Electronic Supplementary Information for

Oxidative dehydrogenation of a tetra-amine N_4 macrocycle tunes the nickel(II) spin state

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Experimental

Elemental analyses were carried out by the Campbell Microanalytical Laboratory at the University of Otago. Infrared spectra were obtained on a Bruker Alpha FT-ATR IR spectrometer with a diamond anvil Alpha-P module. MS spectra were collected on a Bruker MicrOTOF$_Q$ spectrometer. UV-vis spectra were obtained on a Varian 500 Scan UV-vis-NIR spectrophotometer. Magnetic data were recorded using a Quantum Design Physical Property Measurement PPMS magnetometer with an applied field of 1 T, for all of the nickel(II) complexes, except for $[Ni^{II}L^{ia}](BF_4)\cdot H_2O\cdot DCM$ for which data was recorded using a Johnson-Matthey magnetic susceptibility balance MSB-MKI. All magnetic data were corrected for diamagnetic contributions using Pascal's constants.

^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Varian 500 MHz Inova spectrometer. The assignments are based on the atom labelling scheme used in the X-ray crystal structures.

All Evans method experiments were recorded on the Varian 500 MHz NMR spectrometer (i.e. $f = 500 \times 10^6$ Hz) with CD_3CN as the solvent (contains TMS). All samples were prepared with a precisely known mass dissolved in a volume of 0.7 mL of CD_3CN. A special double walled NMR tube was used. A sample of pure CD_3CN was placed in the inner tube while the paramagnetic sample in CD_3CN was placed in the outer tube. The resulting NMR spectrum exhibits two peaks near 2 ppm: one is due to the pure CD_3CN in the inner tube (which occurs at 969.36 Hz) and the other is due to the paramagnetically shifted CD_3CN signal from the outer tube. The chemical shift of these two peaks was determined and the separation between them (Δf) measured in hertz. The following equation[1] was then used to calculate the gram susceptibility χ_g, which was then converted in the usual manner to the molar susceptibility, χ_m.

$$\chi_g = \frac{3\Delta f}{2\pi f m} + \chi_0$$

Where $\chi_0 = -0.534 \times 10^{-6}$ cgs/gram, the gram susceptibility of pure CD_3CN,[2] and m is the concentration of the paramagnetic sample in the outer tube in mol L^{-1}.

In all the reactions MeOH and MeCN were HPLC grade, whereas ethanol and DCM were reagent grade and used without further purification. All reactions were conducted in air unless otherwise stated.

Experimental for the amine macrocycle HL^{aa}

HL^{aa}: To a bright yellow solution of HL^{Et} (254 mg, 0.857 mmol) in a mixture of ethanol (30 mL) and dichloromethane (5 mL) was slowly added small portions solid $NaBH_4$ (260 mg, 6.85 mmol, 8 equivalents) over a 10 minute period. The bright yellow solution slowly faded in colour and became cloudy over about 20 minutes after addition of $NaBH_4$. The resulting mixture was stirred at room temperature for 48 hours. Acetone (10 mL) was added to the off-white cloudy mixture. The solvent was removed by rotary evaporation and the residue was extracted with RT chloroform (3 x 50 mL). The combined chloroform extracts were washed with water (3 x 20 mL), dried over $MgSO_4$ and the solvent removed, giving a pale yellow oil which upon drying *in vacuo* resulted in HL^{aa} as an off-white crystalline solid (252 mg, 93%). (Found: C, 70.81; H, 8.41; N, 17.18%. Calc. for $[C_{18}H_{24}N_4\cdot 0.4EtOH\cdot 0.3H_2O]$ (320.25 g mol^{-1}): C, 70.51; H, 8.50; N, 17.49%). IR (ATR): ν/cm^{-1} = 3275, 3256, 3216, 2838, 1599, 1580, 1502, 1454, 1315, 1285, 1223, 1183, 1158, 1105, 1072, 1018, 979, 965, 940, 857, 840, 794, 742, 727, 646, 613, 593, 540, 466. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ/ppm = 2.10–1.70 (br, 3H, NHb/c/d), 2.71 (m, 4H, H9), 2.84 (m, 4H, H8), 3.79 (s, 4H, H7), 6.85 (apparent td, *J* = 7.4, 1.2 Hz, 2H, H4), 7.18 (m, 4H, H3/5), 7.28 (d, *J* = 8.1, 1.1 Hz, 2H, H6), 8.35 (s, 1H, NHa). ^{13}C NMR (500 MHz, $CDCl_3$, 298 K): δ/ppm = 48.05 (C9), 48.30 (C8), 53.02 (C7), 118.22 (C6), 120.19 (C4), 128.21 (C5), 128.66 (C2), 130.65 (C3), 143.63 (C1). ESI(+) MS (m/z) (MeOH): [$C_{18}H_{24}N_4$+H] expected 297.2084, found 297.2074.

Experimental for the nickel(II) complexes

[$Ni^{II}L^{ia}$](BF_4)•H_2O•DCM (3): To a pale yellow solution of HL^{aa} (71.3 mg, 0.241 mmol) in a mixture of dichloromethane (5 mL) and methanol (10 mL) was added a solution of nickel(II) tetrafluoroborate hexahydrate (81.9 mg, 0.241 mmol) in methanol (3 mL), causing an immediate change to dark blue in colour. To this solution was added triethylamine (24.3 mg, 0.241 mmol) in methanol (1 mL) resulting in a colour change from dark blue to dark green. The dark green solution was stirred at RT for 1 hour, concentrated to 20 mL under reduced pressure and subjected to diethyl ether vapour diffusion. After about 1-2 days the colour of the solution in the ether jar had turned dark red. After 2 days the resulting dark red/black solid was collected by filtration and dried *in vacuo* (98.3 mg, 75%). (Found: C, 42.19; H, 5.02; N, 10.01%. Calc. for [$C_{18}H_{21}N_4BF_4Ni$•H_2O•DCM] (541.83 g mol^{-1}): C, 42.12; H, 4.65; N, 10.34%). ESI(+) MS (m/z) (MeCN): [$Ni^{II}L^{aa}$-2H]$^+$ expected 351.1118, found 351.1114. UV-vis (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) = 364 (4379), 431 (4096), 970 (800). μ (Gouy) = 0 BM. μ (Evans in MeCN at 298 K) = 2.93 BM. Λ_m (MeCN) = 159 Ω^{-1} cm^2 mol^{-1}.

$Ni^{II}L^{aa}$(BF_4)•2H_2O•DCM (4): Under an Ar atmosphere, to a pale yellow solution of HL^{aa} (68.4 mg, 0.231 mmol) in a 1:1 mixture of dichloromethane and acetonitrile (8 mL) was added a solution of nickel(II) tetrafluoroborate hexahydrate (78.6 mg, 0.231 mmol) in acetonitrile (2 mL), causing an immediate colour change to dark blue. To this solution was added triethylamine (23.4 mg, 0.231 mmol) in acetonitrile (1 mL) resulting in a dark green colour. This dark green solution was stirred at RT for 20 minutes, then diethyl ether (150 mL) was added resulting in the formation of a pale green precipitate which was filtered off under a constant flow of Ar and dried *in vacuo* (74 mg, 57%). (Found: C, 40.28; H, 5.31; N, 9.98%. Calc. for [$C_{18}H_{23}N_4BF_4Ni$•2H_2O•DCM] (561.86 g mol^{-1}): C, 40.62; H, 5.20; N, 9.97%. ESI(+) MS (m/z): [$Ni^{II}L^{aa}$]$^+$ expected 353.1271, found 353.1271. UV-vis (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) = 452 (242), 524 (136), 872 (61). μ (Evans in MeCN at 298 K) = 3.42 BM. μ (PPMS at 300 K) = 3.50 BM. Λ_m (MeCN) = 162 Ω^{-1} cm^2 mol^{-1}.

[$Ni^{II}HL^{aa}$($NCS)_2$]•$CHCl_3$ (5): To a pale yellow solution of HL^{aa} (43.4 mg, 0.146 mmol) in chloroform (10 mL) in air was added solid nickel(II) thiocyanate (25.6 mg, 0.146 mmol), resulting in a pale green suspension. Acetonitrile (15 mL) was added to the suspension. The resulting suspension was stirred at RT for 2 days by which time it was much darker in colour. It was filtered, and the filtrate allowed to slowly evaporate, giving pale orange crystals which were collected by filtration and dried *in vacuo* (27 mg, 32 %). (Found: C, 43.12; H, 4.52; N, 14.62; S, 11.26%. Calc. for [$C_{20}H_{24}N_6S_2Ni$•$CHCl_3$] (590.64 g mol^{-1}): C, 42.70; H, 4.27; N, 14.23; S, 10.86%). ESI(+) MS (m/z) (MeCN): [$Ni^{II}L^{aa}$-H]$^+$ expected 353.1280, found 353.1271. UV-vis (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) = 438 (546), 567 (129), 938 (27). μ (Evans in MeCN at 298 K) = 3.25 BM. μ (PPMS at 300 K) = 3.32 BM. Λ_m (MeCN) = 88 Ω^{-1} cm^2 mol^{-1}.

Figure S1. ^{1}H NMR and ^{13}C NMR spectra of H**L**$^{\mathbf{aa}}$ in $CDCl_3$.

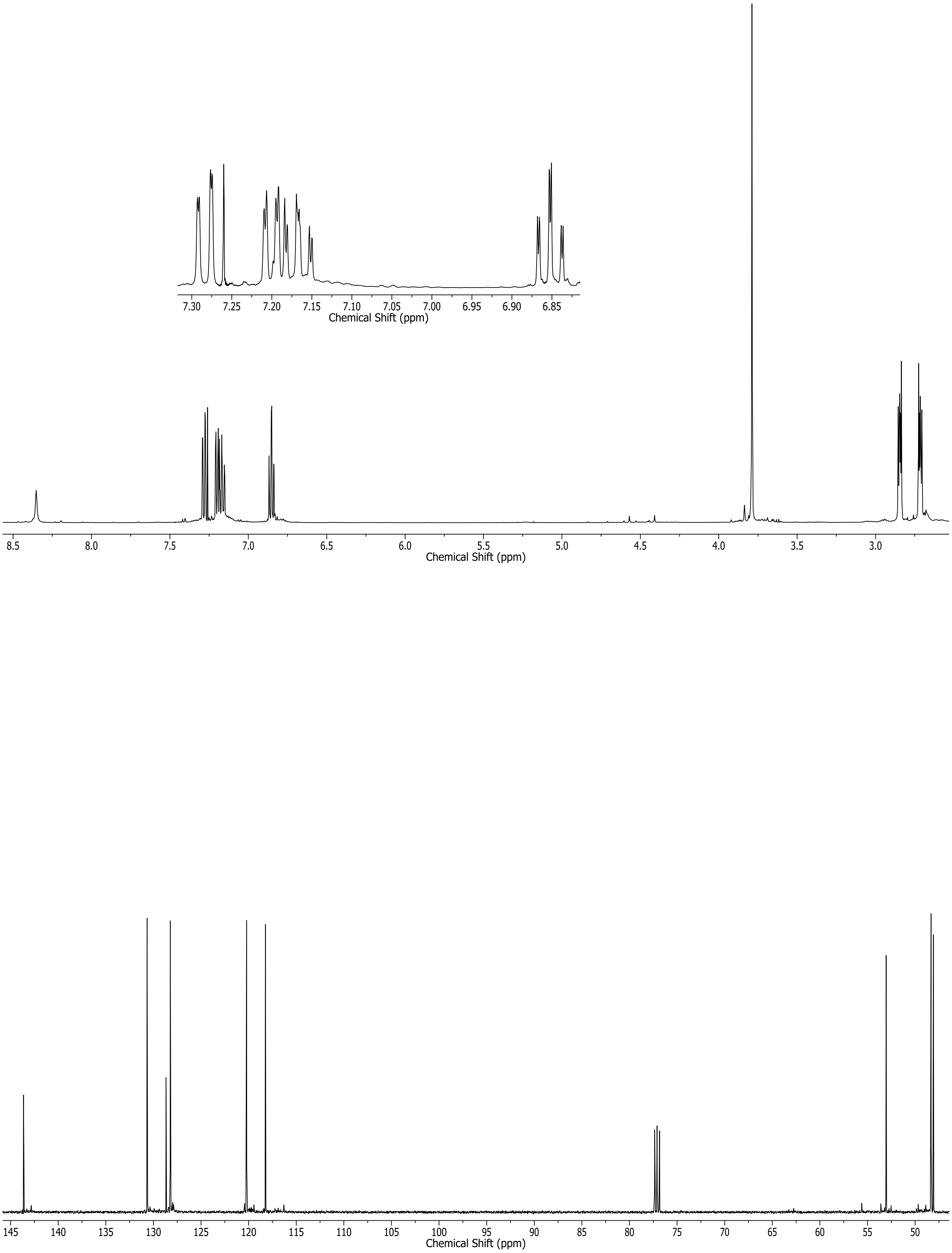
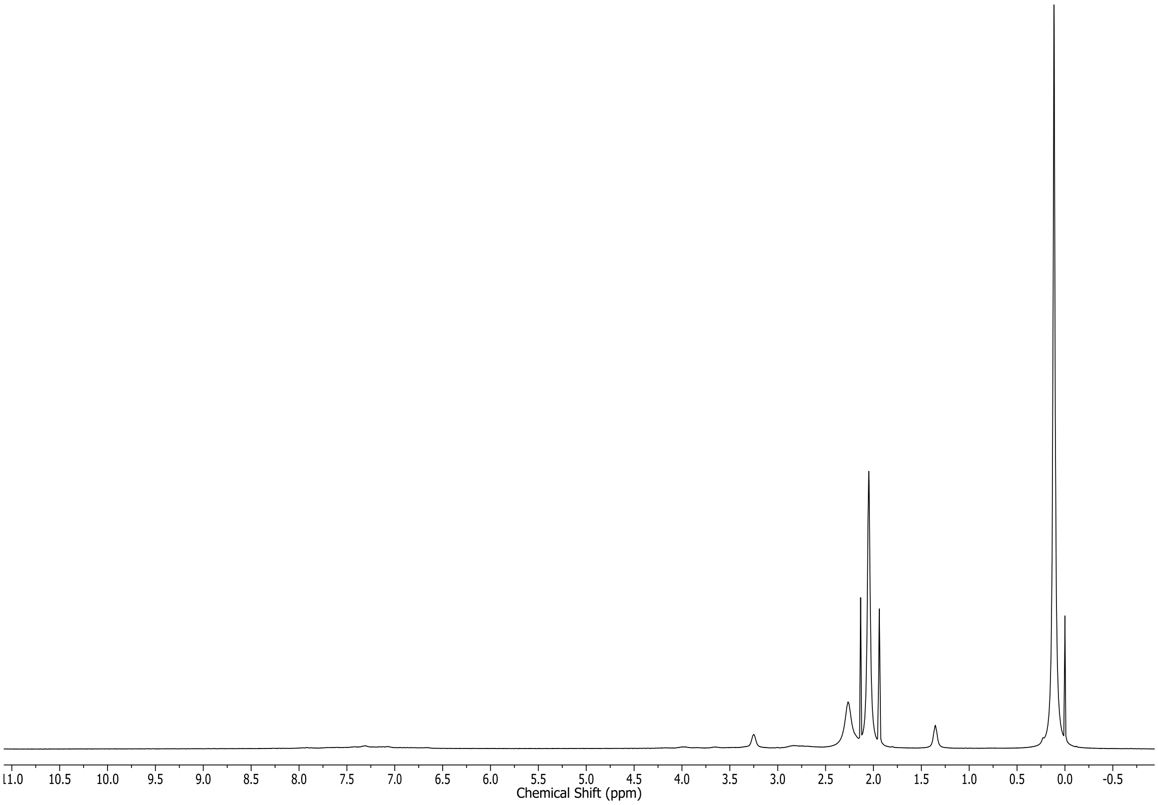


Figure S2. Evans method ^{1}H NMR spectrum, obtained in a double walled NMR tube, for [Ni^{II}**L^{ia}**]$(BF_4)\bullet H_2O\bullet$DCM (**3**) in CD_3CN (outer) *vs.* pure CD_3CN (inner).



Calculation of magnetic moment from the shift of the acetonitrile peak in the NMR spectrum:

Mass = 2.565 mg; Volume = 0.7 mL; χ_0 = -0.534 x 10^{-6}

Concentration = m = $\frac{mass}{MW x\ Volume} = \frac{2.565\ x\ 10^{-3}}{541.83\ x\ 0.0007} = 6.76\ x\ 10^{-3}\ mol\ L^{-1}$

CD_3CN (inner tube) = 969.36 Hz $\qquad$ CD_3CN (outer tube) = 1024.22 Hz

Δf = 1024.22 – 969.36 = 54.86; f = 5 x 10^8 Hz; m = concentration = 6.76 x 10^{-3} mol L^{-1}

$\chi_g = \frac{3\Delta f}{2\pi f m} + \chi_0 = \frac{3\ x\ 54.86}{2\ x\ 3.14\ x\ 5\ x\ 10^8\ x\ 6.76\ x\ 10^{-3}} + (-0.534\ x\ 10^{-6})$ = 7.22 x 10^{-6} $cm^3\ g^{-1}$

$\chi_{mT} = \chi_g\ x\ MW\ of\ sample = 7.22\ x\ 10^{-6}\ x\ 541.83 = 3.91\ x\ 10^{-3}$ $cm^3\ mol^{-1}$

$\chi_{m20} = \chi_{Tm}\ x\ \left(\frac{T}{293}\right) = 3.91\ x\ 10^{-3}\ x\ \left(\frac{291}{293}\right) = 3.89\ x\ 10^{-3}$ $cm^3\ mol^{-1}$

$\chi^{corr} = \chi_{m20} - \chi^{dia} = 3.89\ x\ 10^{-3} + 270.25\ x\ 10^{-6}$ = 4.16 x 10^{-3} $cm^3\ mol^{-1}$

$\mu_{eff} = 2.83\sqrt{293\ x\ \chi_{corr}}$ $= 2.83\sqrt{293\ x\ 4.16\ x\ 10^{-3}}$ = 3.12 BM

Figure S3. Evans method ^{1}H NMR spectrum, obtained in a double walled NMR tube, for $[Ni^{II}\mathbf{L^{aa}}](BF_4)\bullet 2H_2O\bullet DCM$ (**4**) in CD_3CN (outer) *vs.* pure CD_3CN (inner). Mass used: 3.296 mg; CD_3CN positions: 969.41 Hz (inner tube) and 1048.15 Hz (outer tube) so μ_{eff} = 3.42 BM.

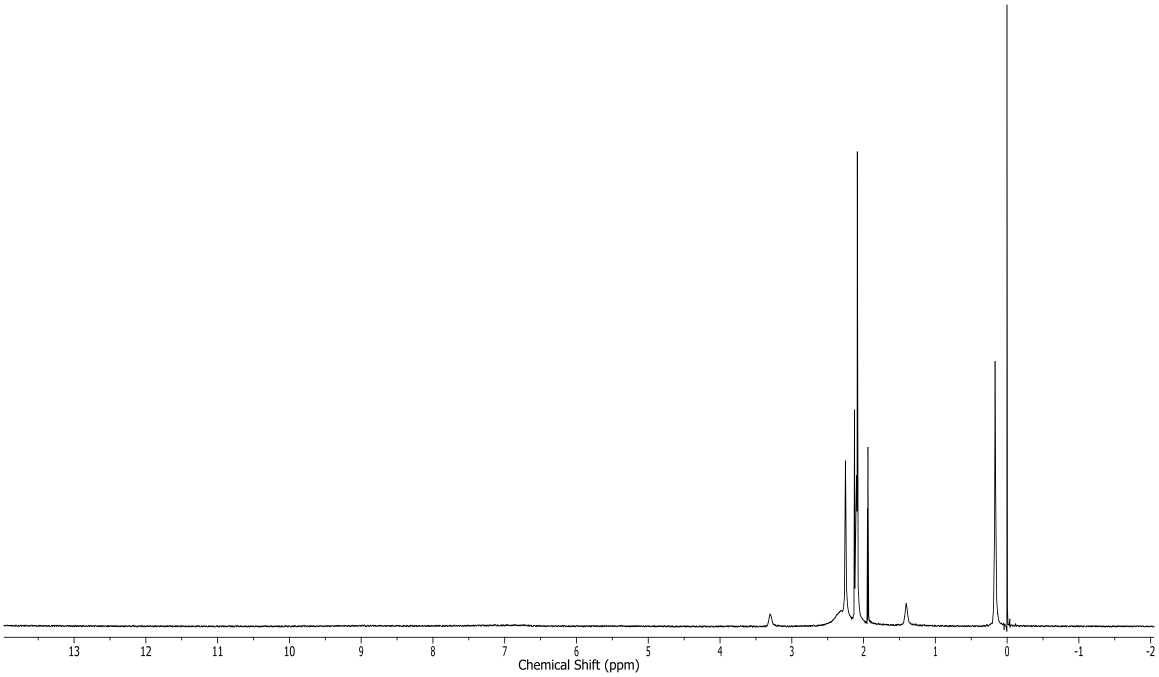


Figure S4. Evans method ^{1}H NMR spectrum, obtained in a double walled NMR tube, for [Ni^{II}**HL^{aa}**(NCS)$_2$]•CHCl$_3$ (**5**) in CD$_3$CN (outer) *vs.* pure CD$_3$CN (inner). Mass used: 2.936 mg; CD$_3$CN positions: 969.36 Hz (inner tube) and 1026.69 Hz (outer tube) so μ_{eff} = 3.25 BM.

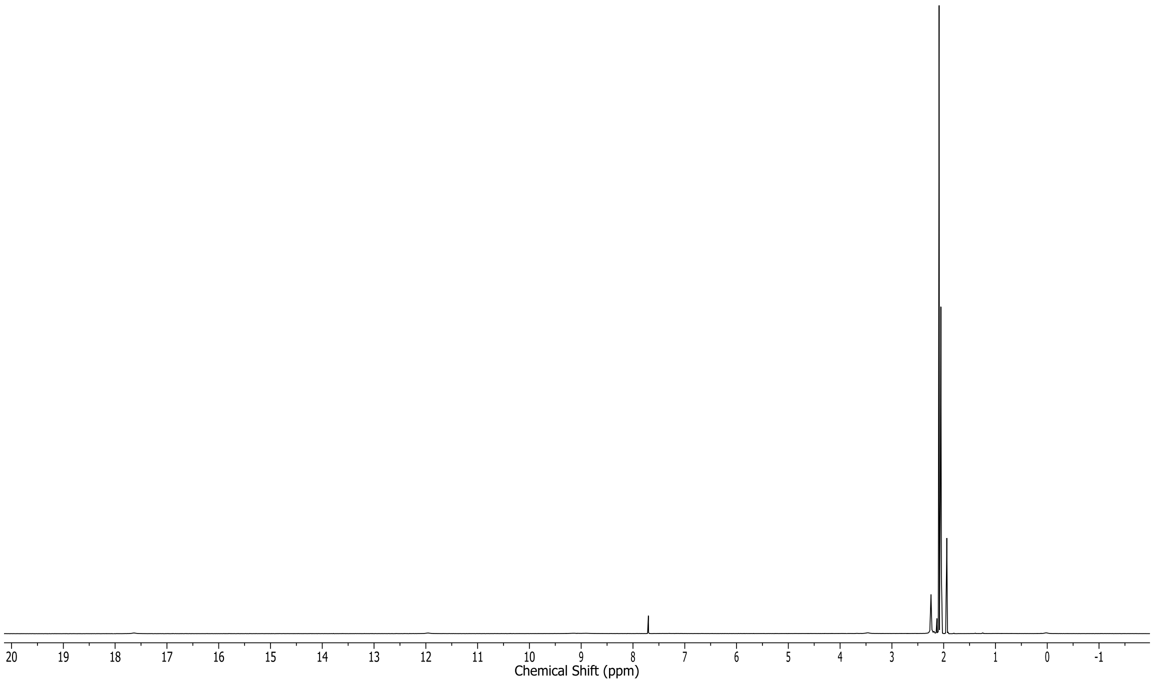


Figure S5. ^{1}H NMR spectrum of [Ni^{II}**L**$^{\mathbf{Et}}$](BF_4)•H_2O (**2**) in CD_3CN (400 MHz) **before** addition of a drop of pyridine.

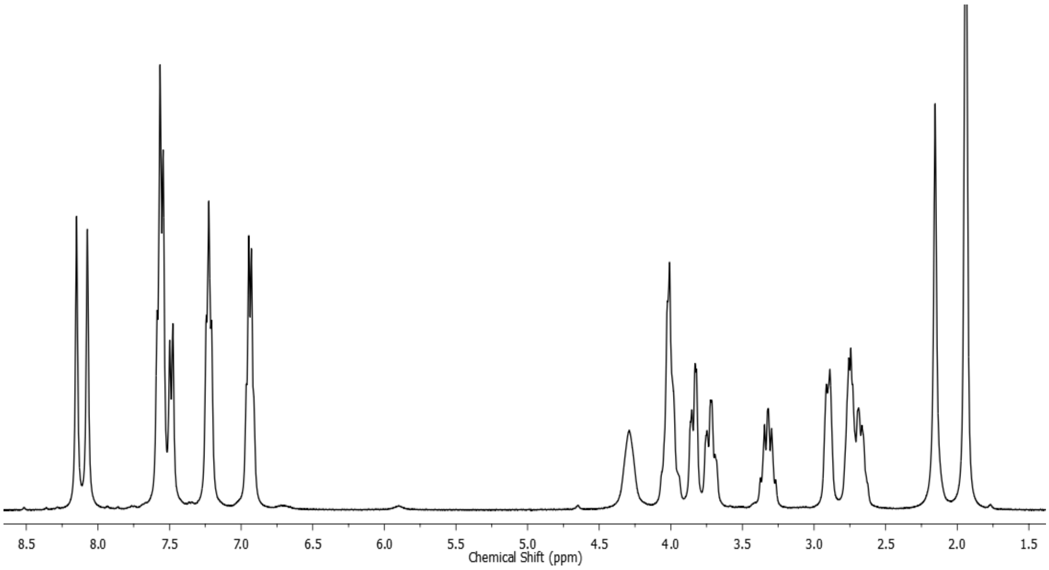
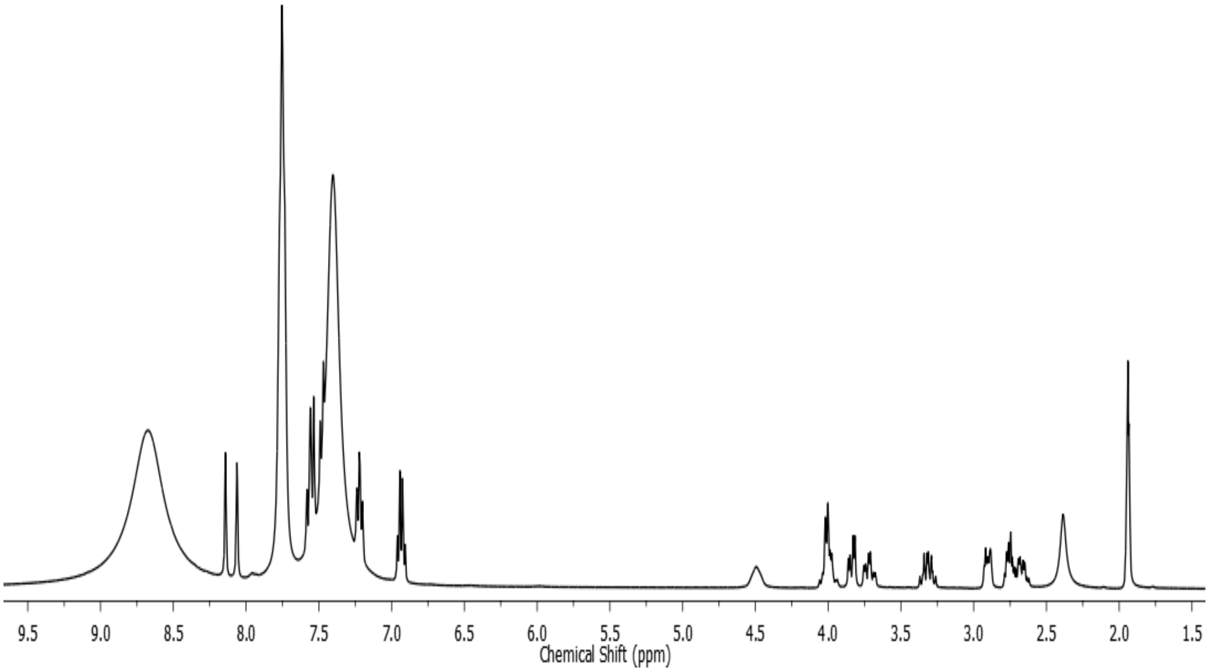


Figure S6. ^{1}H NMR spectrum of [Ni^{II}**L**$^{\mathbf{Et}}$](BF_4)•H_2O (**2**) in CD_3CN (400 MHz) **after** addition of a drop of pyridine.



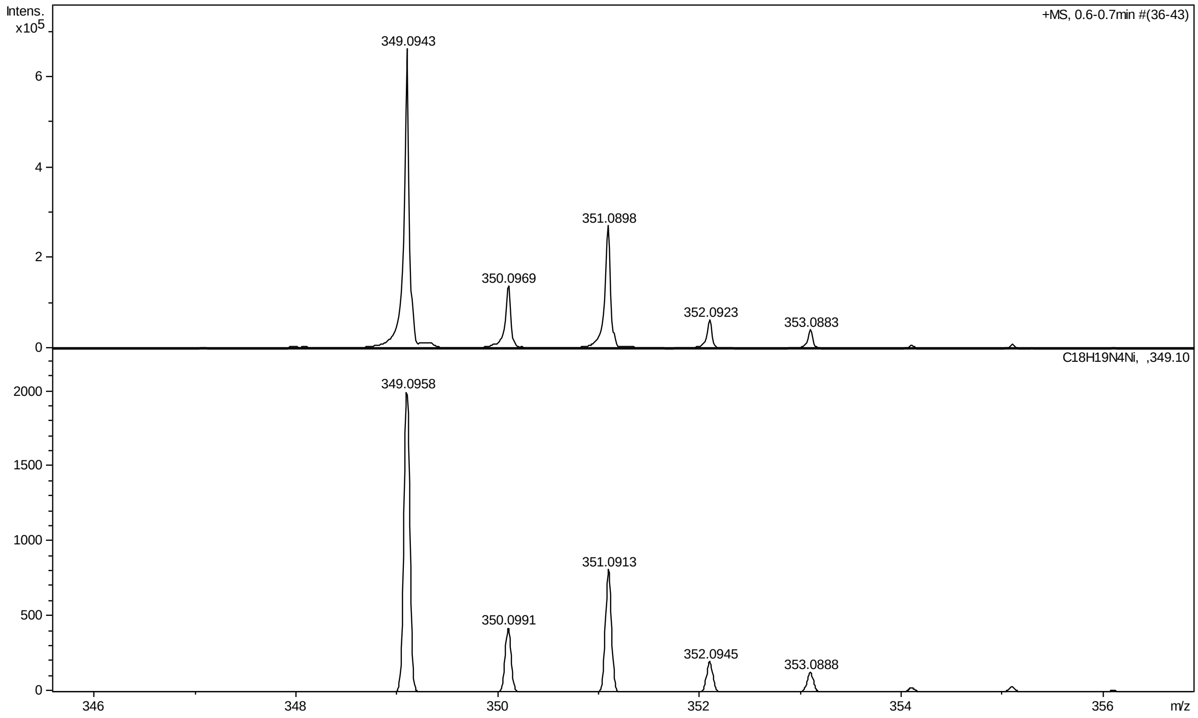


Figure S7. The observed (top) and simulated (bottom) positive ion mass spectrum pattern for the $[Ni^{II}L^{aa}\text{-}4H]^+ = [Ni^{II}L^{Et}]^+$ moiety of $[Ni^{II}\mathbf{L}^{\mathbf{Et}}](BF_4)\bullet H_2O$ (**2**).

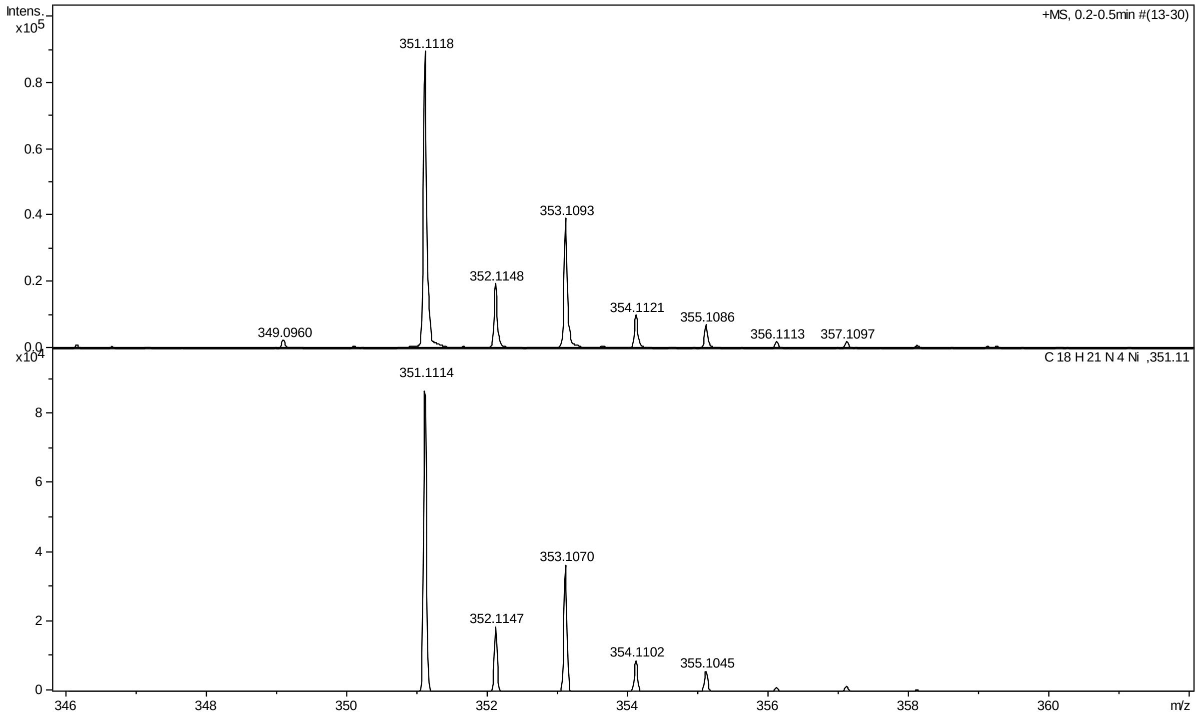


Figure S8. The observed (top) and simulated (bottom) positive ion mass spectrum pattern for the $[Ni^{II}L^{aa}\text{-}2H]^+ = [Ni^{II}L^{ia}]^+$ moiety of $[Ni^{II}\mathbf{L}^{\mathbf{ia}}](BF_4)\bullet H_2O\bullet DCM$ (**3**).

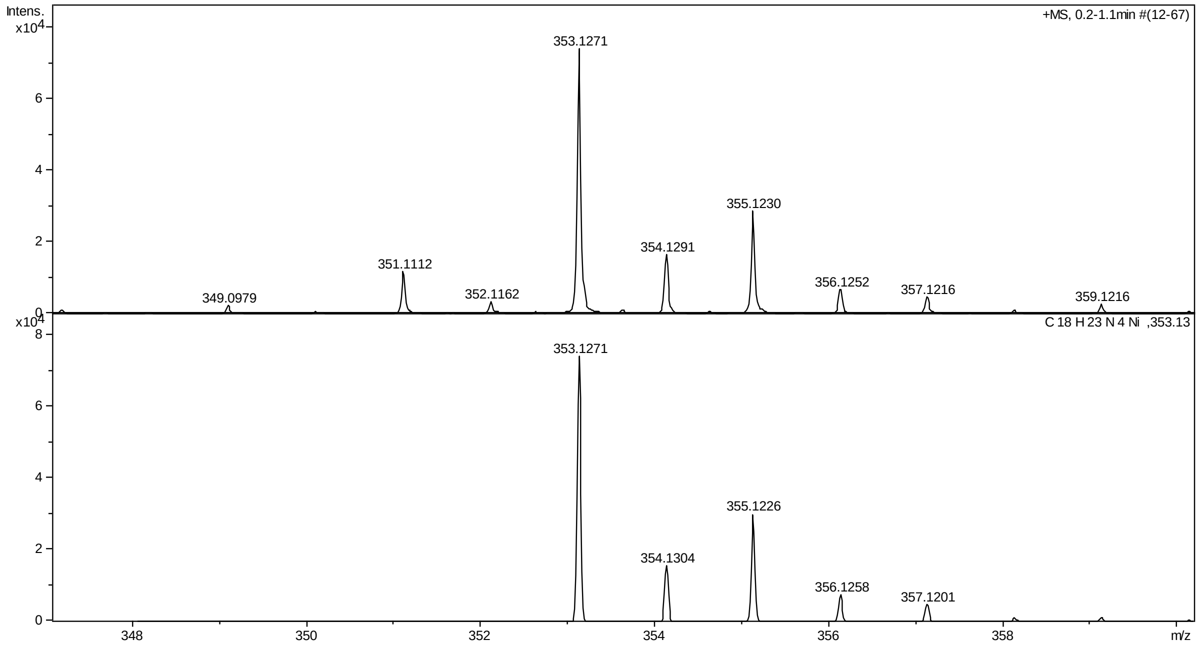


Figure S9. The observed (top) and simulated (bottom) positive ion mass spectrum pattern for the $[Ni^{II}L^{aa}]^+$ moiety in $[Ni^{II}\mathbf{L^{aa}}](BF_4)\cdot2H_2O\cdot DCM$ (**4**).

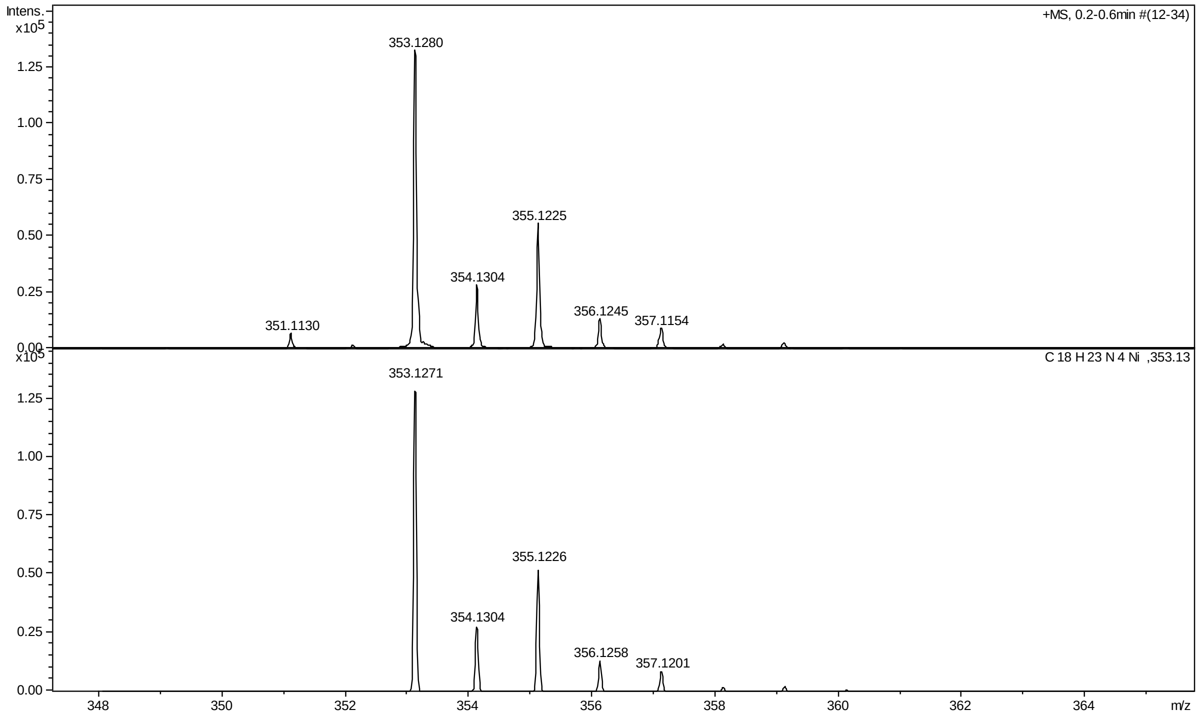


Figure S10. The observed (top) and simulated (bottom) positive ion mass spectrum pattern for the $[Ni^{II}L^{aa}\text{-}H]^+$ moiety of $[Ni^{II}\mathbf{HL^{aa}}(NCS)_2]\cdot CHCl_3$ (**5**).

Table S1. Crystal structure determination details for the complexes, $[\mathrm{Ni^{II}}\mathbf{L}^{\mathbf{Et}}](\mathrm{BF_4})$ (**2**), $[\mathrm{Ni^{II}}\mathbf{L}^{\mathbf{ia}}](\mathrm{BF_4})$ (**3**), and $[\mathrm{Ni^{II}}\mathbf{HL}^{\mathbf{aa}}(\mathrm{NCS})_2]\bullet 0.3\mathrm{DCM}\bullet 0.15\mathrm{MeOH}\bullet 0.15\mathrm{H_2O}$ (**5**).

	$[\mathrm{Ni^{II}}\mathbf{L}^{\mathbf{Et}}](\mathrm{BF_4})$	$[\mathrm{Ni^{II}}\mathbf{L}^{\mathbf{ia}}](\mathrm{BF_4})$	$[\mathrm{Ni^{II}}\mathbf{HL}^{\mathbf{aa}}(\mathrm{NCS})_2]\bullet 0.3\mathrm{DCM}\bullet 0.15\mathrm{MeOH}\bullet 0.15\mathrm{H_2O}$
Emprical formula	$C_{18}H_{19}N_4BF_4Ni$	$C_{18}H_{21}N_4BF_4Ni$	$C_{20.45}H_{25.20}Cl_{0.60}N_6NiO_{0.30}S_2$
M_r	436.89	438.91	503.97
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P_n	$P2_1/c$	$P2_1/c$
a [Å]	7.2737(15)	9.8702(4)	13.7811(9)
b [Å]	10.6471(18)	18.1530(8)	20.5066(14)
c [Å]	11.3778(15)	11.2583(4)	9.1197(5)
α [°]	90	90	90
β [°]	94.181(3)	115.560(1)	106.797(2)
γ [°]	90	90	90
V [Å^3]	878.8(3)	1819.8(2)	2467.3(3)
Z	2	4	4
T [K]	90(2)	90(2)	91(2)
$\rho_{\mathrm{calcd.}}$ [gcm^{-3}]	1.651	1.602	1.357
µ [mm^{-1}]	1.156	1.117	1.041
F(000)	448	904	1050
Crystal size [mm]	0.20 x 0.10 x 0.08	0.50 x 0.39 x 0.37	0.26 x 0.24 x 0.13
Θ range for data collection [°]	1.79 to 26.02	2.29 to 26.11	2.54 to 26.37
Reflections collected	11732	12160	18695
Independent reflections	3339	3496	4882
R(int)	0.0574	0.0342	0.0435
Max. and min. transmission	0.9132 and 0.6614	0.6827 and 0.6051	0.8766 and 0.7736
Data/ restraints/ parameters	3339 / 2 / 257	3496 / 0 / 261	4882 / 2 / 302
Goof (F^2)	1.014	1.043	1.061
R_1 [$I > 2\sigma(I)$]	0.0504	0.0322	0.0494
wR_2 [all data]	0.1169	0.0772	0.1579

References

1. D. F. Evans, *J. Chem. Soc.*, 1959, 2003-2005.
2. R. C. Weast, M. J. Astle and W. H. Beyer, *CRC Handbook of Chemistry and Physics*, 64 edn., CRC Press, 1983.