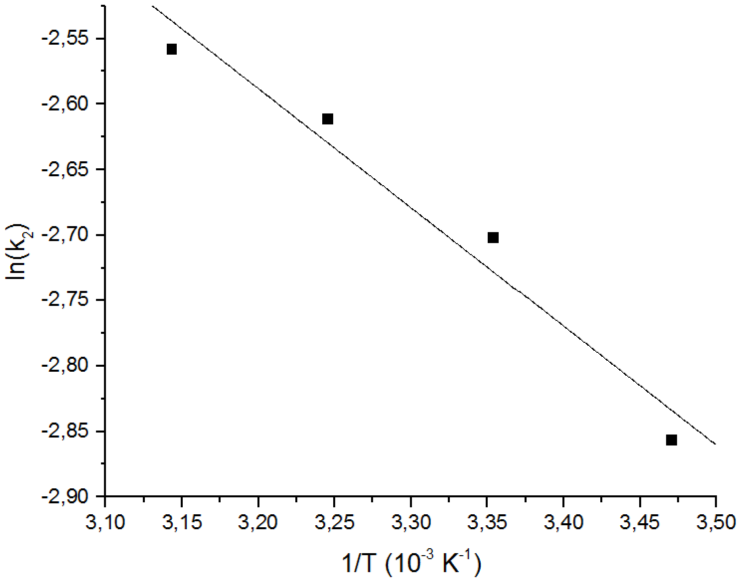

Figure S6: Eyring plot for the reaction of 6 mM complex **3** with carbon dioxide in acetonitrile. Data points are listed in table S5. Linear regression yields the activation parameters shown in table S5.

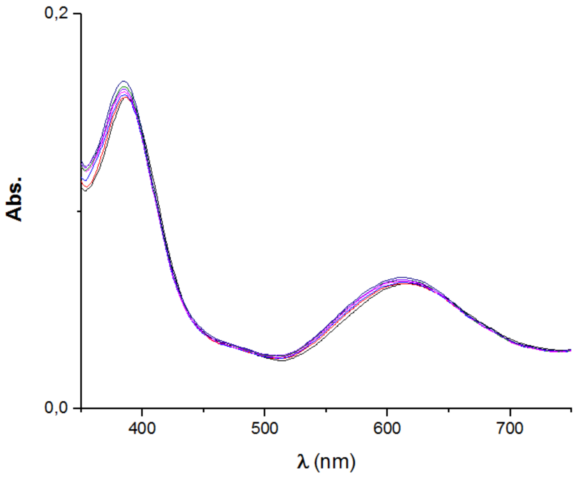

Figure S7: UV-vis spectrum in acetonitrile showing the temperature stability of **5** at 65 °C.

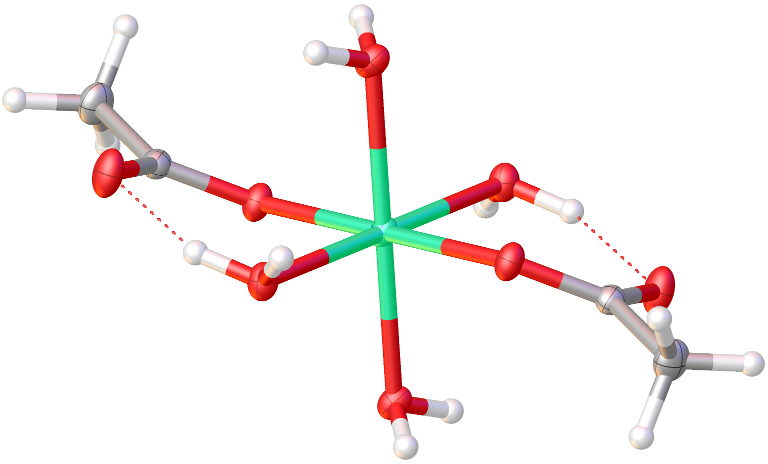

Figure S8: Re-determined molecular structure of $[Ni(OAc)_2(H_2O)_4]$ crystallized from DMF/Et_2O at RT. See also Ref [7].

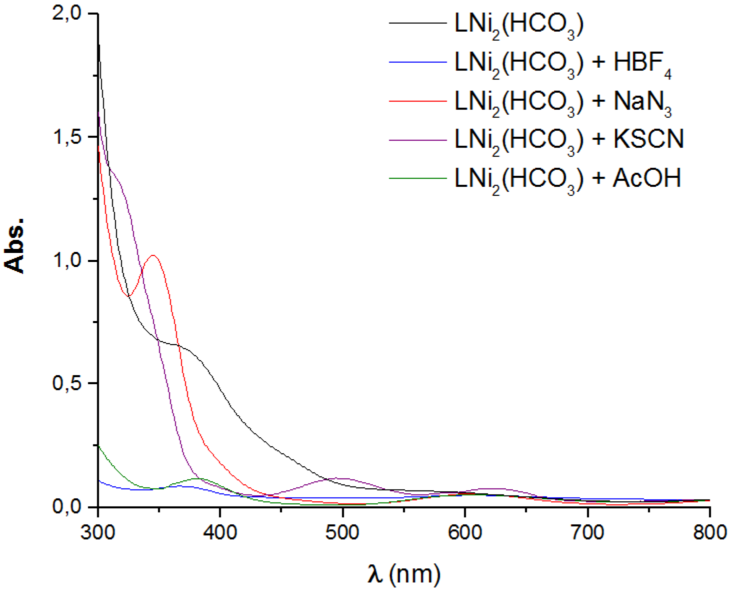

Figure S9a: UV-vis spectra in acetonitrile at RT of the exchange reactions of **5** with N_3^-, SCN^- and HBF_4.

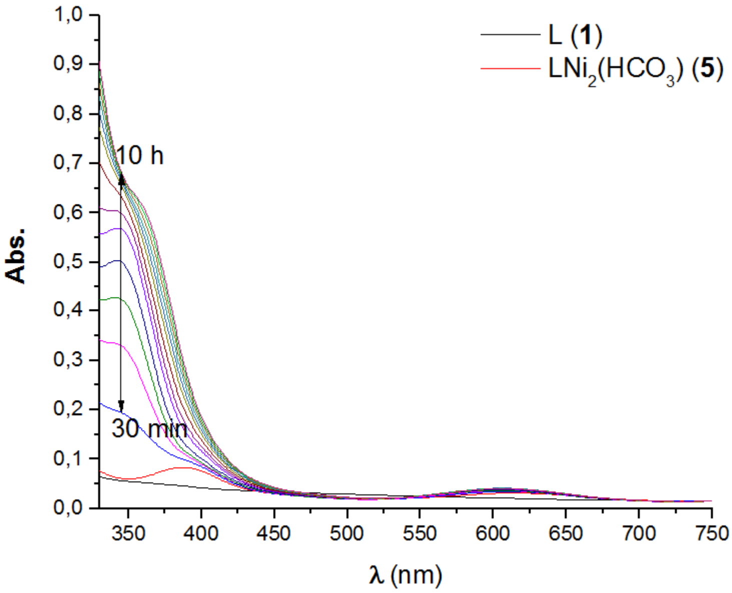

Figure S9b: Time-dependent UV-vis spectra in acetonitrile at RT, of the exchange of HCO_3^- with 1 eq. N_3^-.

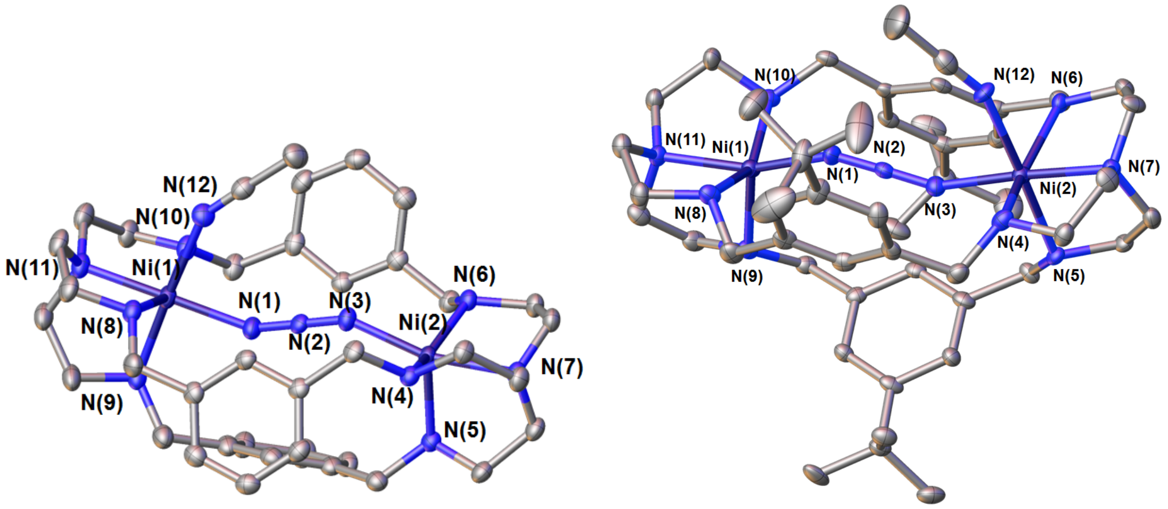

Figure S10: Molecular structure of compound **6** (right) and its *tert*-butyl version **7** (left) (hydrogen atoms were omitted for clarity).

Table S6: Selected bond length [Å] and angles [°] for complex **6**.

N(1)-N(2)	1.161(3)	Ni(2)-N(7)	2.104(2)
N(2)-N(3)	1.171(3)	Ni(1)-N(8)	2.206(2)
Ni(1)-N(1)	2.019(2)	Ni(1)-N(9)	2.113(2)
Ni(2)-N(3)	1.990(2)	Ni(1)-N(10)	2.157(2)
Ni(2)-N(4)	2.114(2)	Ni(1)-N(11)	2.087(2)
Ni(2)-N(5)	2.074(2)	Ni(1)-N(12)	2.184(2)
Ni(2)-N(6)	2.127(2)		
N(1)-N(2)-N(3)	179.4(2)	N(8)-Ni(1)-N(1)	100.33(8)
Ni(1)-N(1)-N(2)	149.83(18)	N(4)-Ni(2)-N(3)	95.42(8)
Ni(2)-N(3)-N(2)	148.08(19)		

Table S7: Selected bond length [Å] and angles [°] for complex **7**. [See also Ref. [8] for comparison]

N(1)-N(2)	1.166(9)	Ni(2)-N(7)	2.072(6)
N(2)-N(3)	1.174(9)	Ni(1)-N(8)	2.098(6)
Ni(1)-N(1)	1.972(6)	Ni(1)-N(9)	2.056(6)
Ni(2)-N(3)	1.988(6)	Ni(1)-N(10)	2.130(6)
Ni(2)-N(4)	2.150(6)	Ni(1)-N(11)	2.098(6)
Ni(2)-N(5)	2.114(5)	Ni(1)-N(12)	2.075(6)
Ni(2)-N(6)	2.247(6)		
N(1)-N(2)-N(3)	179.1(7)	N(8)-Ni(1)-N(1)	149.5(2)
Ni(1)-N(1)-N(2)	150.2(6)	N(4)-Ni(2)-N(3)	158.4(2)
Ni(2)-N(3)-N(2)	153.5(5)		

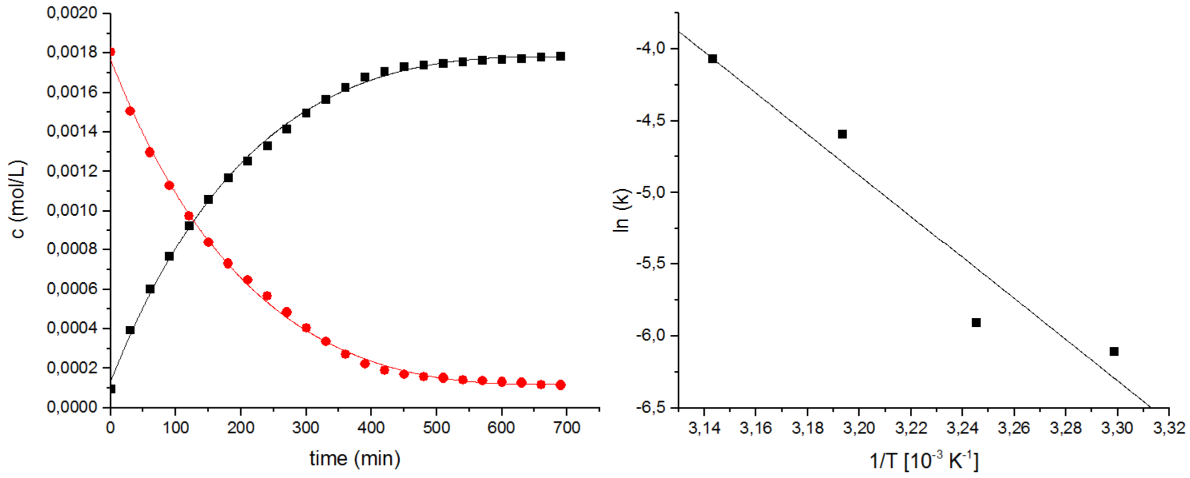

Figure S11: Time-dependent UV-vis spectra of the exchange of HCO_3^- with N_3^- at 25˚C in acetonitrile. The change in absorption at 348 nm was plotted against the time. The data were fitted with a single exponential fit ($k_{obs,\ 303.15K} = 0.00223\ min^{-1}$) (left). The Eyring plot for this exchange reaction at different temperatures is shown on the right. The linear regression yields the activation parameters provided in table S8.

Table S8: Observed k_{obs}-values for different temperatures, obtained from single exponential fit (left). Activation parameters were calculated from the Eyring plot, $\ln k_{obs} = -\Delta H^{‡}/RT + \Delta S^{‡}/R$ (right).

T [K]	k_{obs} [min^{-1}]
303.15	$0.00223 \pm 1.18 \cdot 10^{-3}$
308.15	$0.00272 \pm 2.59 \cdot 10^{-4}$
313.15	$0.01012 \pm 5.17 \cdot 10^{-4}$
318.15	$0.01712 \pm 6.52 \cdot 10^{-4}$

$\Delta H^{‡}$ [kJ/mol]	$\Delta S^{‡}$ [J/mol·K]
118.9 ± 23.6	340.04 ± 75.99

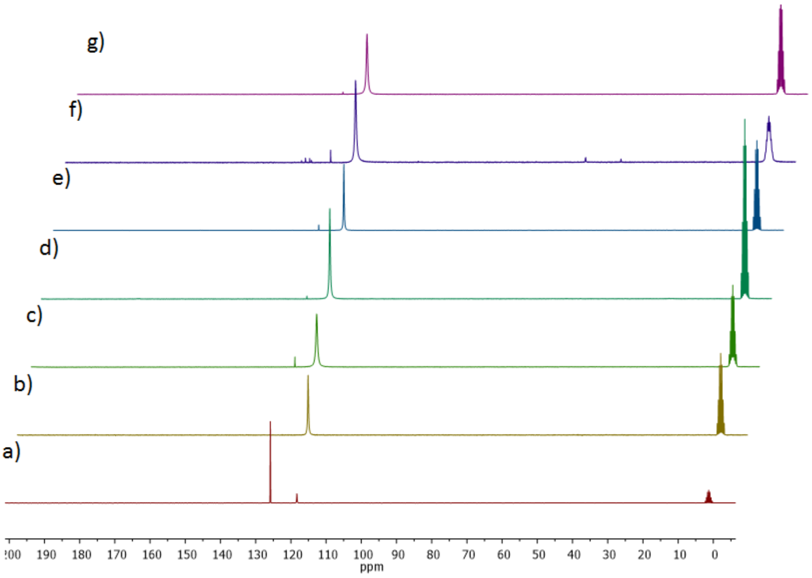

Figure S12a: ^{13}C-NMR spectra (50.3 MHz, MeCN-d_3) of the exchange reactions at RT: a) $^{13}CO_2$ in MeCN-d_3, b) $LNi_2(H^{13}CO_2)$ **^{13}CO$_2$-5**, c) **^{13}CO$_2$-5** with AcOH d) **^{13}CO$_2$-5** with 1 eq. NaN_3, e) **^{13}CO$_2$-5** with 1 eq. KSCN, f) **^{13}CO$_2$-5** with HBF_4, g) **^{13}CO$_2$-5** with 1 eq. $NaHCO_3$; 118.3 ppm and 1.3 ppm are MeCN-d_3 signals.

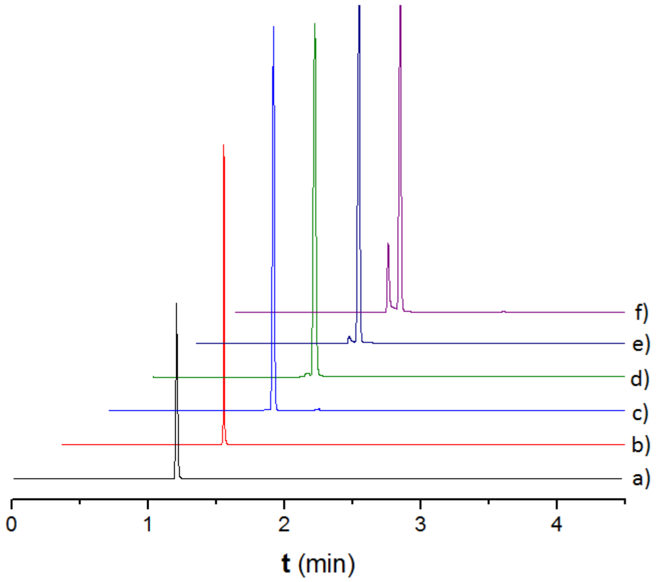

Figure S12b: GC spectra of the exchange reactions, performed in dry acetonitrile under inert conditions: a) CO_2, b) **5** + NaN_3, c) **5** + AcOH d) **5** + KSCN, e) **5** + HBF_4, f) **5** + $NaHCO_3$.

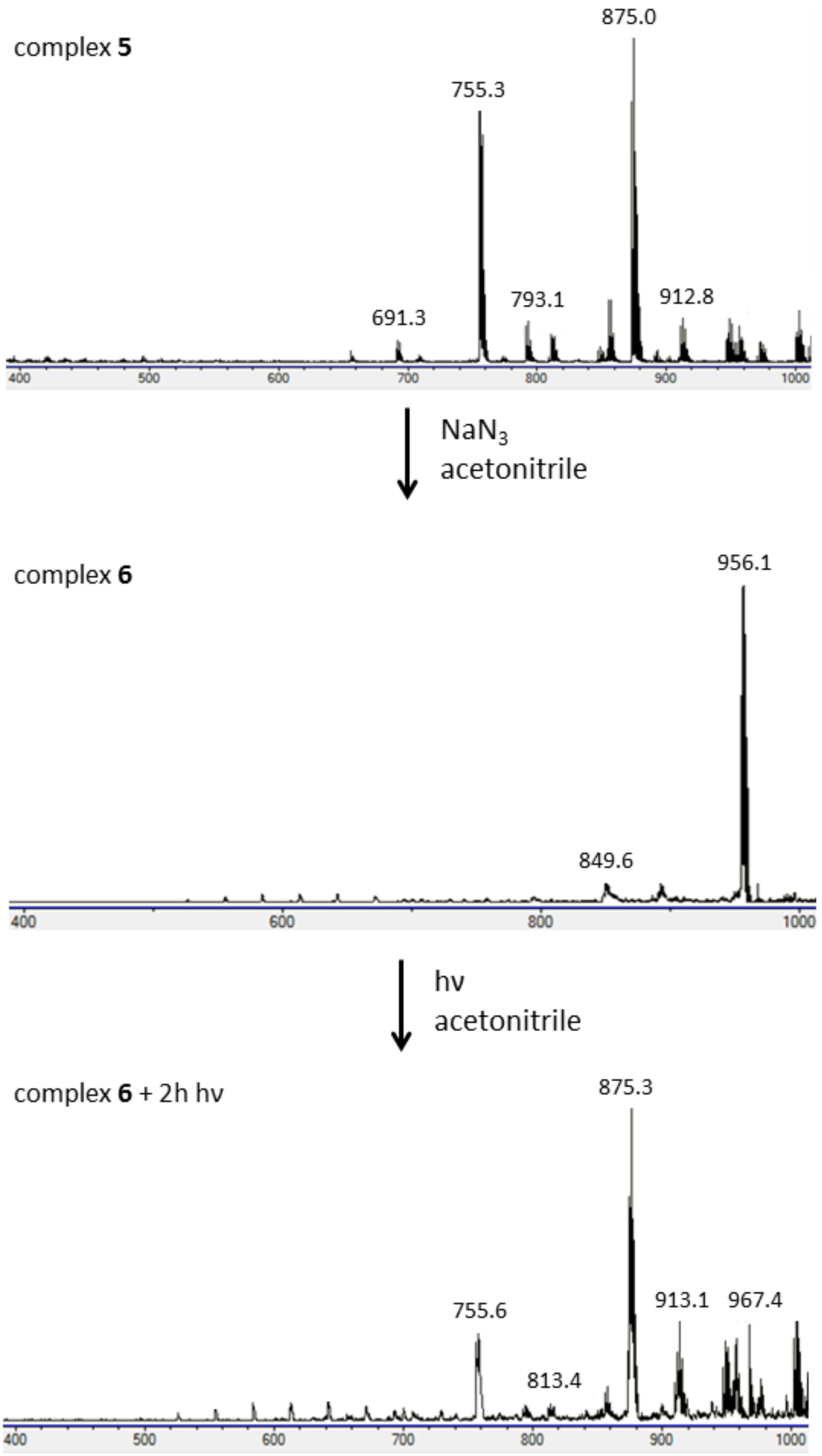

Figure S13: Reaction control via mass spectrometry of the exchange reaction of HCO_3^- with 1 eq. N_3^- and following photolysis of complex **6**.

Table S9: Crystallographic Data of compound **3**, **4**, and **7.**

	3	**4**	**7**
Empirical formular	$C_{46}H_{71}Cl_4N_{13}Ni_2O_{13}$	$C_{50}H_{83}Cl_4N_9Ni_2O_{13}$	$C_{54}H_{87}Cl_3N_{14}Ni_2O_{12}$
Formular weight [g·mol^{-1}]	1273.38	1277.47	1348.15
Temperature [K]	170	170	170
λ (Cu K$_{\alpha}$) [Å]	1.54184	1.54184	1.54184
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1$
a [Å]	12.3126(2)	14.0625(17)	12.7102(6)
b [Å]	20.4330(3)	23.576(2)	12.8900(5)
c [Å]	23.8954(5)	21.767(2)	19.9985(9)
α [°]	90.00	90.00	90.00
β [°]	99.7407(18)	95.325(13)	102.464(4)
γ [°]	90.00	90.00	90.00
V [Å^3]	5925.02(18)	7185.4(13)	3199.2(2)
Z	4	4	2
ρ_{ber} [g·cm^{-3}]	1.428	1.181	1.3994
μ [mm^{-1}]	3.029	0.728	2.452
F(000)	2644.0	2696.0	1424.0
Crystal size [mm^3]	0.31 x 0.24 x 0.14	0.21 x 0.20 x 0.16	0.13 x 0.10 x 0.10
2θ for data collection [deg]	7.28-152.74	1.87-24.22	3.56-74.43
Index-ranges	$-15 \leq h \leq 10$ $-23 \leq k \leq 25$ $-28 \leq l \leq 29$	$-16 \leq h \leq 163$ $-26 \leq k \leq 26$ $-24 \leq l \leq 24$	$-15 \leq h \leq 11$ $-16 \leq k \leq 15$ $-21 \leq l \leq 24$
Reflections collected	23826	54008	13871
Independent	12011	11282	9639
reflections R_{int}	0.0225	0.0978	0.0350
S[a)]	1.062	0.811	1.035
R_1 [$I \geq 2\sigma(I)$][b)]	0.0610	0.0462	0.0446
wR_2 [all data, F^2][c)]	0.1648	0.0803	0.1156
Residual electron density [e Å^{-3}]	1.90/-1.30	0.599/-0.266	0.619/-0.348
CCDC number	1418422	1418423	1418427

[a)] $S = \{\sum[w(F_0^2 - F_c^2)^2]\}/(n-p)\}^{0.5}$, n = number of reflections, p = number of parameters.

[b)] $R_1 = \sum|F_0|| \, |F_c|| \, \sum|F_0|$. [c)] $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2 / \sum[(F_0^2)^s]\}^{0.5}$

Note: Crystals of **4** contained several highly disordered solvent molecules that were removed by SQUEEZE/Platon.

Table S10: Crystallographic Data of compound **5**, **6** and [Ni(OAc)$_2$(H$_2$O)$_4$].

	5	**6**	**[Ni(OAc)$_2$(H$_2$O)$_4$]**
Empirical formular	$C_{41}H_{63}Cl_3N_{10}Ni_2O_{12}$	$C_{42}H_{63}Cl_3N_{14}Ni_2O_{12}$	$C_4H_{14}NiO_8$
Formular weight [g·mol^{-1}]	1111.78	1179.83	248.86
Temperature [K]	173	170	170
λ [Å]	1.54184 (Cu K_α)	1.54184 (Cu K_α)	0.71075 (Mo K_α)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$
a [Å]	17.1218(13)	11.1608(3)	4.74771(14)
b [Å]	15.9325(14)	15.0248(3)	11.7147(3)
c [Å]	19.4659(15)	16.3126(3)	8.3144(3)
α [°]	90.00	112.1643(18)	90
β [°]	115.046(8)	91.4575(18)	93.055(3)
γ [°]	90.00	94.8008(17)	90
V [Å^3]	4810.8(7)	2519.60(9)	461.78(2)
Z	4	2	2
ρ_{ber} [g·cm^{-3}]	1.535	1.555	1.603
μ [mm^{-1}]	1.020	3.026	2.052
F(000)	2328.0	1232.0	230.0
Crystal size [mm^3]	0.20 x 0.10 x 0.10	0.13 x 0.12 x 0.10	0.23 x 0.14 x 0.14
2θ for data collection [deg]	2.12-25.98	3.19-74.27	3.01-36.61
Index-ranges	$-20 \le h \le 20$	$-12 \le h \le 13$	$-7 \le h \le 6$
	$-19 \le k \le 19$	$-18 \le k \le 18$	$-19 \le k \le 18$
	$-23 \le l \le 23$	$-20 \le l \le 20$	$-10 \le l \le 11$
Reflections collected	37246	10101	8698
Independent reflections	9334	8943	1788
R_{int}	0.0531	0.0518	0.0587
S$^{a)}$	0.955	1.024	1.052
R_1 [$I \ge 2\sigma(I)$]$^{b)}$	0.0340	0.0457	0.0370
wR_2 [all data, F^2]$^{c)}$	0.0871	0.1248	0.0652
Residual electron density [e Å^{-3}]	0.663/-0.707	1.324/-0.652	0.516/-0.455
CCDC number	1418424	1418425	1418426

[a)] $S = \{\sum[w(F_0^2 - F_c^2)^2]\}/(n-p)\}^{0.5}$, n = number of reflections, p = number of parameters.

[b)] $R_1 = \sum|F_0|| \; |F_c|| \; \sum|F_0|$. [c)] $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2 / \sum[(F_0^2)^s]\}^{0.5}$

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