Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Rotaxanes composed of dibenzo-24-crown-8 and macrocyclic transition metal complexing tetraimine units.

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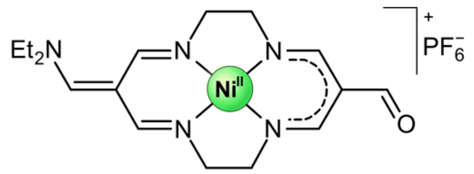
Electronic Supplementary Information

Contents

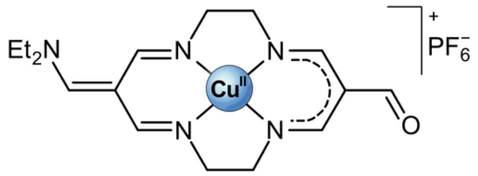
1. Analytical data for new compounds (2-4M and 5-6M$_2$)

Complexes **2-4M**, and **5-6M$_2$** were synthesized according to procedures described in the manuscript, using acetonitrile, dichloromethane and toluene in their anhydrous form. All other solvents and reagents were reagent grade or better and used without purification (methyl trifluoromethanesulfonate / MeOTf (>98%, Aldrich); diethylamine / Et_2NH (TCI Chemicals, >99%); *o*-xylylenediamine hydrochloride (Fluorochem); *m*-xylylenediamine (TCI Chemicals, >99.0%); *p*-xylylenediamine (TCI Chemicals, >99.0%); dibenzo-24-crown-8 / DB24C8 (TCI Chemicals, >98%); triethylamine / Et_3N (ABCR, 99%); trifluoromethanesulfonic acid / TfOH (TCI Chemicals, >98.0%); N,N-dimethylformamide / DMF puriss, absolute, over molecular sieve (Aldrich); nitromethane / CH_3NO_2 (POCh); toluene (POCh); ammonium hexafluorophosphate / NH_4PF_6 (Apollo Scientific, 99.8%); silica gel 60 silanized for column chromatography (0.063-0.200 mm, Merck)).

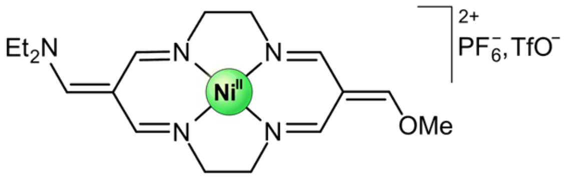
The analytical data were collected with the following equipment: elemental analyzer PERKIN-ELMER type 240; mass spectrometer MALDI Synapt G2-S (*m/z* peaks listed according to decreasing peak intensity); nuclear magnetic resonance spectrometers Varian VNMRS 600 MHz, Varian VNMRS 500 MHz and Varian Mercury 400 MHz (chemical shifts reported in reference to solvent residual peak (1.94 ppm (^{1}H) and 118.26 ppm (^{13}C) for acetonitrile).



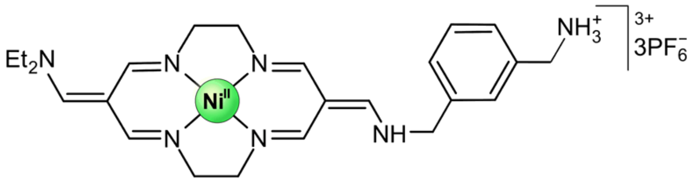
2Ni: *Anal.* Calc. for $C_{16}H_{24}N_5NiO{\cdot}PF_6$ (506.1): C 37.98, H 4.78, N 13.84 %; found C 37.77, H 4.79, N 13.88 %. TOF MS ES$^+$ (CH_3CN, *m/z*): 360.14 $[C_{16}H_{24}N_5NiO]^+$. ^{1}H NMR (400 MHz, CD_3CN) δ 1.31 (t, J = 7.2 Hz, 6 H, CH_3); 3.48 br and 3.54 br (2 × 4 H, NCH_2CH_2N); 3.58 and 3.64 (q, J = 7.2 Hz, 2 × 2 H, $NC\underline{H_2}CH_3$); 7.46 (s, 1 H, =CHN); 7.50 and 7.86 (bs, 2 × 1 H, CH=N on the side of NEt_2); 7.67 (bs, 2 H, CH=N on the side of CHO); 9.21 (s, 1 H, CHO). ^{13}C NMR (100 MHz, CD_3CN) δ 12.5 and 14.5 (CH_3); 47.4 and 55.6 ($N\underline{C}H_2CH_3$); 58.9 br and 60.9 br (NCH_2CH_2N); 104.1 ($\underline{C}$=CHN); 114.2 ($\underline{C}$–CHO); 154.7 br and 160.1 br (CH=N); 161.4 (=CHN); 187.3 (CHO).



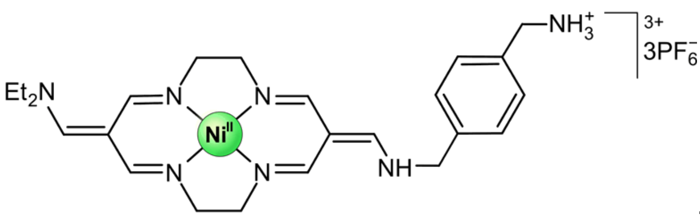
2Cu: *Anal.* Calc. for $C_{16}H_{24}CuN_5O{\cdot}PF_6{\cdot}H_2O$ (528.9): C 36.33, H 4.96, N 13.24%; found C 36.53, H 4.98, N 13.33%. TOF MS ES$^+$ (CH_3CN, *m/z*): 365.13 $[C_{16}H_{24}CuN_5O]^+$. NMR spectra were not measured because of paramagnetic nature of the complex.



In the case of **3Ni**, an NMR spectra were measured to confirm the structure of the product as well as the selectivity and quantitative yield of *O*-methylation: ^{1}H NMR (400 MHz, CD_3CN) δ 1.34 (t, J = 7.2 Hz, 6 H, $CH_2C\underline{H}_3$); 3.61-3.67 (m, 8 H, NCH_2CH_2N); 3.69 (q, J = 7.2 Hz, 4 H, $C\underline{H}_2CH_3$); 4.26 (s, 3 H, OCH_3); 7.64 s, 7.72 bs, 7.78 s, 7.95 s and 8.18 s (Σ 6 H, CH=N and =CHN). ^{13}C NMR (100 MHz, CD_3CN) δ 12.4 and 14.4 (two $CH_2\underline{C}H_3$); 47.4 and 56.0 ($N\underline{C}H_2CH_3$); 60.0, 60.1, 60.3, 60.9 (NCH_2CH_2N); 66.9 (OCH_3); 103.9 ($\underline{C}$=CHN); 114.0 ($\underline{C}$=CHO); 157.0 and 162.7 (CH=N); 161.6 (=CHN); 180.0 (=CHO); signal from triflate anion unobserved.

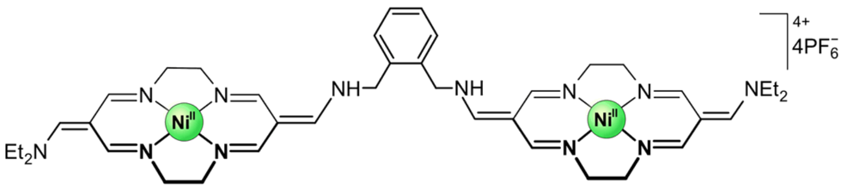


4*m*Ni: *Anal.* Calc. for $C_{24}H_{36}N_7Ni\cdot 3PF_6$ (916.2): C 31.46, H 3.96, N 10.70%; found C 31.40, H 3.74, N 10.49%. TOF MS ES^{+} (CH_3CN, *m/z*): 770.16 $[C_{24}H_{36}N_7Ni\cdot 2PF_6]^{+}$, 478.23 $[C_{24}H_{34}N_7Ni]^{+}$, 239.62 $[C_{24}H_{35}N_7Ni]^{2+}$, 624.20 $[C_{24}H_{35}N_7Ni\cdot PF_6]^{+}$. ^{1}H NMR (400 MHz, CD_3CN) δ 1.33 (t, J = 7.2 Hz, 6 H, CH_3); 3.4-3.7 (comp, 12 H, NCH_2CH_2N and $C\underline{H}_2CH_3$); 4.16 (s, 2 H, $ArC\underline{H}_2NH_3^{+}$); 4.68 (s, 2 H, $ArC\underline{H}_2NH$); 7.41 s, 7.43 s, 7.45-7.53 m, 7.56 s, 7.57 br s, 7.71 br s, 7.79 s, 8.08 br s (10 H, =CHN, CH=N, H_{Ar}). ^{13}C NMR (100 MHz, CD_3CN) δ 12.4, 14.4 (two CH_3); 44.5, 47.5, 54.4, 55.8, 59.4, 60.3 br (NCH_2); 103.9, 104.8 ($\underline{C}$=CHN); 129.9, 130.0, 130.1, 130.6 ($C_{sp2}H$ in benzene ring); 133.8, 137.6 ($\underline{C}_{sp2}C$ in benzene ring); 155.3, 161.0 (CH=N); 162.2, 164.0 (=CHN).

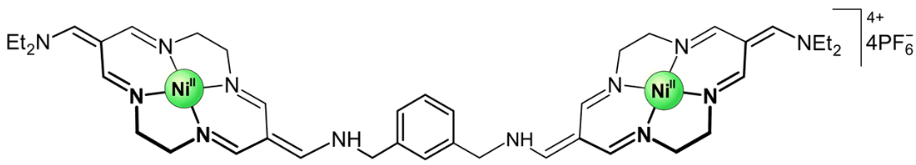


4*p*Ni: *Anal.* Calc. for $C_{24}H_{36}N_7Ni\cdot 3PF_6$ (916.2): C 31.46, H 3.96, N 10.70%; found C 31.45, H 4.07, N 10.75%. TOF MS ES^{+} (CH_3CN, *m/z*): 770.16 $[C_{24}H_{36}N_7Ni\cdot 2PF_6]^{+}$, 478.23 $[C_{24}H_{34}N_7Ni]^{+}$, 624.20 $[C_{24}H_{35}N_7Ni\cdot PF_6]^{+}$. ^{1}H NMR (400 MHz, CD_3CN) δ 1.33 (t, J = 7.2 Hz, 6 H, CH_3); 3.5-3.7 (comp, 12 H, NCH_2CH_2N and $C\underline{H}_2CH_3$); 4.15 (s, 2 H, $ArC\underline{H}_2NH_3^{+}$); 4.68 (s, 2 H, $ArC\underline{H}_2NH$); 5.75-6.75 very broad (3 H, NH_3^{+}); 7.45 (m, 4 H, H_{Ar}); 7.55 s, 7.56 s, 7.70 br s, 7.79 br s, 8.01 s (6 H, =CHN, CH=N); 8.23-8.43 very broad (1 H, NH). ^{13}C NMR (100 MHz, CD_3CN) δ 12.4, 14.4 (two CH_3); 44.3, 47.5, 54.3, 55.8, 59.4, 60.3 (NCH_2); 103.9, 104.8

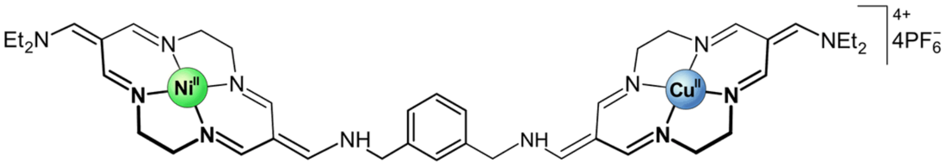
($\underline{C}$=CHN); 129.5, 130.8 (C_{sp2}H in benzene ring); 133.0, 138.0 ($\underline{C}_{sp2}$C in benzene ring); 155.2, 160.9 (CH=N); 162.1, 164.1 (=CHN).



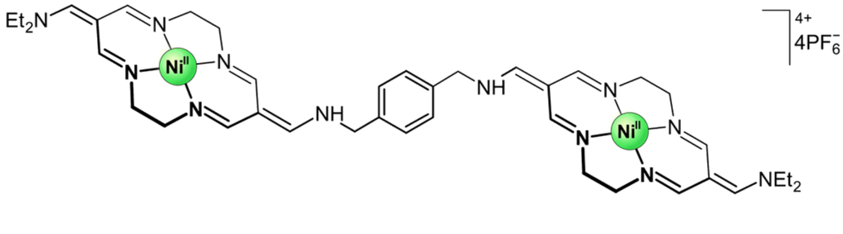
5*o*Ni₂: This compound was obtained in an experiment aimed at obtaining *ortho* isomers of an axle and a rotaxane, however, no formation of the latter was observed (axle **5*o*Ni₂** being the main product). To the intermediate **3Ni**, freshly prepared by methylation of **2Ni** (299.7 mg, 0.591 mmol), DB24C8 (2.656 g, 10 eq.), *o*-xylylenediamine dichloride (61.8 mg, 0.5 eq.), followed by CH_3CN (37.9 ml) were added. The system was degassed, filled with Ar, and stirred until all crown ether dissolved. After cooling to RT, a solution of Et_3N (82.5 μl, 1 eq.) in CH_3CN (1 ml) was added dropwise over 3 h. From time to time the flask was gently heated in order to dissolve DB24C8 which crystallizes from the supersaturated solution. The solution was further stirred for 2 days, followed by evaporation to dryness. Then, the product was isolated according to the recipe for **5*m*Ni₂**/**6*m*Ni₂** (see manuscript). Yield: 151.1 mg (36%) of **5*o*Ni₂**. Anal. Calc. for $C_{40}H_{58}N_{12}Ni_2\cdot4PF_6$ (1404.2): C 34.21, H 4.16, N 11.97%; found C 34.26, H 4.32, N 11.77%. TOF MS ES+ (CH_3CN, *m/z*): 205.59 $[C_{40}H_{58}N_{12}Ni_2]^{4+}$; 410.17 $[C_{40}H_{56}N_{12}Ni_2]^{2+}$. ^{1}H NMR (600 MHz, CD_3CN) δ 1.32-1.36 (m, 12 H, CH_3); 3.53-3.65 (comp, 20 H, NCH_2CH_2N and 2 × CH_2CH_3); 3.68 (q, J = 7.3 Hz, 4 H, 2 × CH_2CH_3); 4.75 (d, J = 4.9 Hz, 4 H, $ArCH_2$); 7.44-7.62 (m, 4 H, H_{Ar}); 7.56 and 8.04 (2 × s, 2 × 2 H, CH=N on the side of Ar); 7.57 (s, 2 H, =CHN on the side of NEt_2); 7.71 (d, J = 15.6 Hz, =CHN on the side of Ar) superimposed with br s (CH=N on the side of NEt_2) (total of 6 H); 8.38 (m, 2 H, NH). ^{13}C NMR (150 MHz, CD_3CN) δ 11.5 and 13.4 (2 × CH_3); 46.6 and 54.9 (2 × CH_2CH_3); 50.9 ($ArCH_2$); 58.5 and 59.4 (NCH_2CH_2N); 103.0 and 104.0 (C=CHN); 129.4 and 130.2 (C_{sp2}–H in Ar); 133.5 (C_{sp2}–C in Ar); 154.4 and 160.0 (CH=N on the side of Ar); 161.2 (=CHN on the side of NEt_2); 162.6 (=CHN on the side of Ar); CH=N on the side of NEt_2 unobserved due to broadening resulting from the rotation of the substituent. The assignment of the signals supported by ^{1}H-^{13}C HSQC spectrum.



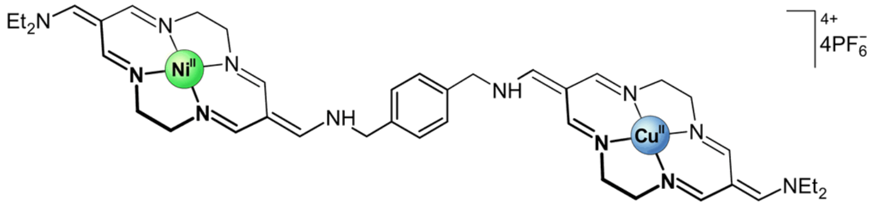
5*m*Ni₂: *Anal.* Calc. for $C_{40}H_{58}N_{12}Ni_2\cdot4PF_6$ (1404.2): C 34.21, H 4.16, N 11.97%; found C 34.19, H 4.23, N 11.95%. TOF MS ES$^+$ (CH_3CN, *m/z*): 205.59 $[C_{40}H_{58}N_{12}Ni_2]^{4+}$; 273.78 $[C_{40}H_{57}N_{12}Ni_2]^{3+}$; 410.18 $[C_{40}H_{56}N_{12}Ni_2]^{2+}$; 556.15 $[C_{40}H_{58}N_{12}Ni_2\cdot2PF_6]^{2+}$. ^{1}H NMR (600 MHz, CD_3CN) δ 1.34 (t, J = 7.2 Hz, 12 H, CH_3); 3.52-3.61 (m, 16 H, NCH_2CH_2N); 3.63 (q, J = 7.3 Hz, 4 H, 2 × $C\underline{H}_2CH_3$); 3.68 (q, J = 7.3 Hz, 4 H, 2 × $C\underline{H}_2CH_3$); 4.68 (d, J = 5.5 Hz, 4 H, $ArCH_2$); 7.37 (s, 1 H, H_{Ar} ortho to both CH_2); 7.38 (d, J = 7.1 Hz, 2 H, H_{Ar} ortho/para to CH_2); 7.48 (m, 1 H, H_{Ar} meta to CH_2); 7.566 (s, 2 H, =CHN on the side of NEt_2); 7.575 and 8.06 (2 × s, 2 × 2 H, CH=N on the side of Ar); 7.71 (br s, 4 H, CH=N on the side of NEt_2); 7.80 (d, J = 15.6 Hz, 2 H, =CHN on the side of Ar); 8.50 (m, 2 H, NH). ^{13}C NMR (150 MHz, CD_3CN) δ 11.5 and 13.4 (2 × CH_3); 46.6 and 54.9 (2 × $\underline{C}H_2CH_3$); 53.6 ($ArCH_2$); 58.5 and 59.3 (NCH_2CH_2N); 103.0 and 103.8 ($\underline{C}$=CHN); 127.9 and 128.1 (C_{sp2} in Ar "*ortho*" to both CH_2 and C_{sp2} in Ar "*ortho*/*para*" to CH_2); 129.6 (C_{sp2} in Ar "*meta*" to CH_2); 136.5 ($\underline{C}_{sp2}$–C in Ar); 154.3 and 160.0 (CH=N on the side of Ar); 161.2 (=CHN on the side of NEt_2); 163.0 (=CHN on the side of Ar); CH=N on the side of NEt_2 unobserved due to broadening resulting from the rotation of the substituent. The assignment of the signals supported by ^{1}H-^{13}C HSQC spectrum.



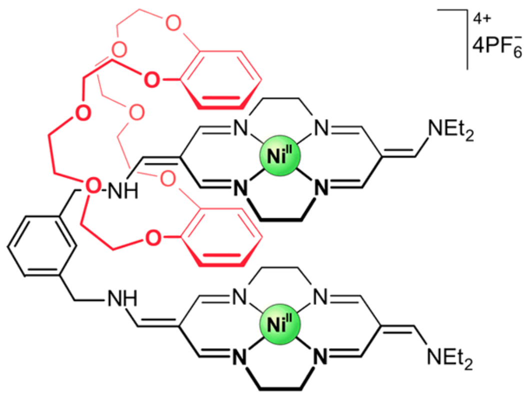
5*m*CuNi: *Anal.* Calc. for $C_{40}H_{58}CuN_{12}Ni·4PF_6$ (1409.1): C 34.10, H 4.15, N 11.93%; found C 34.14, H 4.38, N 11.67. TOF MS ES^{+} (CH_3CN, *m/z*): 206.84 $[C_{40}H_{58}CuN_{12}Ni]^{4+}$; 275.45 $[C_{40}H_{57}CuN_{12}Ni]^{3+}$; 412.67 $[C_{40}H_{56}CuN_{12}Ni]^{2+}$; 1262.25 $[C_{40}H_{58}CuN_{12}Ni·3PF_6]^{+}$; 558.64 $[C_{40}H_{58}CuN_{12}Ni·2PF_6]^{2+}$; 970.30 $[C_{40}H_{56}CuN_{12}Ni·PF_6]^{+}$; 485.65 $[C_{40}H_{57}CuN_{12}Ni·PF_6]^{2+}$. ^{1}H NMR (600 MHz, CD_3CN) δ 1.24-1.30 (br); 1.33 (t, J = 7.2 Hz); 3.48-3.64 (very br); 3.62 (br q, J = 7.3 Hz); 3.67 (br q, J = 7.2 Hz); 4.62-4.66 (br); a set of broad signals with visible maxima at 7.23, 7.34, 7.41, 7.70, 7.76, 8.01. 8.33; 7.55 (s); 8.7-10.7 (very br). ^{13}C NMR (150 MHz, CD_3CN) a set of weak and broad signals at δ 12.5, 14.5, 47.6, 54.5, 55.9, 60.2-60.5 (very br), 104.0, 104.8, 128.8, 129.0, 130.3, 137.7, 162.2, 164.0.



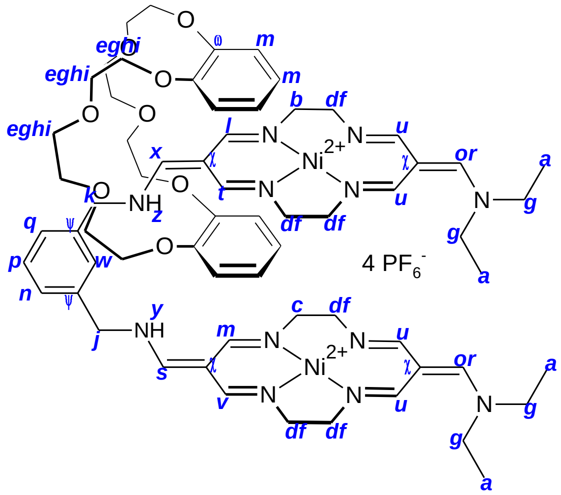
5*p*Ni$_2$: *Anal.* Calc. for $C_{40}H_{58}N_{12}Ni_2·4PF_6$ (1404.2): C 34.21, H 4.16, N 11.97%; found C 34.14, H 3.89, N 12.00%. TOF MS ES^{+} (CH_3CN, *m/z*): 205.59 $[C_{40}H_{58}N_{12}Ni_2]^{4+}$; 410.17 $[C_{40}H_{56}N_{12}Ni_2]^{2+}$; 556.15 $[C_{40}H_{58}N_{12}Ni_2·2PF_6]^{2+}$. ^{1}H NMR (600 MHz, CD_3CN) δ 1.34 (t, J = 7.3 Hz, 12 H, CH_3); 3.51-3.61 (m, 16 H, NCH_2CH_2N); 3.63 (q, J = 7.3 Hz, 4 H, 2 × $C\underline{H}_2CH_3$); 3.68 (q, J = 7.3 Hz, 4 H, 2 × $C\underline{H}_2CH_3$); 4.68 (d, J = 5.8 Hz, 4 H, $ArCH_2$); 7.42 (s, 4 H, H_{Ar}); 7.566 (s, 2 H, =CHN on the side of NEt_2); 7.571 and 8.04 (2 × s, 2 × 2 H, CH=N on the side of Ar); 7.71 (br s, 4 H, CH=N on the side of NEt_2); 7.80 (d, J = 15.7 Hz, 2 H, =CHN on the side of Ar); 8.47 (m, 2 H, NH). ^{13}C NMR (150 MHz, CD_3CN) δ 11.5 and 13.4 (2 × CH_3); 46.6 and 54.9 (2 × <u>C</u>H_2CH_3); 53.5 ($ArCH_2$); 58.5 and 59.3 (NCH_2CH_2N); 103.0 and 103.8 (<u>C</u>=CHN); 128.6 (C_{sp2}–H in Ar); 136.0 (<u>C</u>$_{sp2}$–C in Ar); 154.3 and 160.0 (CH=N on the side of Ar); 161.2 (=CHN on the side of NEt_2); 163.0 (=CHN on the side of Ar); CH=N on the side of NEt_2 unobserved due to broadening resulting from the rotation of the substituent. The assignment of the signals supported by ^{1}H-^{13}C HSQC spectrum.



5*p*CuNi: *Anal.* Calc. for $C_{40}H_{58}CuN_{12}Ni·4PF_6$ (1409.1): C 34.10, H 4.15, N 11.93%; found C 33.96, H 4.03, N 11.80%. TOF MS ES$^+$ (CH_3CN, *m/z*): 206.84 $[C_{40}H_{58}CuN_{12}Ni]^{4+}$; 275.45 $[C_{40}H_{57}CuN_{12}Ni]^{3+}$; 412.67 $[C_{40}H_{56}CuN_{12}Ni]^{2+}$; 1262.25 $[C_{40}H_{58}CuN_{12}Ni·3PF_6]^+$; 558.64 $[C_{40}H_{58}CuN_{12}Ni·2PF_6]^{2+}$; 970.30 $[C_{40}H_{56}CuN_{12}Ni·PF_6]^+$; 485.65 $[C_{40}H_{57}CuN_{12}Ni·PF_6]^{2+}$. ^{1}H NMR (600 MHz, CD_3CN) δ 1.28 (br); 1.34 (t, J = 7.3 Hz); 3.51-3.61 (br); 3.63 and 3.68 (2 × q, J = 7.3 Hz); 4.68 (br); set of broad signals with maxima at 7.29, 7.35, 7.42, 7.56, 7.71, 7.80, 8.02, 8.37; 8.9-10.3 (very br). ^{13}C NMR (150 MHz, CD_3CN) a set of weak and broad signals at δ 11.5, 13.5, 46.6, 54.9, 53.6, 58.5, 59.3, 103.0, 103.8, 128.4, 128.5, 128.6, 136.0, 154.3, 159.9, 160.0, 161.2, 163.0.

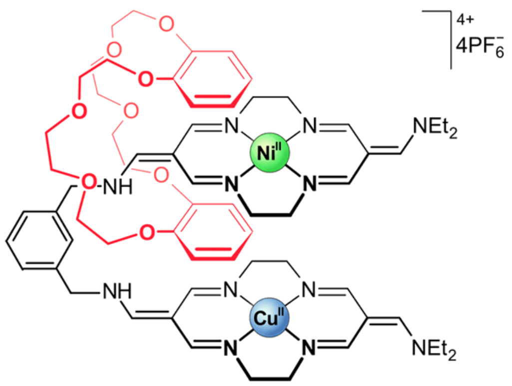


6*m*Ni$_2$: *Anal.* Calc. for $C_{64}H_{90}N_{12}Ni_2O_8·4PF_6$ (1852.7): C 41.49, H 4.90, N 9.07%; found C 41.65, H 4.85, N 8.96%. TOF MS ES$^+$ (CH_3CN, *m/z*): 317.64 $[C_{64}H_{90}N_{12}Ni_2O_8]^{4+}$; 423.19 $[C_{64}H_{89}N_{12}Ni_2O_8]^{3+}$; 707.26 $[C_{64}H_{89}N_{12}Ni_2O_8·PF_6]^{2+}$; 780.24 $[C_{64}H_{90}N_{12}Ni_2O_8·2PF_6]^{2+}$; 1705.46 $[C_{64}H_{90}N_{12}Ni_2O_8·3PF_6]^+$. ^{1}H NMR and ^{13}C NMR (interpretation supported by ^{1}H-^{13}C HSQC and ^{1}H-^{1}H COSY spectra):

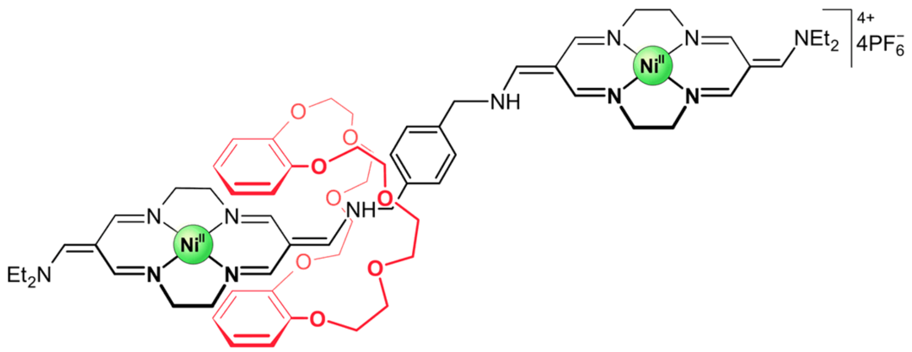


#	^{1}H NMR (600 MHz, CD_3CN)	HSQC corr.	^{13}C NMR (150 MHz, CD_3CN)	group
a	1.30-1.36 (comp, 12 H)	↔ ↔	12.48, 12.51 14.46, 14.52	CH_3
b	2.94 (t, *J* = 6.6 Hz, 2 H)	↔	58.53	NCH_2CH_2N
c	3.16 (t, *J* = 6.6 Hz, 2 H)	↔	59.29	NCH_2CH_2N
d	3.23-3.29 (comp, 4 H)	↔	59.59	NCH_2CH_2N
e	3.37-3.42 (comp, 4 H)	↔	71.04	OCH_2
f	3.42-3.49 (6 H) and 3.52-3.57 br (2 H)	↔ ↔	60.24 60.15 br	NCH_2CH_2N
g	3.58-3.72 (comp, 16 H)	↔ ↔ ↔	47.46, 47.56 55.90, 55.82 70.87	$NC\underline{H}_2CH_3$ $NC\underline{H}_2CH_3$ OCH_2
h	3.76-3.85 (comp, 8 H)	↔ ↔	68.43 70.87	OCH_2
i	4.04-4.10 (4 H)	↔	68.43	OCH_2
j	4.72 (d, *J* = 5.7 Hz, 2 H)	↔	55.75	$ArCH_2N$ at the side of TAM^{2+} unit neighbouring DB24C8
k	4.95 (d, *J* = 6.0 Hz, 2 H)	↔	54.60	$ArCH_2N$ at the side of TAM^{2+} unit enclosed by DB24C8
l	6.59 (s, 1 H)	↔	158.50	one of two CH=N enclosed by DB24C8
m	6.82-6.90 (comp, 9 H)	↔ ↔	112.72, 122.03 160.11	all H_{Ar} in DB24C8 and one of two CH=N neighbouring DB24C8
n	7.38 („d", *J* = 6.90 Hz, 1 H)	↔	129.07	H_{Ar} in xylyl *ortho/para*
o	7.48 (s, 1 H)	↔	161.69	one of two =CHN on the side of NEt_2
p	7.48 („t", 1 H)	↔	129.93	H_{Ar} in xylyl *meta* to CH_2N
q	7.50 („d", 1 H)	↔	129.62	H_{Ar} in xylyl *ortho/para* close to DB24C8
r	7.54 (s, 1 H)	↔	162.15	one of two =CHN on the side of NEt_2

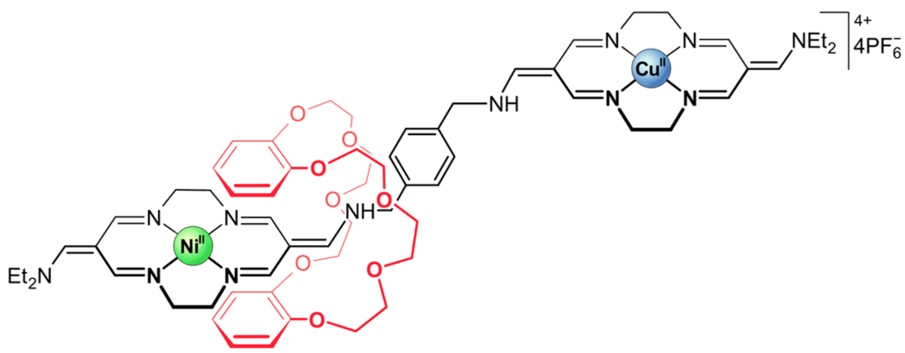
s	7.56 (d, *J* = 16.8 Hz, 1 H)	↔	163.94	one of two =CHN on the side of xylyl, the one neighboring DB24C8
t	7.58 (s, 1 H)	↔	154.64	one of two CH=N enclosed by DB24C8
u	7.60-7.72 very br (4 H)	undetected		four CH=N on the side of NEt_2
v	7.84 (s, 1 H)	↔	154.53	one of two CH=N neighbouring DB24C8
w	7.90 („s", 1 H)	↔	128.88	H_{Ar} in xylyl *ortho/ortho* to CH_2N
x	8.30 (d, *J* = 16.8 Hz, 1 H)	↔	166.92	one of two =CHN on the side of xylyl, the one enclosed by DB24C8
y	8.40-8.48 (m, 1 H)	n/a	n/a	NH neighbouring DB24C8
z	8.92-9.01 (m, 1 H)			NH enclosed by DB24C8
χ	n/a		103.92, 103.94, 104.40, 104.41	quaternary C=CHN (first C underlined)
ψ			139.12, 136.77	quaternary C atoms in xylyl ring
ω			148.90	quaternary C atoms in catechol ring



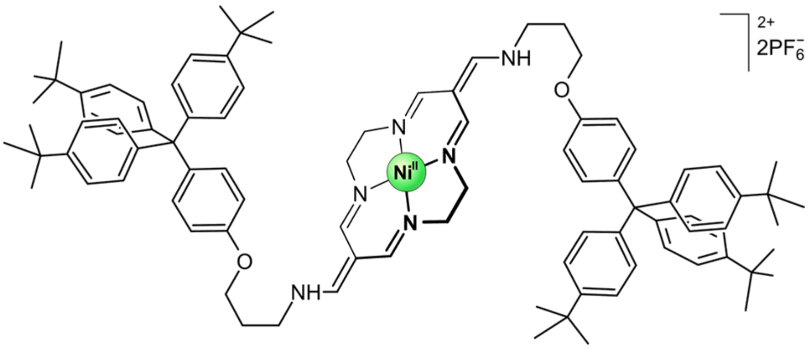
6*m*CuNi: *Anal.* Calc. for $C_{64}H_{90}CuN_{12}NiO_8 \cdot 4PF_6$ (1857.6): C 41.38, H 4.88, N 9.05%; found C 41.21, H 4.90, N 8.87%. TOF MS ES$^+$ (CH_3CN, *m/z*): 318.90 $[C_{64}H_{90}CuN_{12}NiO_8]^{4+}$; 424.86 $[C_{64}H_{89}CuN_{12}NiO_8]^{3+}$; 709.79 $[C_{64}H_{89}CuN_{12}NiO_8 \cdot PF_6]^{2+}$; 636.80 $[C_{64}H_{88}CuN_{12}NiO_8]^{2+}$. ^{1}H NMR (600 MHz, CD_3CN) a set of broad signals with visible maxima at δ 1.27, 1.34, 3.02, 3.31, 3.38, 3.50, 3.62, 3.80, 3.89, 4.14, 4.70, 4.93, 6.66, 6.74-7.20 (very br), 7.27, 7.35, 7.41, 7.50, 7.57, 7.62, 7.71, 7.77, 7.89, 8.32, 8.96, 9.1-10.5 (bery br). ^{13}C NMR (150 MHz, CD_3CN) weak and broad signals at δ 12.5 and 71.1 (other signals unobserved due to paramagnetic nature of the complex, despite 656 repetitions with relax. delay 0.500 sec).



6*p*Ni2: *Anal.* Calc. for $C_{64}H_{90}N_{12}Ni_2O_8{\cdot}4PF_6$ (1852.7): C 41.49, H 4.90, N 9.07%; found C 41.31, H 4.96, N 9.19%. TOF MS ES$^+$ (CH_3CN, *m/z*): 317.64 $[C_{64}H_{90}N_{12}Ni_2O_8]^{4+}$; 423.19 $[C_{64}H_{89}N_{12}Ni_2O_8]^{3+}$. ^{1}H NMR (600 MHz, CD_3CN) δ 1.33 and 1.34 (2 × t, 2 × 6 H, CH_3); 2.94 (t, J = 6.6 Hz, 2 H, NC$\underline{H}_2$CH$_2$N in TAM^{2+} unit enclosed by the DB24C8); 3.20-3.90 (comp, 46 H, all NCH_2 and OCH_2 but xylyl and the one corresponding to the 2.94 ppm signal); 4.68 (s, 2 H, NCH_2Ar at the side of DB24C8); 4.91 (d, J = 6.0 Hz, 2 H, NCH_2Ar at the opposite side of DB24C8); 6.63 s, 7.48 s, 7.55 s, 7.63 s, 7.69 br s, 7.80 s, 8.33 d (J = 15.8 Hz) and 8.40 br s (CH=N and =CHN); 6.81-6.88 (m, 8 H, H_{ar} in DB24C8); 7.41 and 7.73 (2 × d, 2 × J = 7.8 Hz, 2 × 2 H, H_{ar} in xylyl linker); 8.96 (m, 2 H, NH). ^{13}C NMR (150 MHz, CD_3CN) δ 12.44, 12.47, 14.41 and 14.47 (CH_3); 47.41, 47.53, 54.24, 54.65, 55.78, 55.85, 58.48, 59.53 and 60.26 br (NCH_2); 68.28 ($ArOCH_2$); 70.78 (ArOCH$_2\underline{C}$H$_2$); 70.98 (ArO(CH$_2$)$_2$O$\underline{C}$H$_2$); 103.91, 104.45 and 104.71 ($\underline{C}$=CHN); 112.64 (C *ortho* to O); 121.81 (C *meta* to O); 128.99 and 129.92 ($\underline{C}_{sp2}$C in xylyl); 136.33 and 138.43($\underline{C}_{sp2}$H in xylyl); 148.92 (C_{sp2}O); 154.74, 158.62, 161.62, 162.12, 163.94 and 167.10 (CH=N and =CHN). The assignment of the signals supported by ^{1}H-^{13}C HMBC spectrum.

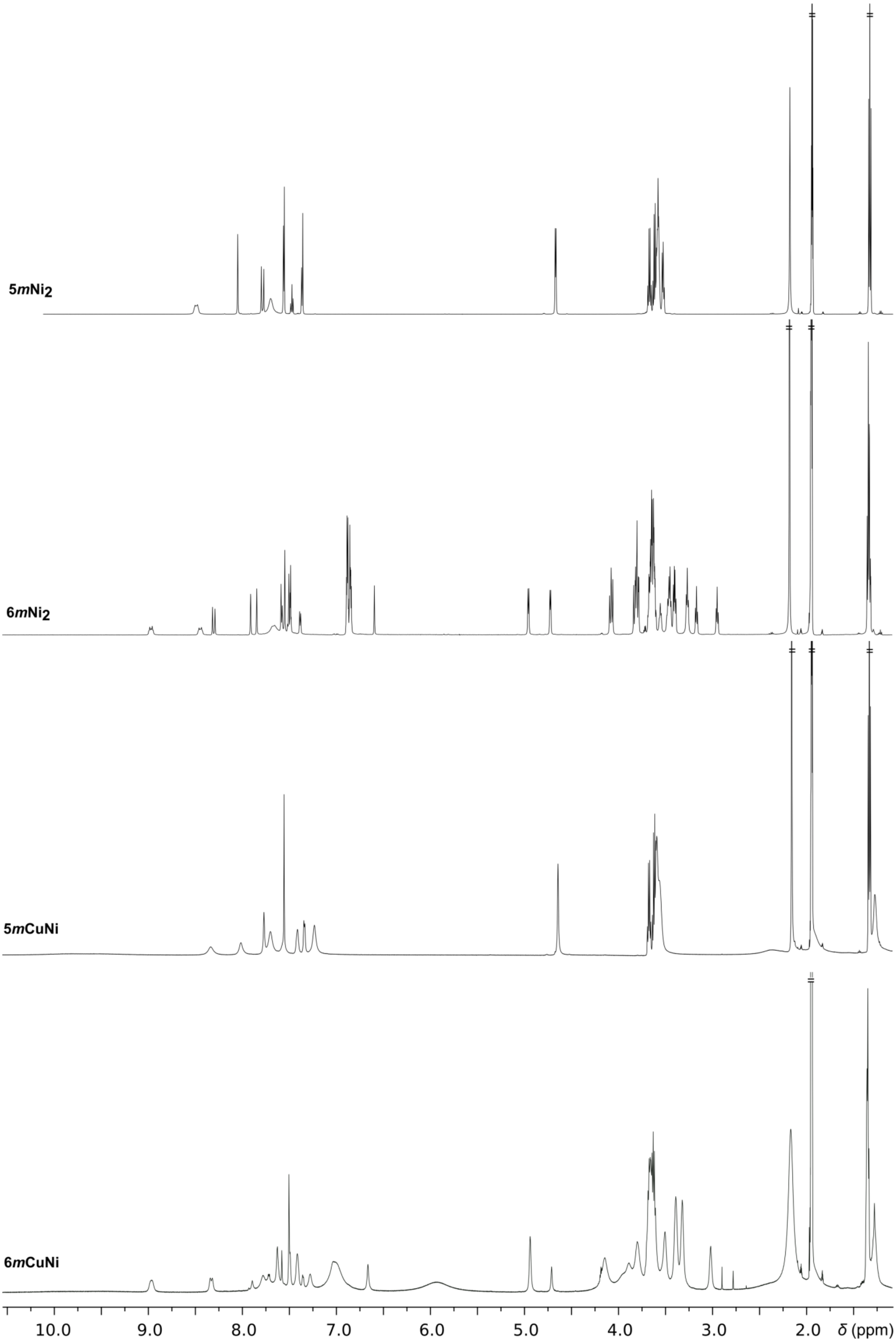


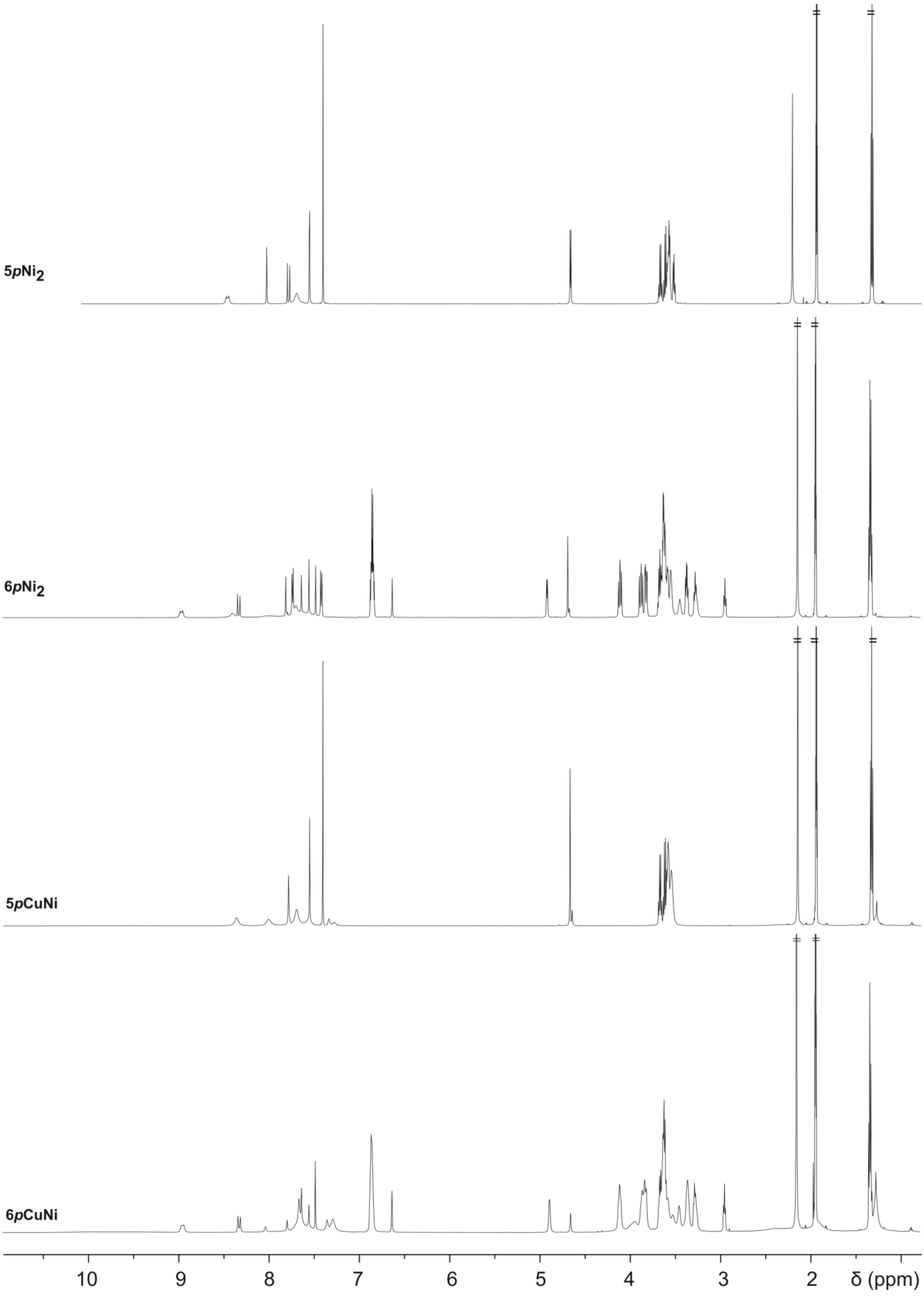
6*p*CuNi: *Anal.* Calc. for $C_{64}H_{90}CuN_{12}NiO_8{\cdot}4PF_6{\cdot}2H_2O$ (1893.6): C 40.59, H 5.00, N 8.88%; found C 40.45, H 5.13, N 8.60%. TOF MS ES$^+$ (CH_3CN, *m/z*): 318.89 $[C_{64}H_{90}CuN_{12}NiO_8]^{4+}$; 424.86 $[C_{64}H_{89}CuN_{12}NiO_8]^{3+}$; 709.79 $[C_{64}H_{89}CuN_{12}NiO_8{\cdot}PF_6]^{2+}$. ^{1}H NMR (600 MHz, CD_3CN) δ 1.27 (br); 1.34 (t, J = 7.2 Hz); 2.95 (t, J = 6.4 Hz); 3.22-3.31 (br); 3.32-3.40 (br); 3.42-3.49 (br); 3.49-3.54 (br); 3.54-3.70 (br); 3.78-3.90 (br); 3.90-4.02 (br); 4.07-4.15 (br); set of broad signals with visible maxima at δ 7.29, 7.35, 7.48, 7.55, 7.63, 7.66, 7.79, 8.03; 8.32 (d br, J = 15.7 Hz); 8.90-9.00 (br); 8.7-10.7 (very br). ^{13}C NMR (150 MHz, CD_3CN) a set of weak and broad signals at *δ* 12.5, 14.5, 47.5, 54.3, 55.8, 58.5, 59.6, 68.3, 70.9, 71.1, 103.9, 104.5, 112.7, 121.9, 128.9, 129.7, 138.2, 149.0, 154.8, 158.7, 161.7, 167.1.



8Ni: *Anal.* Calc. for $C_{92}H_{114}N_6NiO_2{\cdot}2PF_6$ (1684.6): C 65.60, H 6.82, N 4.99%; found C 65.49, H 6.80, N 5.07%. TOF MS ES+ (CH_3CN, *m/z*): 696.41 $[C_{92}H_{114}N_6NiO_2]^{2+}$, 1391.82 $[C_{92}H_{113}N_6NiO_2]^+$, 1537.80 $[C_{92}H_{114}N_6NiO_2{\cdot}PF_6]^+$. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29 (s, 54 H, $C(CH_3)_3$); 2.08 (p, *J* = 6.0 Hz, 4 H, $CH_2C\underline{H}_2CH_2$); 3.40-3.65 (m, 8 H, NCH_2CH_2N); 3.70 (m, 4 H, $NC\underline{H}_2(CH_2)_2$); 4.04 (br t, 4 H, CH_2OAr); 6.79 (m, 4 H, C_{sp2}–H *ortho* to ether bond); 7.13 (comp, 16 H, (C_{sp2}–H *meta* to ether bond and C_{sp2}–H *meta* to *t*Bu group); 7.26 (m, 12 H, C_{sp2}–H *ortho* to *t*Bu group); 7.40-8.60 (comp br, 8 H, CH=N, =CHN, NH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.6 ($CH_2C\underline{H}_2CH_2$); 31.4 ($C(\underline{C}H_3)_3$); 34.5 (quaternary carbon atom in *t*Bu group); 48.6 ($N\underline{C}H_2(CH_2)_2$); 58.8, 59.0, 59.7 and 59.9 (NCH_2CH_2N); 63.4 (central, quaternary carbon atom in tritylphenol group); 64.6 (CH_2OAr); 103.9 ($\underline{C}$=CHN); 113.6 (C_{sp2}–H "*ortho*" to ether bond); 124.7 (C_{sp2}–H "*ortho*" to *t*Bu group); 130.7 (C_{sp2}–H "*meta*" to *t*Bu group); 132.3 (C_{sp2}–H "*meta*" to ether bond); 140.3 (C_{sp2} "*para*" to ether bond); 144.7 (C_{sp2} "*para*" to *t*Bu group); 148.7 (C_{sp2} bonded to *t*Bu group); 154.7, 160.1 and 163.5 (CH=N and =CHN); 156.7 (O–C_{sp2}).

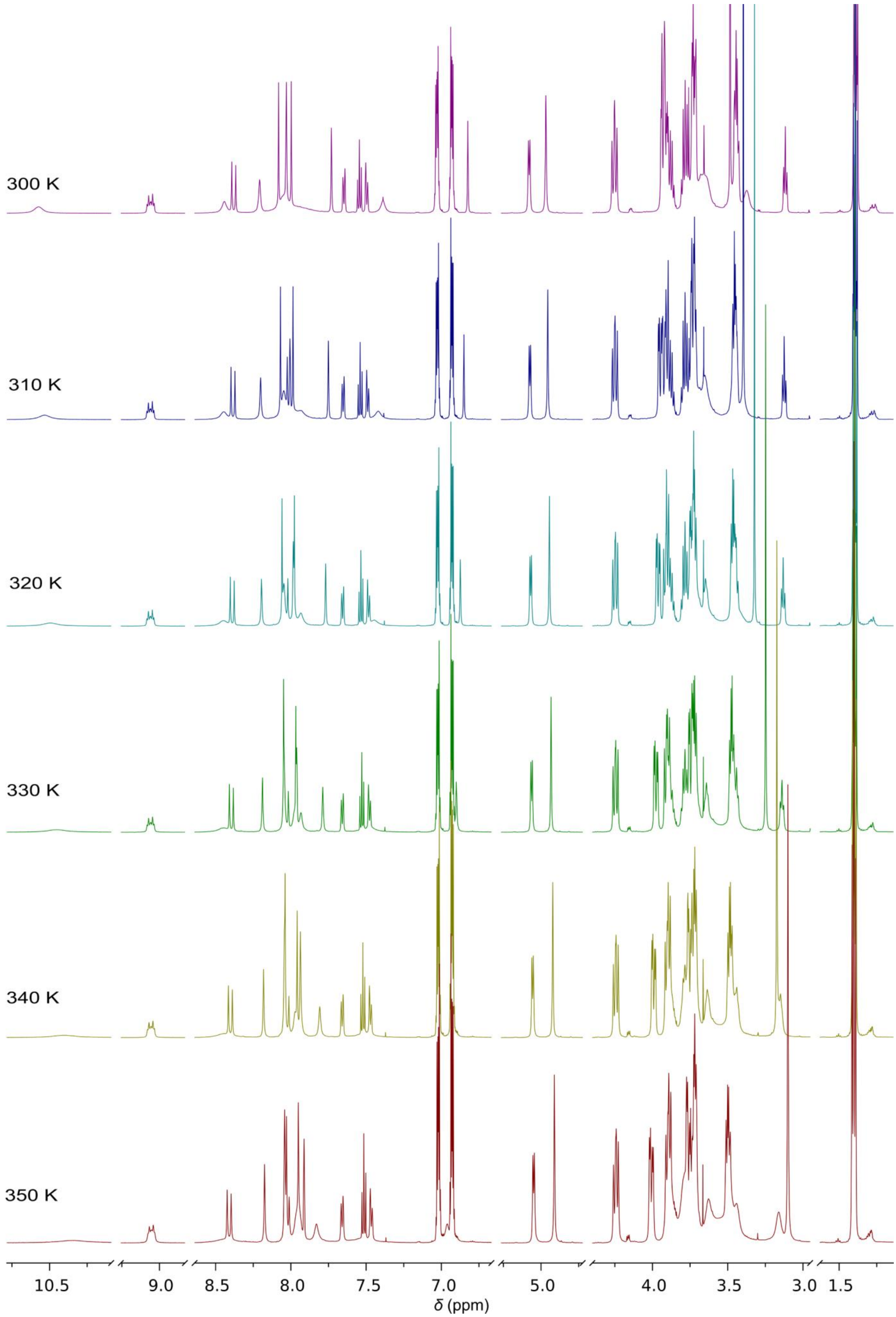
2. [1]H NMR spectra of axles and rotaxanes (600 MHz, CD_3CN)



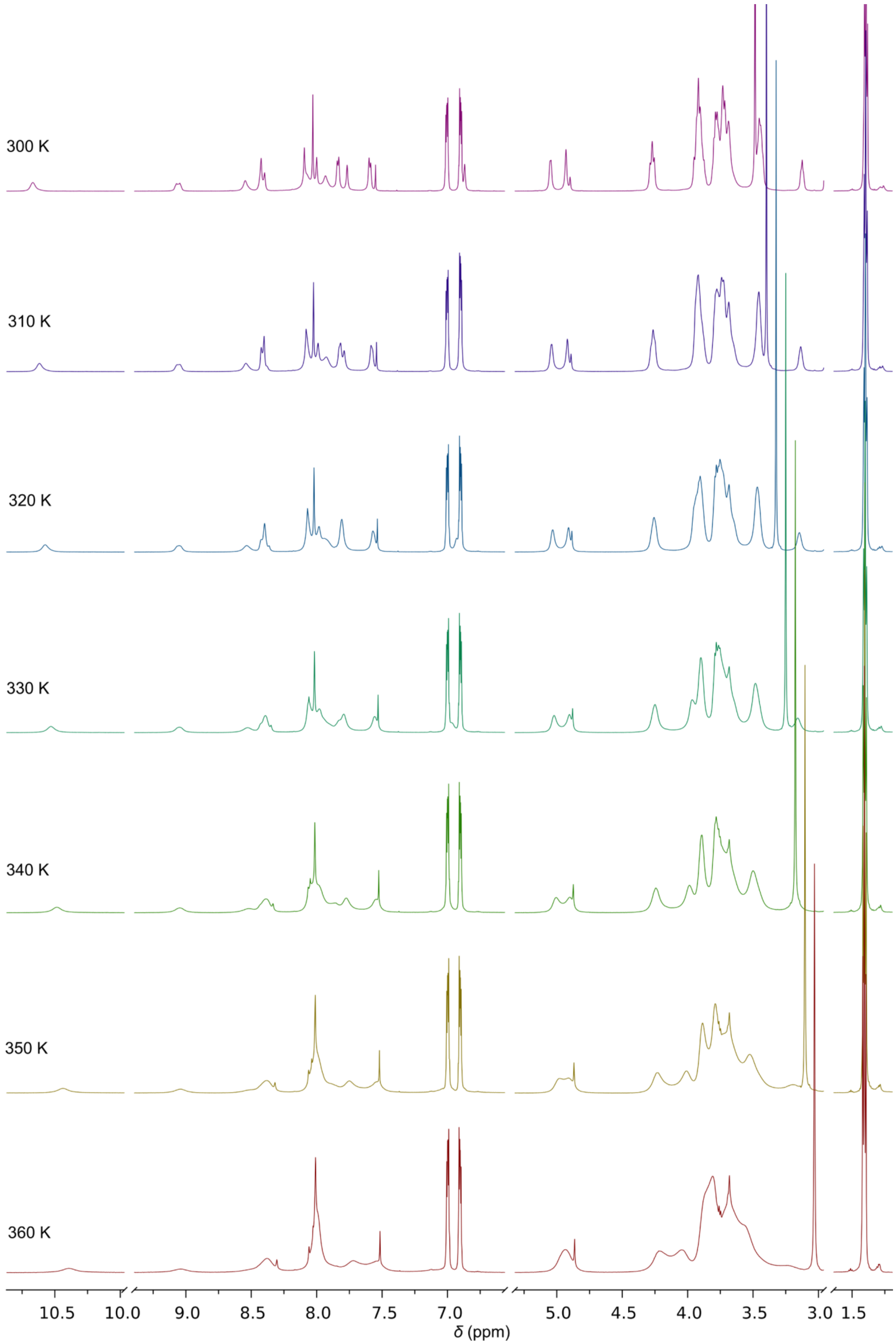


5pNi2
6pNi2
5pCuNi
6pCuNi
10
9
8
7
6
5
4
3
2
δ (ppm)

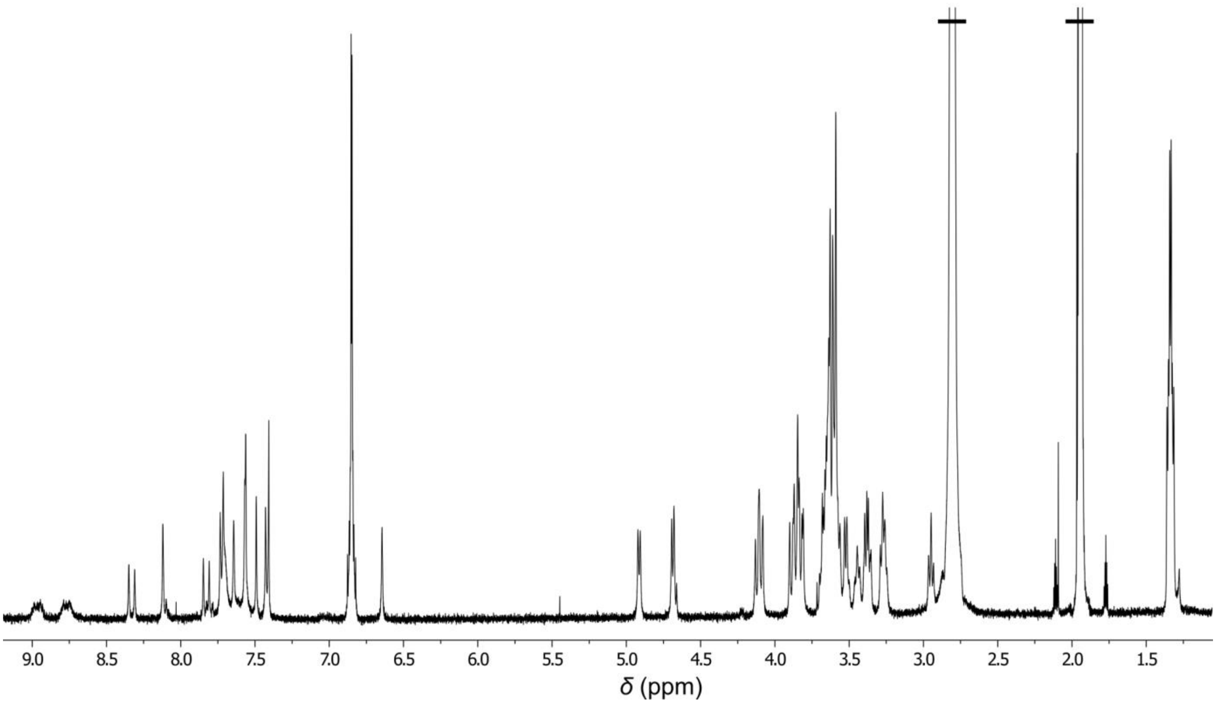
3. VT NMR spectra of 6*m*Ni_2 (600 MHz, DMF-d7)



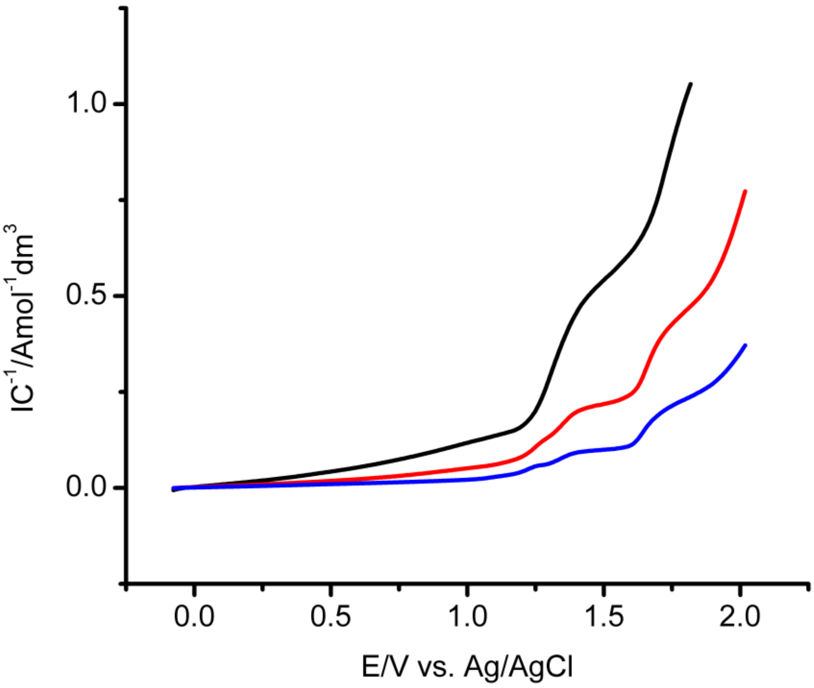
4. VT NMR spectra of 6*p*Ni_2 (600 MHz, DMF-d7)



5. [1]H NMR spectrum of **6*p*Ni$_2$** after addition of trifluoroacetic acid (400 MHz, CD_3CN)

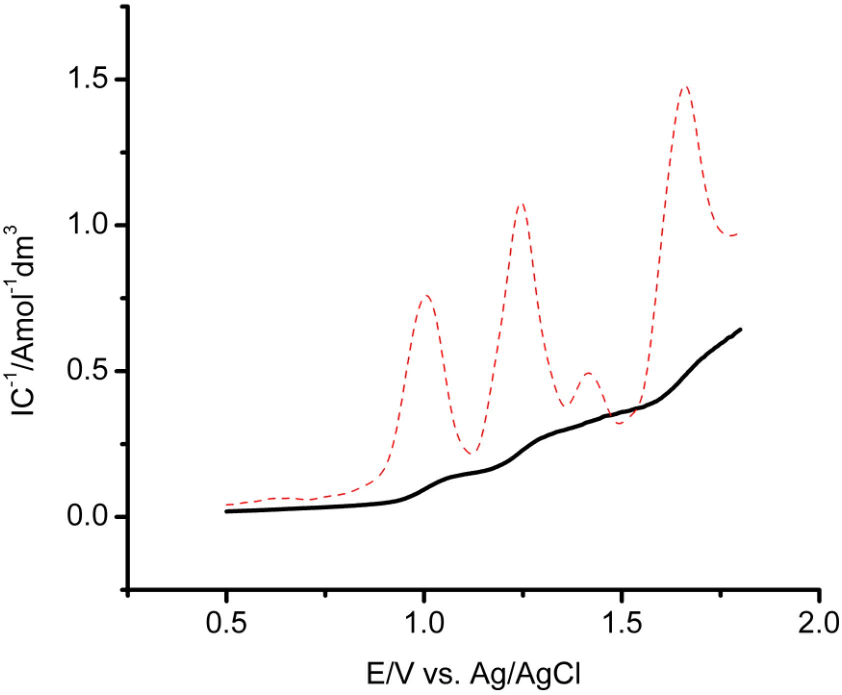


6. **NP voltammograms for 6*m*Ni$_2$ at different time scale of experiment**



NP voltammograms for **6*m*Ni$_2$** recorded at T = 45°C tp = 30 ms (blue line), tp = 70 ms red line),tp = 200ms (black line), 0.1 M TBAHFP/AN.

7. NP voltammogram for 6*p*CuNi



NPV Voltammogram for **6*p*CuNi** recorded atT = 50°C and tp = 70 ms (black line) Derivative of the NP voltammogram (red line**).**

Table 1S. Crystal structure parameters and details of single crystal X-ray diffraction data collection.

Identification code	6*m*Ni_2	6*m*CuNi	6*p*Ni_2	6*p*CuNi
Empirical formula	$C_{65.36}H_{96.17}F_{24}N_{12}Ni_2O_{10.18}P_4$	$C_{70.7}H_{103.4}CuF_{24}N_{12}NiO_{10.23}P_4$	$C_{66}H_{93.5}Cl_2F_{24}N_{12.5}Ni_2O_8P_4$	$C_{65}H_{92}Cl_2CuF_{24}N_{12}NiO_8P_4$
Moiety formula	$C_{64}H_{90}N_{12}O_8Ni_2^{4+}$ $4PF_6^-$ · 0.45 C_3H_6O, 1.72 H_2O	$C_{64}H_{90}N_{12}O_8NiCu^{4+}$ $4PF_6^-$ · 2.23 C_3H_6O	$C_{64}H_{90}N_{12}O_8Ni_2^{4+}$ $4PF_6^-$ · 0.5 C_2H_3N	$C_{64}H_{90}N_{12}O_8NiCu^{4+}$ $4PF_6^-$ · CH_2Cl_2
Formula weight	1910.27	1987.33	1958.23	1942.53
Temperature/K	100			
Crystal system	triclinic			
Space group	P-1			
a/Å	15.8575(2)	13.7274(3)	12.7226(4)	12.5399(2)
b/Å	16.3923(2)	16.1814(4)	16.6566(6)	16.3862(3)
c/Å	17.6221(2)	21.4063(4)	20.9375(6)	20.9420(3)
α/°	82.118(1)	74.016(2)	76.752(3)	80.969(1)
β/°	63.717(1)	88.018(2)	87.027(3)	86.279(1)
γ/°	88.168(1)	69.385(2)	81.031(3)	79.954(1)
Volume/Å^3	4066.22(9)	4268.1(2)	4265.5(2)	4181.6(1)
Z	2	2	2	2
ρ_{calc}g/cm^3	1.560	1.546	1.525	1.543
μ/mm^{-1}	2.369	0.660	2.816	0.729
F(000)	1972.0	2053.0	2014.0	1994.0
Crystal size/mm^3	0.582 × 0.159 × 0.094	0.364 × 0.229 × 0.109	0.502 × 0.295 × 0.204	0.293 × 0.243 × 0.151
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.446 to 153.86	3.862 to 61.016	4.336 to 136.488	3.448 to 56.564
Index ranges	$-19 \le h \le 20$, $-20 \le k \le 20$, $-22 \le l \le 22$	$-19 \le h \le 20$, $-23 \le k \le 24$, $-31 \le l \le 32$	$-15 \le h \le 15$, $-20 \le k \le 20$, $-26 \le l \le 26$	$-17 \le h \le 17$, $-22 \le k \le 23$, $-29 \le l \le 29$
Reflections collected	120445	101860	89025	84252
Independent reflections	17080 R_{int} = 0.0510, R_{sigma} = 0.0502	26052 R_{int} = 0.0472, R_{sigma} = 0.0976	15599 R_{int} = 0.0359, R_{sigma} = 0.0437	20735 R_{int} = 0.0320, R_{sigma} = 0.0612
Data / restraints / parameters	17080/1644/1466	26052/844/1553	15599/724/1025	20735/1026/1227
Goodness-of-fit on F^2	1.029	0.923	1.635	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0794, wR_2 = 0.2270	R_1 = 0.0403, wR_2 = 0.0998	R1 = 0.1061, wR2 = 0.3443	R_1 = 0.0762, wR_2 = 0.2516
Final R indexes [all data]	R_1 = 0.0895, wR_2 = 0.2364	R_1 = 0.0802, wR_2 = 0.1066	R1 = 0.1154, wR2 = 0.3602	R_1 = 0.1011, wR_2 = 0.2663
Largest diff. peak/hole / e Å^{-3}	1.12/-0.71	0.68/-0.60	1.40/-1.72	1.22/-2.00

Table 2S. Selected hydrogen bonds [Å] for rotaxanes (symmetry operations: $1: 1-X,1-Y,1-Z; $2: 1-X,-Y,1-Z; $3 1-X,1-Y,2-Z ; $4: 2-X,1-Y,-Z).

Compound	**Bond**	**D-H**	**H…A**	**D…A**	**DHA**
6*m*Ni$_2$	**N11-H11A...O2A**	0.88	2.39	2.918(10)	118.5
	N11-H11A...O2B	0.88	2.45	3.086(19)	129.4
	N11-H11A...O3A	0.88	2.09	2.929(15)	160.3
	N11-H11A...O3B	0.88	2.34	3.14(2)	152.0
	N12-H12...O10	0.88	1.98	2.838(5)	165.6
	O10-H10A...F17A_$1	0.85	2.10	2.822(6)	142.6
	O10-H10B...F19B_$2	0.85	2.31	3.03(9)	142.4
	O10-H10B...O11_$2	0.85	2.02	2.813(6)	155.9
	O11-H11B...F19A	0.85	1.95	2.797(7)	178.8
6*m*CuNi	**N11-H11...O2B**	0.88	2.62	3.05(4)	110.9
	N11-H11...O3	0.88	2.11	2.976(2)	169.7
	N12-H12...O9_$3	0.88	1.96	2.826(2)	168.0
6*p*Ni$_2$	**N11A-H11A...O2**	0.88	2.15	2.884(6)	140.1
	N11A-H11A...O3	0.88	2.50	3.198(6)	137.3
	N11B-H11B...O7	0.88	2.15	2.89(2)	141.5
	N12-H12...F1_$4	0.88	2.25	3.084(6)	158.2
	N12-H12...F3A_$4	0.88	2.52	3.270(8)	143.4
	N12-H12...F6A_$4	0.88	2.58	3.146(7)	123.1
6*p*CuNi	**N11A-H11A...O2**	0.88	2.13	2.844(6)	137.3
	N11A-H11A...O3	0.88	2.47	3.173(6)	137.7
	N11B-H11B...O7	0.88	2.12	2.89(1)	146.1
	N12-H12...F1	0.88	2.10	2.962(4)	165.3
	N12-H12...F4A	0.88	2.62	3.146(9)	119.3
	N12-H12...F4B	0.88	2.45	3.00(2)	120.4