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"Electrochemically switchable foldamer – surprising feature of rotaxane with equivalent stations"

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1. Synthesis

All solvents and reagents used in these studies were reagent grade or better (used without purification), excluding acetonitrile (dried over P_2O_5 and distilled under argon) and dibenzo-24-crown-8 (dried and kept over P_2O_5 *in vacuo*). Complexes **1Ni** and **1Cu** were synthesized according to known procedures (*J. Am. Chem. Soc.* **2001**, *123*, 9356-9366; and *J. Phys. Org. Chem.* **2001**, *14*, 63-73).

1.1. Monoaldehydes **2Ni** *and* **2Cu**

2Ni: 356.1 mg (0.570 mmol) of **1Ni** was dissolved in 12 ml of anhydrous CH_3CN, and a solution of 1 eq (73.7 mg) of dibutylamine in 1 ml of CH_3CN was added. The mixture was left for 5 minutes, followed by the addition of 1.5 g of silanized silica gel 60 (Merck). The suspension was evaporated to dryness and solids transferred to the top of the silanized silica gel column. Chromatography was performed by means of elution with 10 g NH_4PF_6 : 650 ml H_2O : 350 ml CH_3CN mixture. CH_3CN was evaporated from the main fraction, resulting in secretion of an orange-colored oil, which was filtered, washed with 50 ml H_2O, dissolved in CH_2Cl_2, separated from excessive water in separatory funnel, and dried over $MgSO_4$. After 1 h the organic phase was filtered and evaporated to dryness. The oil obtained

was again dissolved in 10 ml CH_2Cl_2 and 10 ml of hexane was added. Evaporation of solvents left the product in form of non-crystalline film. Yield 137.8 mg (43%). Melting point 83-87 °C.

Anal. Calc. for $C_{20}H_{32}N_5NiO{\cdot}PF_6$ (562.2): C 42.73, H 5.74, N 12.46%; found C 42.67, H 5.55, N 12.43%. TOF MS ES$^+$ (CH_3CN, *m/z*): 416.20 $[C_{20}H_{32}N_5NiO]^+$. ^{1}H NMR (500 MHz, CD_3CN) δ 0.95 (m, 6 H, CH_3), 1.33 (m, 2 H, $C\underline{H}_2CH_3$), 1.40 (m, 2 H, $C\underline{H}_2CH_3$), 1.68 (m, 4 H, $C\underline{H}_2CH_2CH_3$), 3.42-3.56 (comp, 12 H, NCH_2), 7.43 (s, 1 H, =CHN), 7.49 (bs, 2 H, CH=N), 7.85 (bs, 2 H, CH=N), 9.20 (s, 1 H, CHO). ^{13}C NMR (125 MHz, CD_3CN) δ 12.88 and 12.91 (CH_3), 19.1 and 19.5 ($\underline{C}H_2CH_3$), 28.3 and 30.4 ($\underline{C}H_2CH_2CH_3$), 51.5 ($NCH_2\underline{C}H_2N$ at the side of NBu_2), 57.6 and 58.0 (NCH_2 within NBu_2), 60.2 ($N\underline{C}H_2CH_2N$ at the side of CHO), 103.0 ($\underline{C}$=CHN), 113.2 ($\underline{C}$–CHO), 153.7 and 159.2 (bs, CH=N), 160.8 (=CHN), 186.3 (CHO). Redox (CV, 50 mVs^{-1}, 0.1 M TBAHFP/CH_2Cl_2, $E^{\circ'}_{Fc/Fc+}$ = 0.425 V, Ag/AgCl reference and GC working electrode): 1.125 V.

2Cu: This compound was synthesized from **1Cu** following the procedure for **2Ni**. Yield 42%. Mp 82-86 °C. *Anal.* Calc. for $C_{20}H_{32}CuN_5O{\cdot}PF_6$ (567.0): C 42.36, H 5.69, N 12.35%; found C 42.32, H 5.49, N 12.23%. TOF MS ES$^+$ (CH_3CN, *m/z*): 421.19 $[C_{20}H_{32}CuN_5O]^+$. Redox (CV, 50 mVs^{-1}, 0.1 M TBAHFP/CH_2Cl_2, $E^{\circ'}_{Fc/Fc+}$ = 0.425 V, Ag/AgCl reference and GC working electrode): 0.847 V.

1.2. Intermediates **3Ni** *and* **3Cu**

Although isolation and purification of hydrolytically unstable intermediates **3Ni** and **3Cu** seems impossible, it turned out to be unnecessary because of the selectivity and quantitative yield of *O*-methylation. Both enolethers **3Ni** and **3Cu** were prepared right before subsequent syntheses of axles or rotaxanes in a following way: 362.3 mg of **2Ni** (0.644 mmol) was dissolved in 1.8 ml of anhydrous CH_2Cl_2 and 106 µl of methyl trifluoromethanesulfonate (1.5 eq) was added; the mixture was left overnight, evaporated to dryness, and immediately used in the subsequent reaction with putrescine and DB24C8.

In case of **3Ni** a controlling NMR spectra were measured: ^{1}H NMR (400 MHz, CD_3CN) δ 0.96 (m, 6 H, $CH_2C\underline{H}_3$); 1.34 (m, 2 H, $C\underline{H}_2CH_3$); 1.42 (m, 2 H, $C\underline{H}_2CH_3$); 1.71 (m, 4 H, $C\underline{H}_2CH_2CH_3$); 3.48-3.64 (comp, 12 H, NCH_2); 4.25 (s, 3 H, OCH_3); 7.63 m, 7.69 bs, 7.79 m, 7.97 s, 8.18 s and 8.25 m (Σ 6 H, CH=N and =CHN). ^{13}C NMR (100 MHz, CD_3CN) δ 13.77 and 13.80 ($CH_2\underline{C}H_3$); 20.0 and 20.3 ($\underline{C}H_2CH_3$); 29.1 and 31.2 ($\underline{C}H_2CH_2CH_3$); 52.6, 59.9, 60.2, 60.5, 60.8 and 61.3 (NCH_2); 66.9 (OCH_3); 103.8 ($\underline{C}$=CHN); 113.9 ($\underline{C}$=CHO); 156.9 and 163.0 (CH=N); 161.5 (=CHN); 179.9 (=CHO).

1.3. Axles **4M$_2$** *and* **4'Ni$_2$**

4Ni$_2$: Intermediate **3Ni**, freshly prepared by methylation of 61.1 mg (0.109 mmol) of **2Ni**, was dissolved in 0.5 ml of anhydrous CH_3CN. The solution of 0.51 eq of putrescine (4.9 mg) in 0.5 ml CH_3CN was added. After 10 minutes the mixture was poured to the solution of 150 mg of NH_4PF_6 in 20 ml of H_2O. CH_3CN was evaporated and the suspension filtered. The precipitate was washed with 15 ml of H_2O and dissolved in 4 ml CH_3CN. 1.5 g of silanized silica gel 60 was added and the suspension was evaporated. The solid was transferred to the top of silanized silica gel column and eluted with 2 g NH_4PF_6 : 200 ml H_2O : 300 ml CH_3CN solution. The first, main fraction was collected and evaporated. The precipitate formed was filtered, washed with 5 × 10 ml H_2O and dried *in vacuo* over P_2O_5. Yield 55.1 mg (67%).

Anal. Calc. for $C_{44}H_{74}N_{12}Ni_2{\cdot}4PF_6{\cdot}CH_3CN$ (1509.4): C 36.60, H 5.14, N 12.06%; found C 36.59, H 4.96, N 12.11%. TOF MS ES$^+$ (CH_3CN, *m/z*): 221.61 $[C_{44}H_{74}N_{12}Ni_2]^{4+}$, 295.14 $[C_{44}H_{73}N_{12}Ni_2]^{3+}$, 442.19 $[C_{44}H_{72}N_{12}Ni_2]^{2+}$, 515.17 $[C_{44}H_{73}N_{12}Ni_2{\cdot}PF_6]^{2+}$, 588.15 $[C_{44}H_{74}N_{12}Ni_2{\cdot}2PF_6]^{2+}$, 1321.27 $[C_{44}H_{74}N_{12}Ni_2{\cdot}3PF_6]^+$. ^{1}H NMR (500 MHz, CD_3CN) δ 0.97 (comp, 12 H, CH_3); 1.35 (m, 4 H, $C\underline{H}_2CH_3$); 1.42 (m, 4 H, $C\underline{H}_2CH_3$); 1.69 (comp, 12 H, CH_2 β to N); 3.47-3.62 (comp, 28 H, NCH_2); 7.52 s, 7.66 bs and 8.00 bs (14 H, =CHN, CH=N, NH). ^{13}C NMR (125 MHz, CD_3CN) δ 13.8 and 13.9 (CH_3); 20.1 and 20.4 ($\underline{C}H_2CH_3$); 27.2 (CH_2 β to N in the linker); 29.2 and 31.3 (CH_2 β to N in NBu_2); 51.1 and 52.6 (NCH_2CH_2N); 59.4, 60.4 and 61.3 (NCH_2 in the linker and NBu_2); 103.9 and 104.3

(C=CHN); 155.1 and 160.7 (br, CH=N); 162.5 and 164.0 (=CHN). The assignment of the signals supported by ^{1}H-^{13}C HSQC spectrum.

4Cu$_2$: This compound was synthesized from **3Cu** following the procedure for **4Ni$_2$**. Yield 65%. *Anal.* Calc. for $C_{44}H_{74}Cu_2N_{12}\cdot 4PF_6\cdot 3H_2O$ (1532.1): C 34.49, H 5.26, N 10.97%; found C 34.43, H 5.04, N 10.95%. TOF MS ES$^+$ (CH_3CN, *m/z*): 447.19 $[C_{44}H_{72}Cu_2N_{12}]^{2+}$, 1331.19 $[C_{44}H_{74}Cu_2N_{12}\cdot 3PF_6]^+$, 1185.26 $[C_{44}H_{73}Cu_2N_{12}\cdot 2PF_6]^+$, 1039.42 $[C_{44}H_{72}Cu_2N_{12}\cdot PF_6]^+$. ^{1}H NMR (500 MHz, CD_3CN) δ 0.88 (br, 6H, CH_3), 1.08 (br, 6H, CH_3), 1.19 and 1.30 (br, 2 × 4H, CH_2CH_3), 1.46 and 1.65 (br, 2 × 4H, CH_2 β to N in NBu_2); 8.75-11.00 br.

4'Ni$_2$: This compound was synthesized from **3Ni** and *p*-xylylenediamine (instead of putrescine), following the procedure for **4Ni$_2$**. Yield 64%. *Anal.* Calc. for $C_{48}H_{74}N_{12}Ni_2\cdot 4PF_6$ (1516.4): C 38.02, H 4.92, N 11.08%; found C 38.06, H 4.93, N 10.85%. TOF MS ES$^+$ (CH_3CN, *m/z*): 233.60 $[C_{48}H_{74}N_{12}Ni_2]^{4+}$, 311.13 $[C_{48}H_{73}N_{12}Ni_2]^{3+}$, 466.20 $[C_{48}H_{72}N_{12}Ni_2]^{2+}$, 612.16 $[C_{48}H_{74}N_{12}Ni_2\cdot 2PF_6]^{2+}$, 1369.32 $[C_{48}H_{74}N_{12}Ni_2\cdot 3PF_6]^+$. ^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 0.94 (t, J = 7.4 Hz, 6 H, CH_3); 0.99 (t, J = 7.4 Hz, 6 H, CH_3); 1.38 and 1.49 (m, 2 × 4 H, C$\underline{H}_2$CH$_3$); 1.77-1.88 (comp, 8 H, CH_2 β to N); 3.65-3.88 (comp, 24 H, NCH_2CH_2N and N$\underline{CH}_2(CH_2)_2CH_3$); 4.85 (s, 4 H, NCH_2Ar); 7.48 (s, 4 H, H_{Ar}); 7.96 and 8.22 (s, 4 H, =CHN); 8.02 and 8.12 (bs, 8 H, CH=N). ^{13}C NMR (150 MHz, $(CD_3)_2CO$) δ 13.9 and 14.0 (CH_3); 20.2 and 20.5 ($\underline{C}H_2CH_3$); 29.7, 31.6 (CH_2 β to N in NBu_2); 52.6, 59.9, 60.5 and 61.5 (NCH_2 but NCH_2Ar); 54.8 (NCH_2Ar); 104.4 and 105.2 ($\underline{C}$=CHN); 129.7 ($C_{sp2}H$ in benzene ring); 137.2 ($\underline{C}_{sp2}C$ in benzene ring); 162.9 and 164.5 (=CHN); expected broad CH=N signals unobserved. The assignment of the signals supported by ^{1}H-^{13}C HSQC spectrum.

1.4. Rotaxanes **5M$_2$** *and* **5'Ni$_2$**

5Ni$_2$: Intermediate **3Ni**, freshly prepared by methylation of 362.3 mg (0.644 mmol) of **2Ni**, was dissolved in 45.5 ml of anhydrous CH_3CN. Molecular sieves 3Å (1 g), followed by 10 eq of dibenzo-24-crown-8 (2.889 g) were added. The system was degassed and filled with argon, then heated until all crown ether dissolved. After cooling to room temperature, a solution of 0.52 eq (30.1 mg) of putrescine in 1 ml of CH_3CN was added dropwise over the period of 3 h. From time to time the flask was gently heated in order to dissolve DB24C8 which crystallizes from the supersaturated solution. When the addition of putrescine was complete, the mixture was left for 5 h, followed by evaporation to dryness. Solids were washed by shaking with 5 × 15 ml of anhydrous benzene (extracted DB24C8 was afterwards recovered by crystallization). The orange-colored oil remaining in the flask was dried *in vacuo*, dissolved in 10 ml CH_3CN and poured to the solution of 1 g of NH_4PF_6 in 50 ml H_2O. The immediately formed precipitate was filtered, washed with 15 ml of H_2O and dissolved in 8 ml CH_3CN, adsorbed on 3 g of silanized silica gel and evaporated to dryness. The solid was transferred to the top of silanized silica gel column. Solutions of 150 µl 60% HPF_{6aq} in 1 l of distilled water (A), and 15 g of NH_4PF_6 in 1 l CH_3CN (B) were prepared. The product was isolated by means of gradient elution with 20, 30, 40 and 50% B in A. The main fraction was collected. The precipitate formed during evaporation of CH_3CN was filtered, washed with 5 × 10 ml H_2O, 2 × 3 ml CH_3OH and 2 × 3 ml Et_2O, and dried *in vacuo* over P_2O_5. Yield 147.4 mg (22%).

Anal. Calc. for $C_{68}H_{106}N_{12}O_8Ni_2\cdot 4PF_6\cdot H_3OPF_6$ (2080.9): C 39.25, H 5.28, N 8.08%; found C 39.29, H 5.12, N 8.08%. TOF MS ES$^+$ (CH_3CN, *m/z*): 333.68 $[C_{68}H_{106}N_{12}Ni_2O_8]^{4+}$, 444.56 $[C_{68}H_{105}N_{12}Ni_2O_8]^{3+}$, 666.34 $[C_{68}H_{104}N_{12}Ni_2O_8]^{2+}$, 739.34 $[C_{68}H_{105}N_{12}Ni_2O_8\cdot PF_6]^{2+}$. ^{1}H NMR (500 MHz, CD_3CN) δ 0.98 (comp, 12 H, CH_3); 1.35 (m, 4H, C$\underline{H}_2$CH$_3$); 1.42 (m, 4H, C$\underline{H}_2$CH$_3$); 1.71 (m, 8 H, CH_2 β to N in NBu_2); 1.83 (br, 4 H, CH_2 β to N in the linker); 3.10 br, 3.36 br, 3.44 br, 3.55 m, 3.61 br (28 H, NCH_2); 3.78 (s, 8 H, $ArO(CH_2)_2OC\underline{H}_2$); 3.85 (m, 8 H, $ArOCH_2C\underline{H}_2$); 3.97 (m, 8 H, $ArOCH_2$); 6.84 (comp, 8 H, H_{ar}); 6.97 br, 7.48 br, 7.59 br, 7.76 br, 7.91 br and 8.43 br (14 H, =CHN, CH=N, NH). ^{13}C NMR (125 MHz, CD_3CN) δ 13.8 and 13.9 (CH_3); 20.1 and 20.4 ($\underline{C}H_2CH_3$); 27.8 (CH_2 β to N in the linker); 29.2 and 31.3 (CH_2 β to N in NBu_2); 50.9, 52.5, 61.3 and 58.3-60.2 – a set of broad signals (NCH_2); 68.4 ($ArOCH_2$); 71.0 ($ArOCH_2\underline{C}H_2$); 71.4 ($ArO(CH_2)_2O\underline{C}H_2$); 103.8 and 104.3 ($\underline{C}$=CHN); 112.9 (C *ortho* to O); 121.9 (C *meta* to O); 148.8 ($C_{sp2}O$); 154.7 and 159.6 (bs, CH=N); 162.2 and 165.5 (=CHN). The assignment of the signals supported by ^{1}H-^{13}C HSQC spectrum.

5Cu$_2$: This compound was synthesized from **3Cu** following the procedure for **5Ni$_2$**. Yield 13%. *Anal.* Calc. for $C_{68}H_{106}Cu_2N_{12}O_8 \cdot 4PF_6$ (1926.6): C 42.39, H 5.55, N 8.72%; found C 42.39, H 5.40, N 8.71%. TOF MS ES$^+$ (CH_3CN, *m/z*): 336.15 $[C_{68}H_{106}Cu_2N_{12}O_8]^{4+}$, 447.85 $[C_{68}H_{105}Cu_2N_{12}O_8]^{3+}$, 744.24 $[C_{68}H_{105}Cu_2N_{12}O_8 \cdot PF_6]^{2+}$, 817.22 $[C_{68}H_{106}Cu_2N_{12}O_8 \cdot 2PF_6]^{2+}$. ^{1}H NMR (500 MHz, CD_3CN) δ 0.89 br, 1.10 br, 1.21 br, 1.32 br, 1.66 br (CH_2CH_3, CH_2 β to N); 3.20-4.75 – a set of broad signals with discernible maxima at 3.73 and 3.86 (OCH_2); 6.75-8.50 br (H_{ar}); 8.75-11.00 br.

5'Ni$_2$: This compound was synthesized from **3Ni** and *p*-xylylenediamine (instead of putrescine), following the procedure for **5Ni$_2$**. Yield 25%. *Anal.* Calc. for $C_{72}H_{106}N_{12}O_8Ni_2 \cdot 4PF_6$ (1964.9): C 44.01, H 5.44, N 8.55%; found C 44.00, H 5.37, N 8.48%. TOF MS ES$^+$ (CH_3CN, *m/z*): 345.64 $[C_{72}H_{106}N_{12}O_8Ni_2]^{4+}$, 460.52 $[C_{72}H_{105}N_{12}O_8Ni_2]^{3+}$, 763.28 $[C_{72}H_{105}N_{12}O_8Ni_2 \cdot PF_6]^{2+}$, 836.26 $[C_{72}H_{106}N_{12}O_8Ni_2 \cdot 2PF_6]^{2+}$. ^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 0.92-1.02 (comp, 12 H, CH_3); 1.39 and 1.48 (m, 2 × 4 H, $C\underline{H}_2CH_3$); 1.76-1.87 (comp, 8 H, CH_2 β to N); 3.09 (t, J = 6.5 Hz, 2 H, $NC\underline{H}_2CH_2N$ in TAM^{2+} unit enclosed by DB24C8, in ethylenediamine bridge related *trans* to xylyl linker); 3.35-4.30 [comp, 46 H = 22 H in NCH_2 (without CH_2 of the xylyl linker and without CH_2 corresponding to 3.09 ppm signal) + 3 × 8 H from OCH_2 groups in DB24C8]; 4.90 (s, 2 H, NCH_2Ar at the side of DB24C8); 5.04 (m, 2 H, NCH_2Ar at the opposite side of DB24C8); 6.85, 7.81, 7.85 and 7.96 (s, 4 × 1 H, CH=N at the side of xylyl linker); 6.87-6.91 (m, 4 H, H_{ar} meta to O in DB24C8); 6.94-6.98 (m, 4 H, H_{ar} ortho to O in DB24C8); 7.54 (d, J = 8.1 Hz, 2 H, H_{ar} in xylyl linker, at the opposite side of DB24C8); 7.83 (d, J = 8.1 Hz, 2 H, H_{ar} in xylyl linker, at the side of DB24C8); 8.26 and 8.48 (2 × 1 H, =CHN at the side of xylyl linker); 7.70-8.30 (br, 6 H, =CHN and CH=N at the sides of NBu_2 groups); 9.12 (m, 1 H, NH at the side of DB24C8); 9.51 (bs, 1 H, NH at the opposite side of DB24C8). ^{13}C NMR (150 MHz, $(CD_3)_2CO$) δ 13.95, 13.98, 14.03 and 14.07 (CH_3); 20.22, 20.25, 20.54 ($\underline{C}H_2CH_3$); 29.41, 31.61, 31.68 (CH_2 β to N in NBu_2); 52.52, 52.63, 54.41, 55.07, 58.69, 59.73, 59.98, 60.54, 61.44 and 61.53 (NCH_2); 68.34 ($ArOCH_2$); 70.95 ($ArOCH_2\underline{C}H_2$); 71.11 ($ArO(CH_2)_2O\underline{C}H_2$); 104.36, 104.39, 104.68, 105.19 ($\underline{C}$=CHN); 112.76 (C *ortho* to O); 121.04 (C *meta* to O); 129.03 ($\underline{C}_{sp2}$C in xylyl at the opposite side of DB24C8); 130.18 ($\underline{C}_{sp2}$C in xylyl at the side of DB24C8); 136.71 ($\underline{C}_{sp2}$H in xylyl at the opposite side of DB24C8); 138.50 ($\underline{C}_{sp2}$H in xylyl at the side of DB24C8); 149.21 (C_{sp2}O); 155.05, 158.92, 162.41, 162.89, 164.65 and 167.26 (CH=N and =CHN). The assignment of the signals supported by ^{1}H-^{13}C HMBC spectrum.

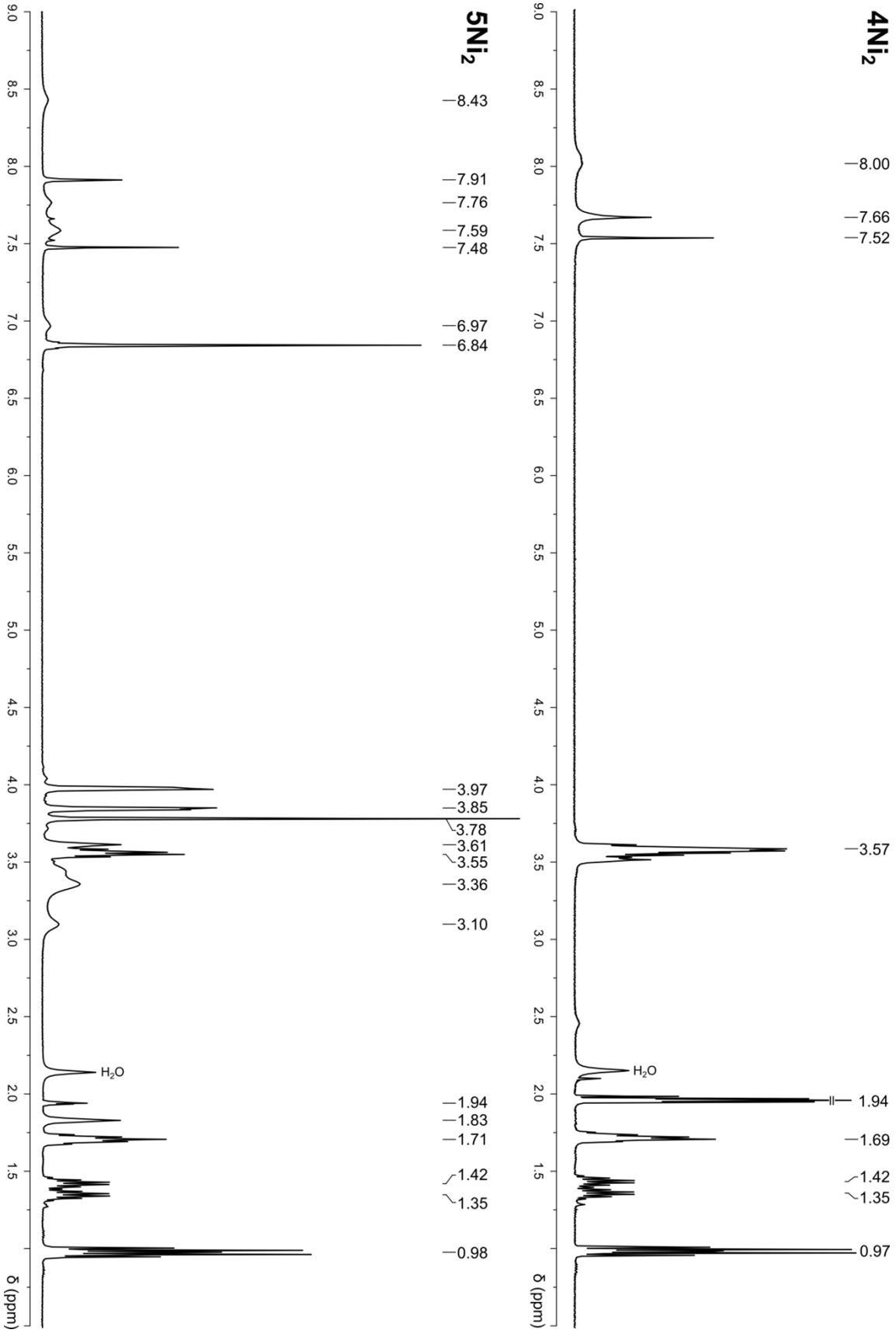
1.5. Complex **6Ni**

Intermediate **3Ni**, freshly prepared by methylation of 41.0 mg (0.073 mmol) of **2Ni**, was dissolved in 0.5 ml of anhydrous CH_3CN and 7.2 µl (0.073 mmol) of *n*-butylamine was added. The mixture was left for 10 minutes. Then 3 ml of CH_3CN and 0.3 g of silanized silica gel were added and the suspension was evaporated to dryness. The solid was transferred to the top of silanized silica gel column and eluted with 10 g NH_4PF_6 : 550 ml H_2O : 450 ml CH_3CN mixture. The main fraction was collected and concentrated. The precipitate formed during evaporation of CH_3CN was filtered, washed with 5 × 3 ml H_2O and dried *in vacuo* over P_2O_5. Yield 25.4 mg (46%).

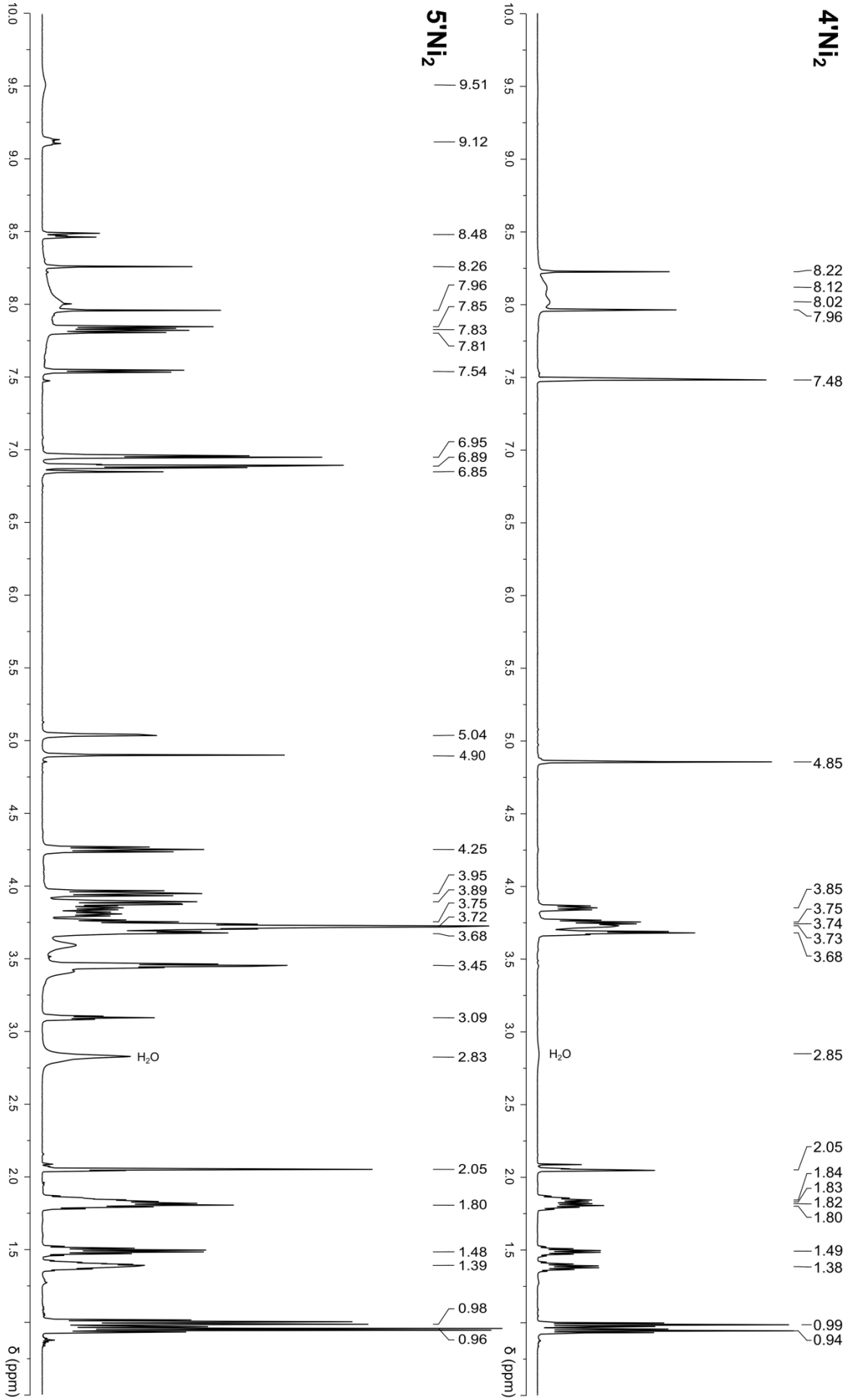
Anal. Calc. for $C_{24}H_{42}N_6Ni \cdot 2PF_6 \cdot H_2O$ (780.3): C 36.94, H 5.56, N 10.77%; found C 37.14, H 5.59, N 10.72%. TOF MS ES$^+$ (CH_3CN, *m/z*): 236.14 $[C_{24}H_{42}N_6Ni]^{2+}$, 471.27 $[C_{24}H_{41}N_6Ni]^+$. ^{1}H NMR (400 MHz, CD_3CN) δ 0.93-1.00 (comp, 9 H, CH_3); 1.30-1.47 (comp, 6 H, $C\underline{H}_2CH_3$); 1.60-1.75 (comp, 6 H, CH_2 β to N); 3.48 (t, J = 7 Hz, 2 H, NCH_2 in NHBu); 3.51-3.60 (comp, 12 H, other NCH_2); 7.52 s, 7.66 s, 7.67 bs, 8.06 bs (6 H, =CHN, CH=N). ^{13}C NMR (100 MHz, CD_3CN) δ 13.76, 13.83 and 13.86 (CH_3); 20.07, 20.11 and 20.45 ($\underline{C}H_2CH_3$); 29.23, 31.34 and 32.39 (CH_2 β to N); 51.4, 52.6, 61.3 (NCH_2 in NHBu and NBu_2); 60.4 br (NCH_2 in NCH_2CH_2N); 103.9 and 104.2 ($\underline{C}$=CHN); 155.1 br and 160.6 br (CH=N); 162.5 and 164.0 (=CHN). Redox (CV, v = 50 mVs^{-1}, in 0.1 M TBAHFP/AN): +1.30 V vs. Ag/AgCl.

2. Reprints of NMR spectra

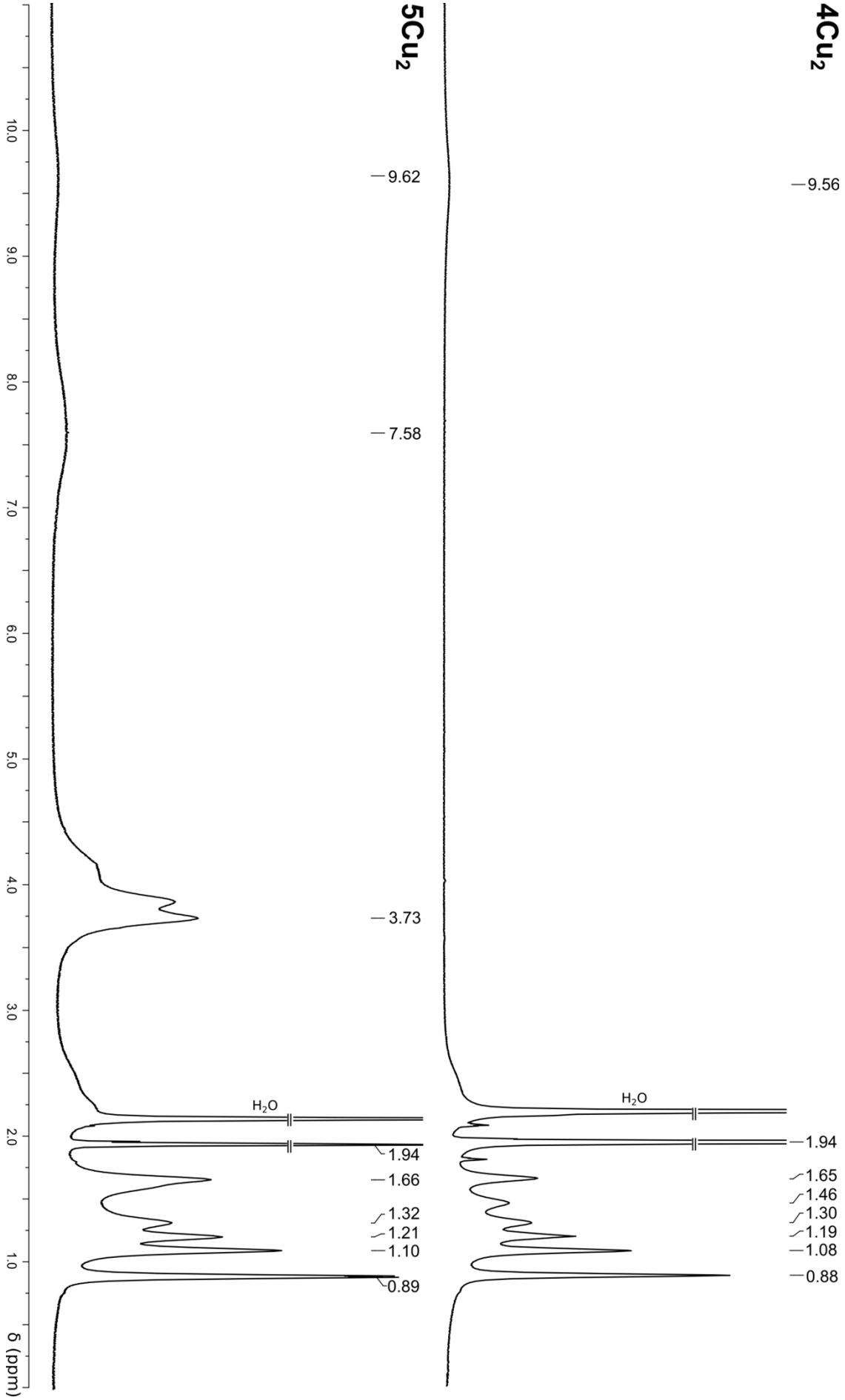
2.1. ^1H NMR spectra of **$4Ni_2$** *and* **$5Ni_2$** *(500 MHz, CD_3CN, 298 K)*



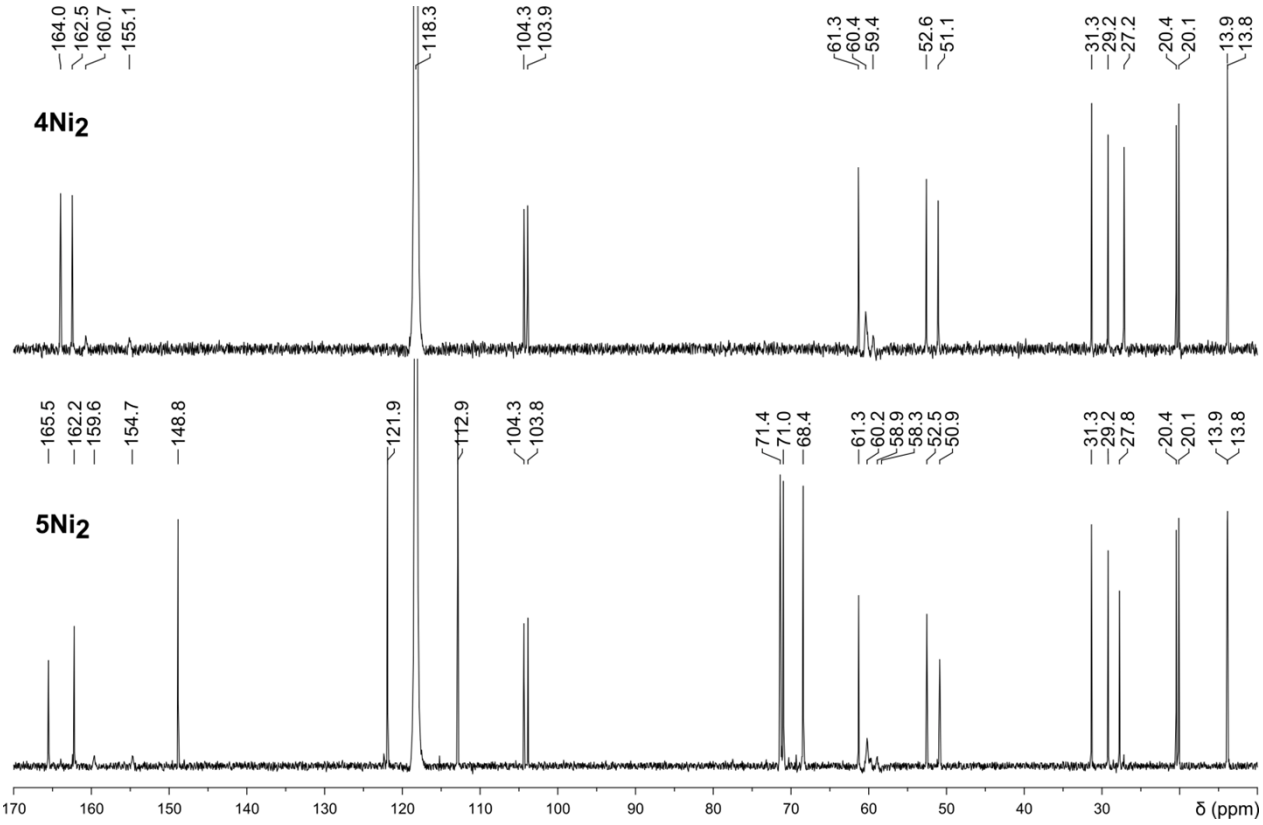
2.2. ^{1}H NMR spectra of **4'Ni$_2$** *and* **5'Ni$_2$** *(600 MHz, (CD$_3$)$_2$CO, 298 K)*



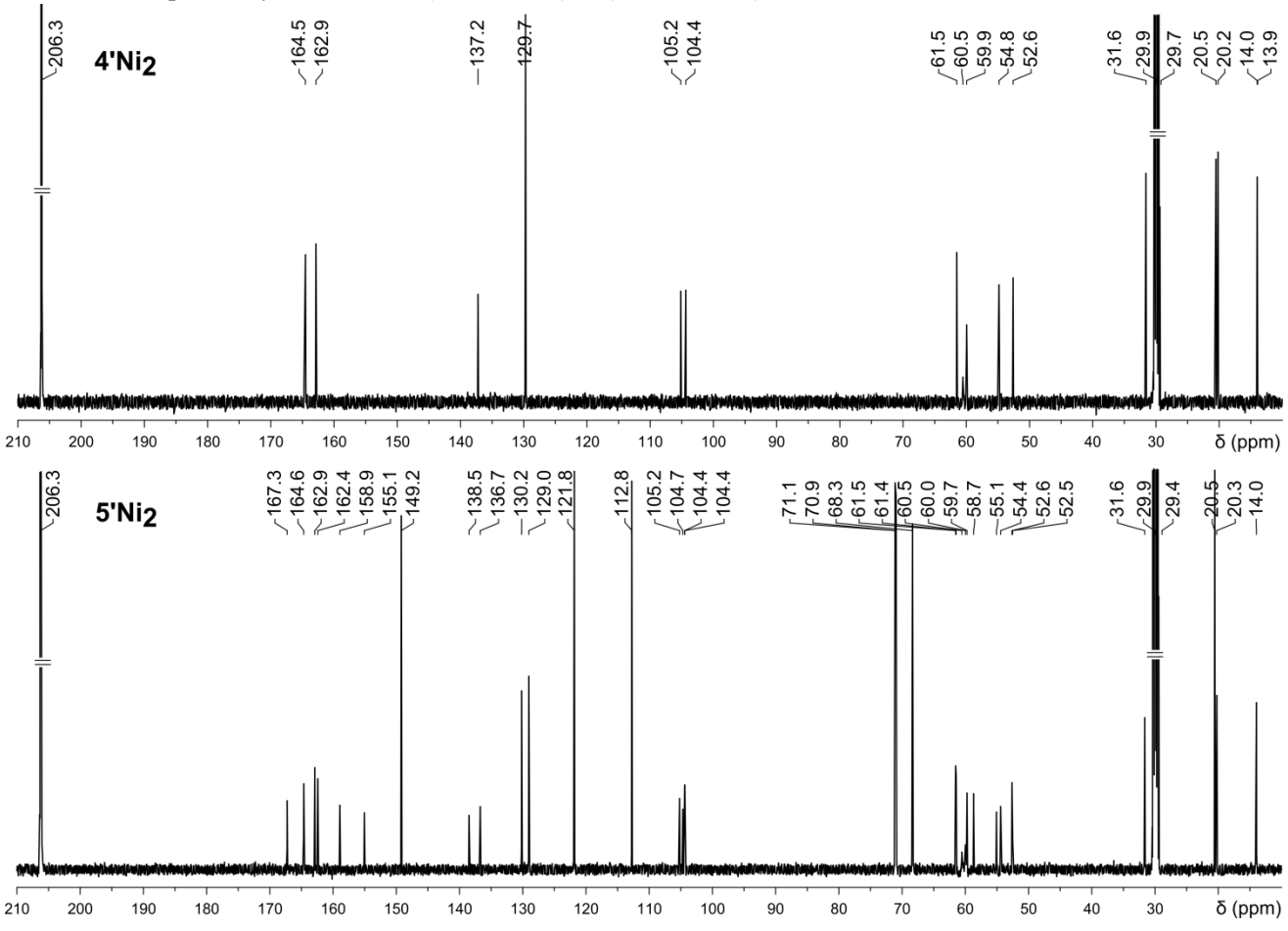
2.3. ^{1}H NMR spectra of **$4Cu_2$** *and* **$5Cu_2$** *(500 MHz, CD_3CN, 298 K)*



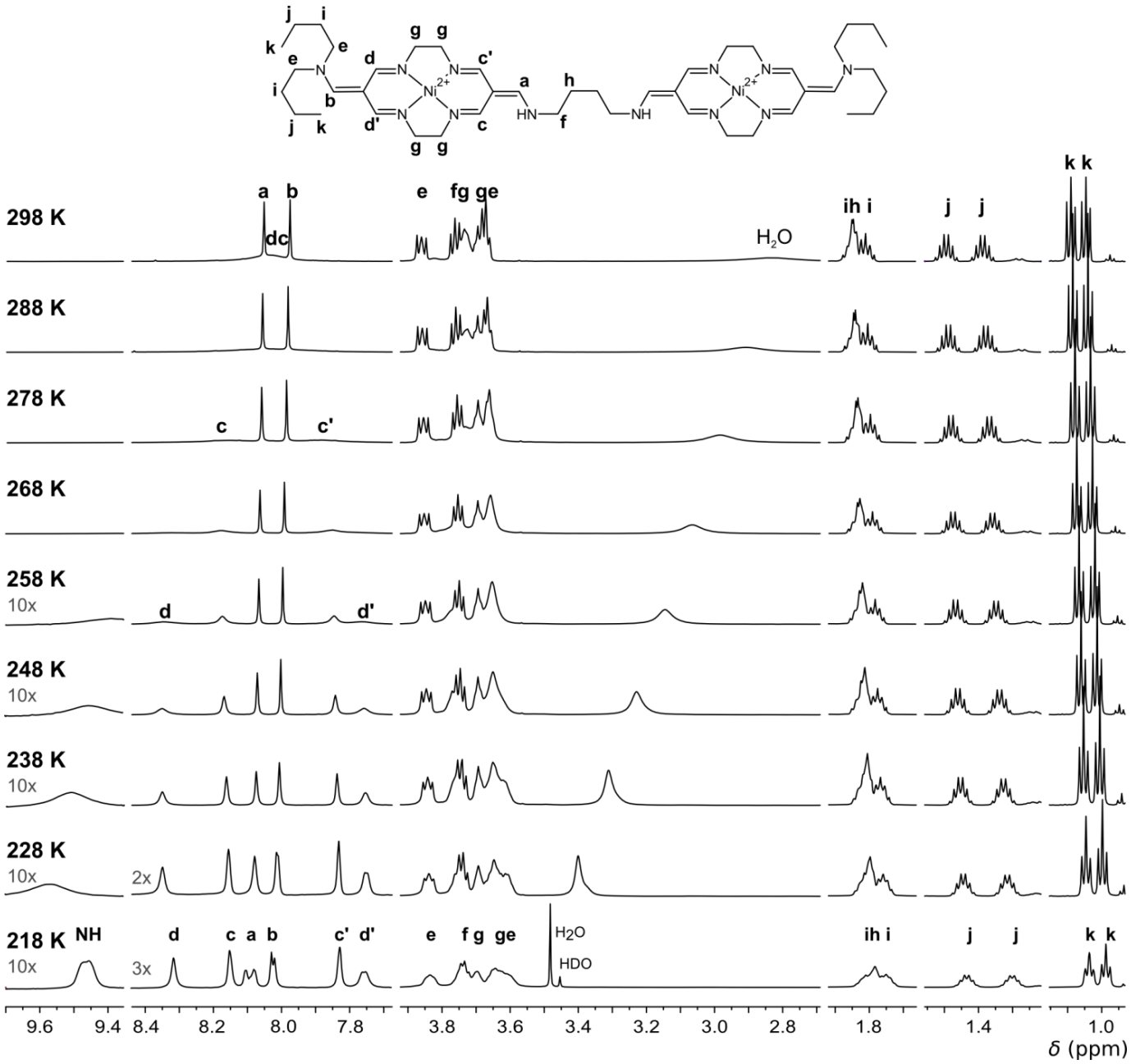
2.4 ^{13}C NMR spectra of **$4Ni_2$**, **$5Ni_2$** *(125 MHz, CD_3CN, 298 K)*



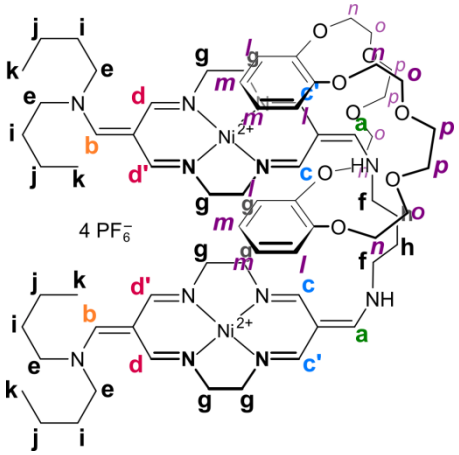
2.5 ^{13}C NMR spectra of **$4'Ni_2$**, **$5'Ni_2$** *(150 MHz, $(CD_3)_2CO$, 298 K)*

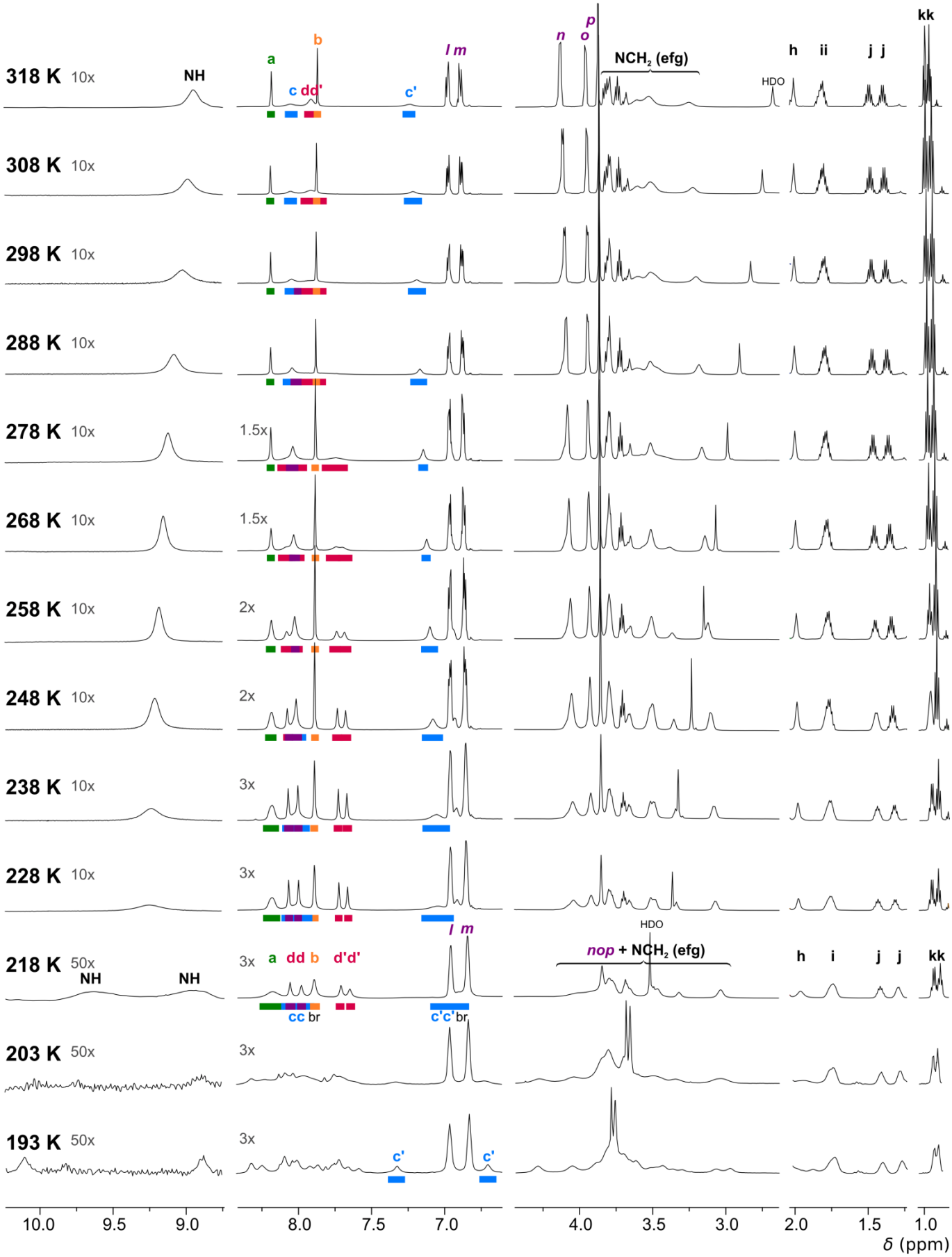


2.6 Variable temperature ^1H NMR spectra of **$4Ni_2$** *(600 MHz, $(CD_3)_2CO$).*

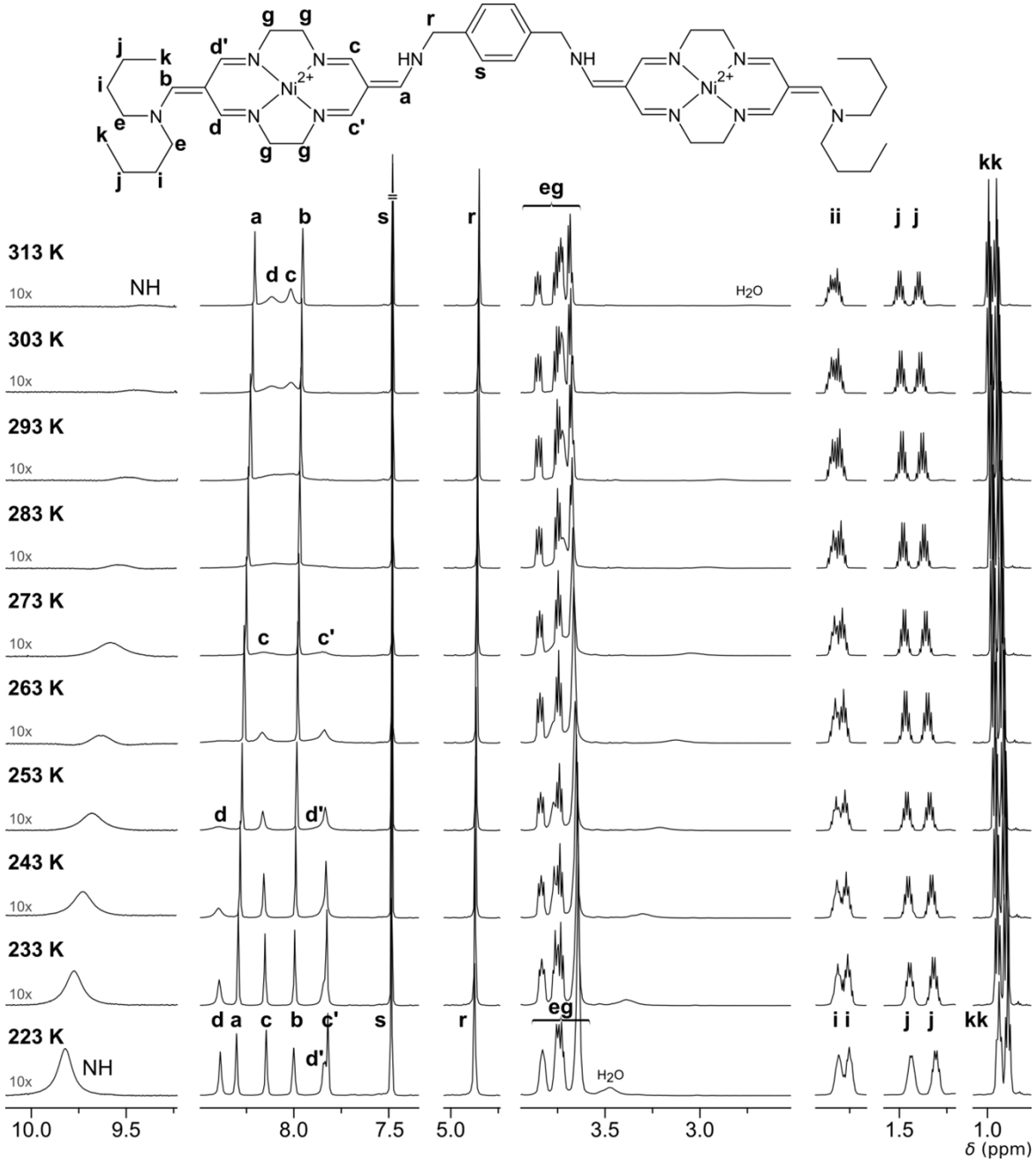


2.7 Variable temperature ^1H NMR spectra of **$5Ni_2$** *(600 MHz, $(CD_3)_2CO$).*

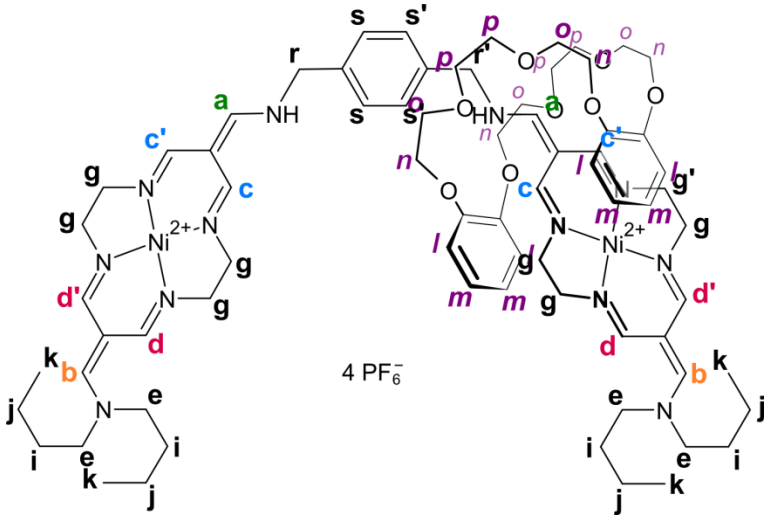


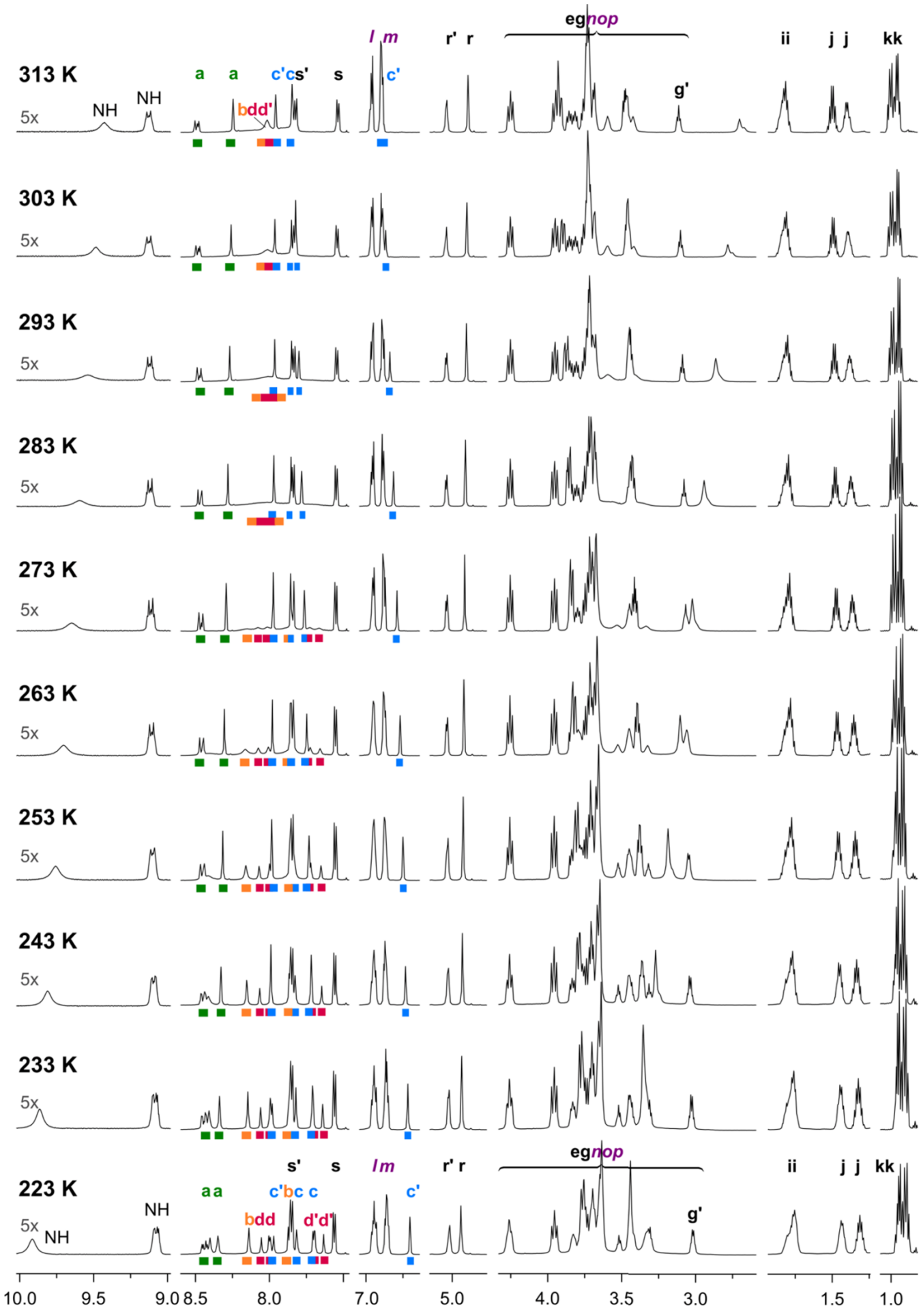

318 K 10x
308 K 10x
298 K 10x
288 K 10x
278 K 10x
268 K 10x
258 K 10x
248 K 10x
238 K 10x
228 K 10x
218 K 50x
203 K 50x
193 K 50x
NH
NH
NH
a
b
c dd'
c'
l m
n
o
p
NCH2 (efg)
HDO
h
ii
j j
kk
1.5x
2x
3x
a dd b d'd'
cc br
c'c' br
nop + NCH2 (efg)
h
i
j j
kk
10.0
9.5
9.0
8.0
7.5
7.0
4.0
3.5
3.0
2.0
1.5
1.0
δ (ppm)

2.8 Variable temperature ^1H NMR spectra of **4'Ni$_2$** *(600 MHz, $(CD_3)_2CO$).*

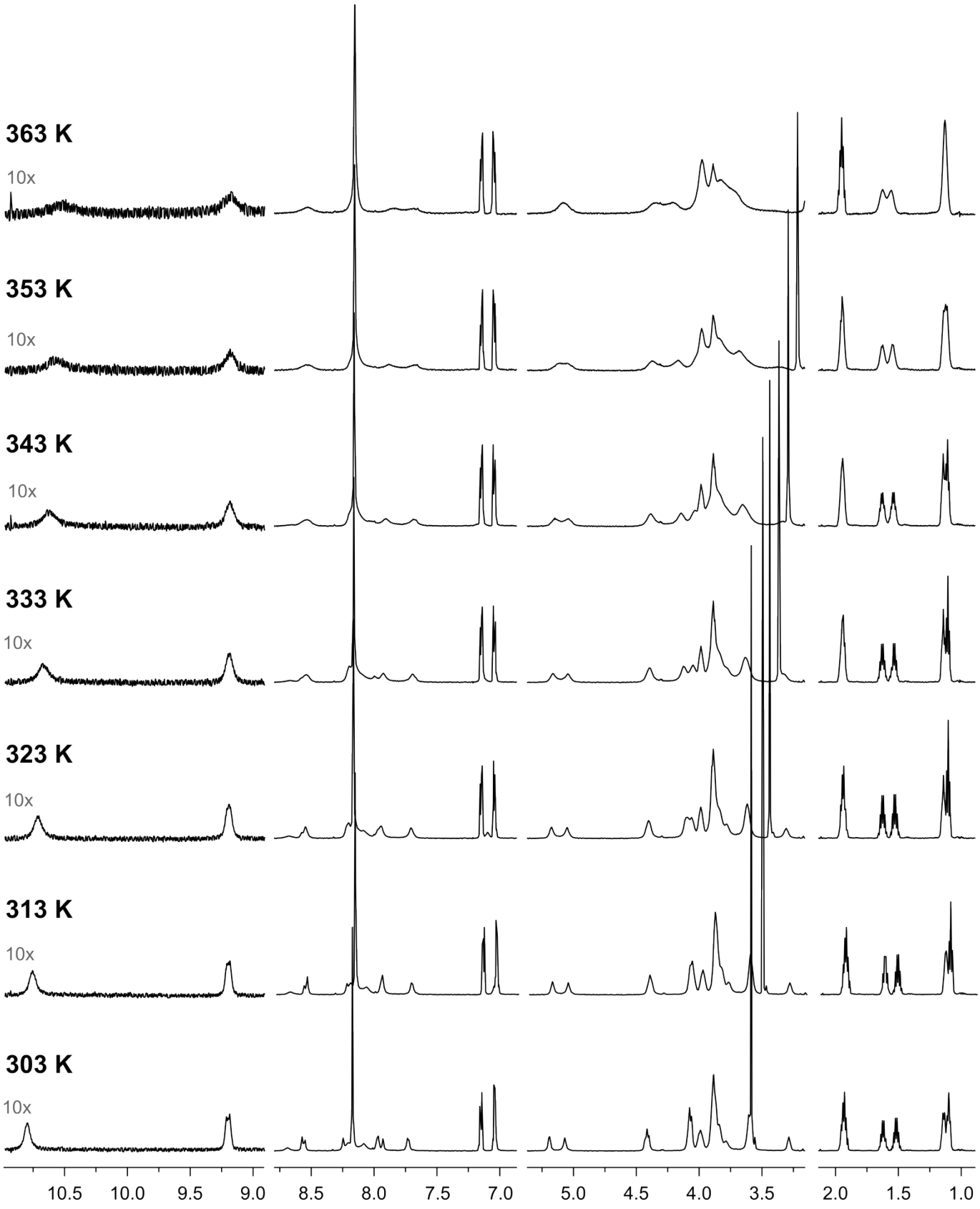


2.9 Variable temperature ^1H NMR spectra of **5'Ni$_2$** *(600 MHz, $(CD_3)_2CO$).*

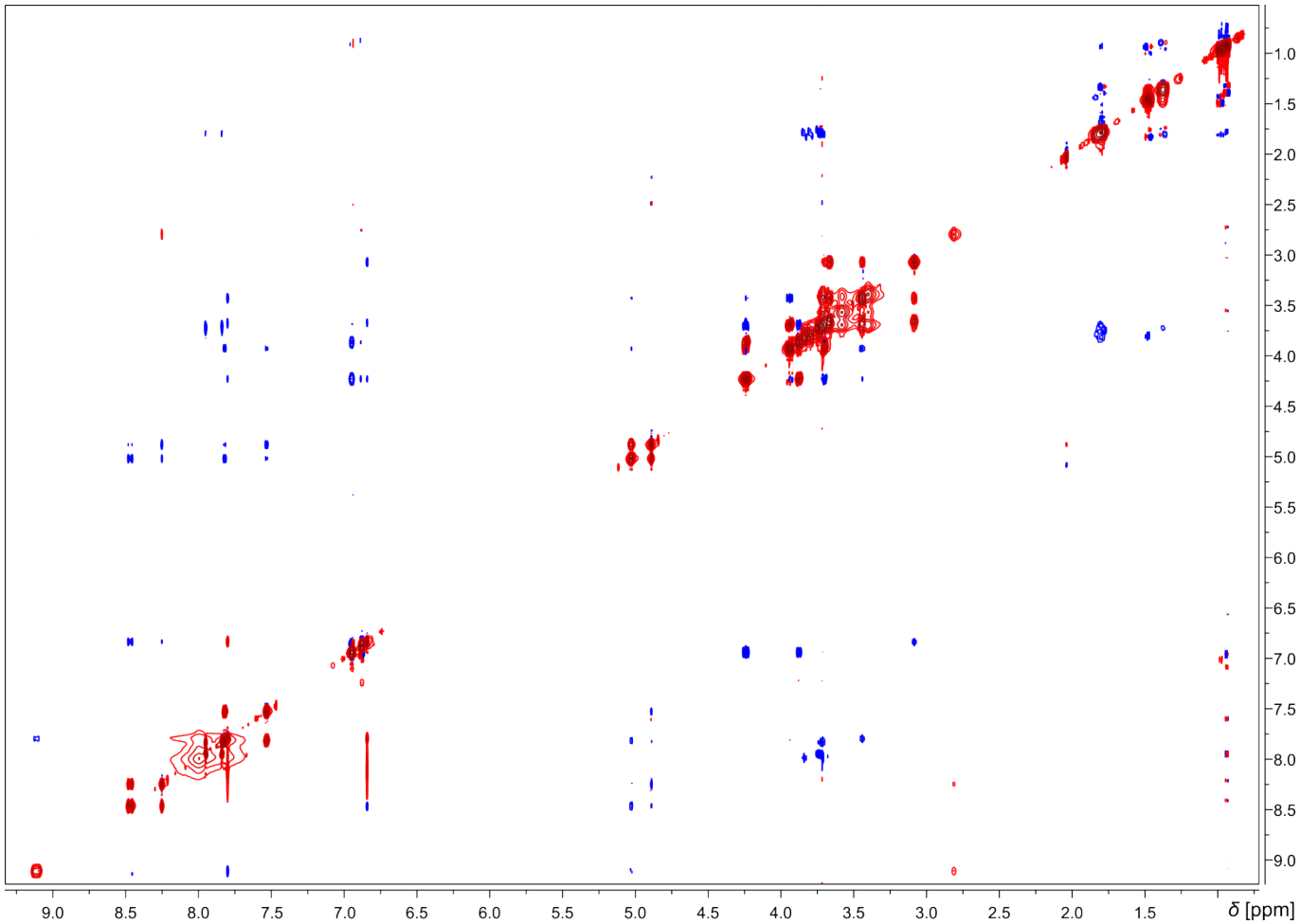



313 K
303 K
293 K
283 K
273 K
263 K
253 K
243 K
233 K
223 K
5x
NH
NH
a a c'c s' s
l m
c'
r' r
egnop
g'
ii j j kk
bdd'
s' s
a a
c'bc c
bdd
d'd'
10.0 9.5 9.0 8.5 8.0 7.0 5.0 4.0 3.5 3.0 1.5 1.0

2.10 Variable temperature ^{1}H NMR spectra of **5'Ni$_2$** *(600 MHz, DMF-d_7)*



2.11 ^{1}H-^{1}H ROESY spectra of **5'Ni$_2$** *(600 MHz, $(CD_3)_2CO$, 298 K)*



3. Electroanalytical measurements

Square wave voltammetry (SWV) and cyclic voltammetry (CV) experiments were carried out using the Autolab potentiostat (ECO Chemie, Netherlands) in a three electrode arrangement, with a silver/silver chloride (Ag/AgCl) electrode as the reference, platinum foil as the counter and the glassy carbon electrode (GCE, BAS, 3 mm diameter) as the working electrode. The reference electrode were separated from the working solution by an electrolytic bridge filled with 0.1 M tetrabutylammonium hexafluorophosphate/acetonitryl (TBAHFP/AN) solution. The reference potential electrode was calibrated by using the ferrocene oxidation process in the same TBAHFP/AN solution. 0.1 M TBAHFP/AN was used as the supporting electrolyte solution. Argon was used to deaerate solution and an argon blanket was maintained over the solution during the experiments. All experiments were carried out at 25 °C. The GC electrode was polished mechanically with 1.0, 0.3 and 0.05 μm alumina powder on a Buehler polishing cloth to a mirror-like surface. Finally, it was rinsed with acetonitrile and sonificated in pure acetonitrile.

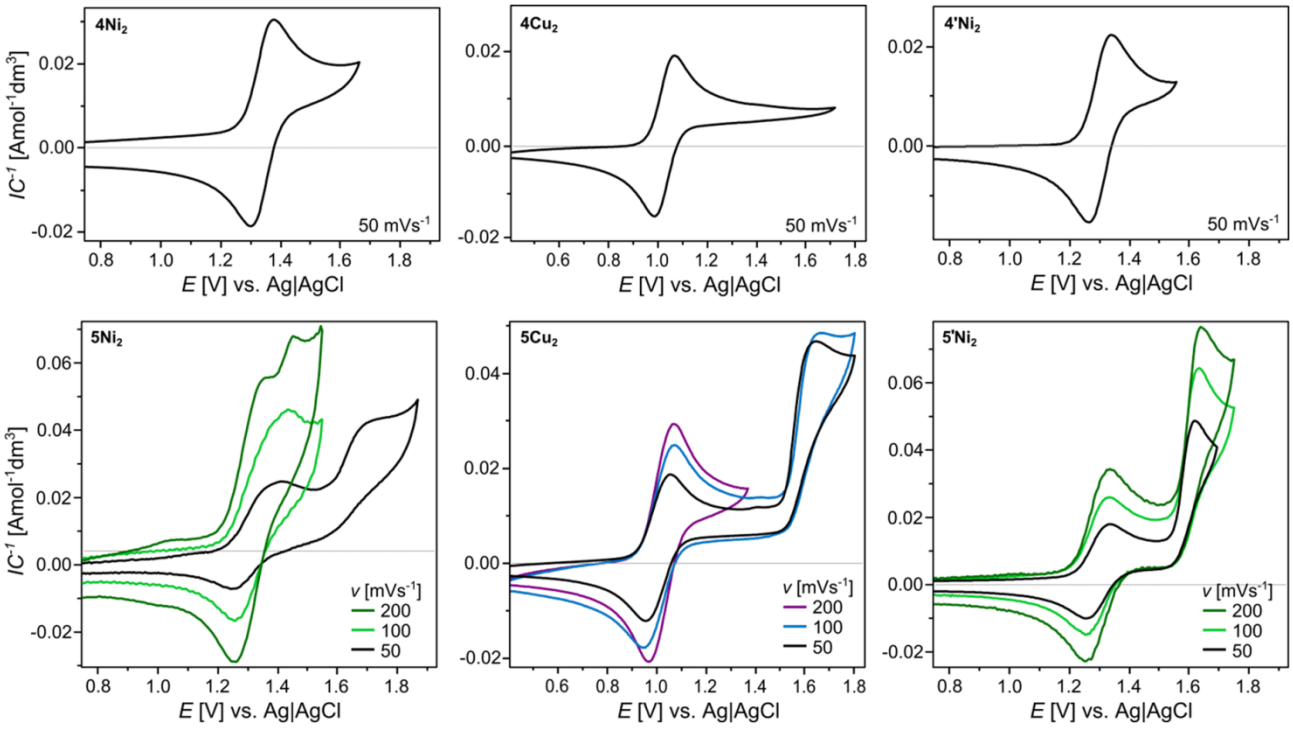


Fig. 1. Cyclic voltammograms of axles **4M$_2$**, **4'Ni$_2$**, molecular switches **5M$_2$** and molecular shuttle **5'Ni$_2$** in 0.1 M TBAHFP/AN.

Table 1. Peak potentials of all investigated compounds from CV (v = 50 mVs^{-1}).

Compound	***E*pa** [V]	***E*pc** [V]	***E*pa crown** [V]	***E*pc crown** [V]
4Ni$_2$	1.377	1.303	-	-
5Ni$_2$	1.405	1.252	1.708	1.581
4Cu$_2$	1.067	0.990	-	-
5Cu$_2$	1.054	0.957	1.661	-
4'Ni$_2$	1.344	1.269	-	-
5'Ni$_2$	1.333	1.251	1.627	-
6Ni	1.338	1.253	-	-

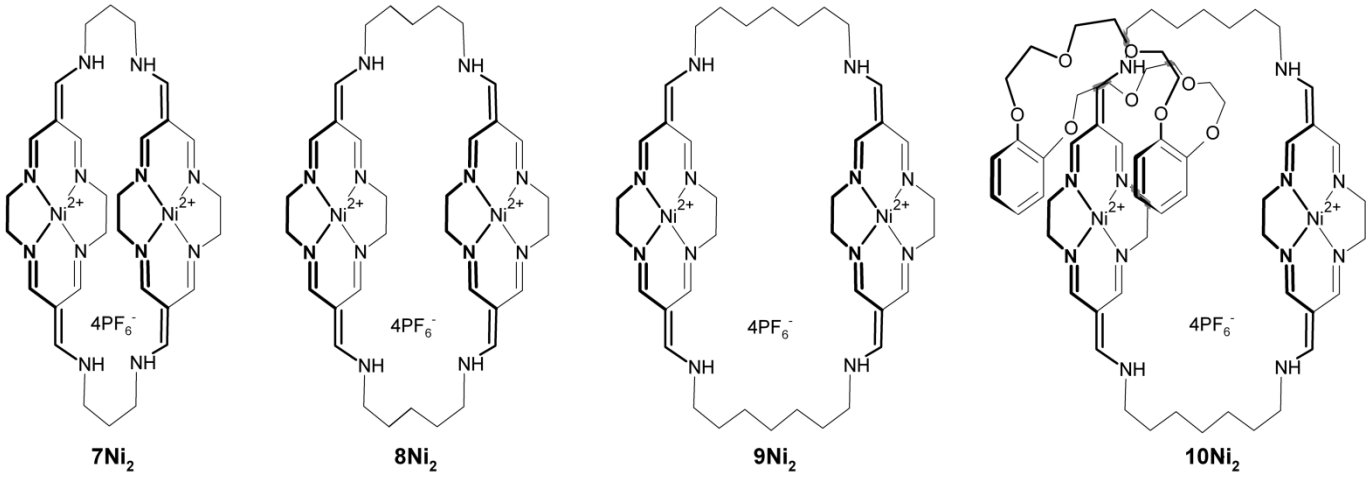


Fig. 2. Structures of macrocyclic compounds **7-9Ni$_2$** and the catenane **10Ni$_2$** (see ref. 7, 12).

Table 2. Redox potentials of macrocyclic compounds **7-9Ni$_2$** and the catenane **10Ni$_2$**.

Compound	***E*°'** [V]	ref.
7Ni$_2$	1.485 and 1.585	7, 12
8Ni$_2$	1.383	
9Ni$_2$	1.326	
10Ni$_2$	1.250 and 1.391	