The Tyranny of Arm-Wrestling Methyls on Iron(II) Spin State in Pseudo-Octahedral [Fe(didentate)$_3$] Complexes.

Neel Deorukhkar, Timothée Lathion, Laure Guénée, Céline Besnard and Claude Piguet*

Supporting Information

(22 pages)

Table S1. Elemental Analysis of the primary $[Fe(\mathbf{L5})_3](CF_3SO_3)_2 \cdot 1.5H_2O$, $[Ni(\mathbf{L5})_3](BF_4)_2 \cdot 1.5H_2O \cdot 1.5CH_3CN$ and $[Zn(\mathbf{L5})_3](BF_4)_2 \cdot 4H_2O$ complexes.

Molecular formula, Mw /g·mol^{-1}	Elemental analysis
$[Fe(\mathbf{L5})_3](CF_3SO_3)_2 \cdot 1.5H_2O$	calcd. %C 46.69 %H 3.71 %N 15.94
MM = 1053.9 g/mol	found %C 47.03 %H 3.52 %N 15.58
$[Ni(\mathbf{L5})_3](BF_4)_2 \cdot 1.5H_2O \cdot 1.5CH_3CN$	calcd. %C 50.70 %H 4.41 %N 18.98
MM = 993.6 g/mol	found %C 50.59 %H 4.26 %N 19.13
$[Zn(\mathbf{L5})_3](BF_4)_2 \cdot 4H_2O$	calcd. %C 47.66 %H 4.50 %N 17.10
MM = 983.8 g/mol	found %C 47.22 %H 4.02 %N 17.53

Table S2 Crystal data and structure refinement for **L5**.

CCDC number	1988655
Empirical formula	$C_{13}H_{12}N_4$
Formula weight	224.27
Temperature	180 K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 19.8873(10) Å b = 3.90974(16) Å c = 14.8924(7) Å α = 90° β = 107.876(5)° γ = 90°
Volume	1102.04(9) Å^3
Z	4
Density (calculated)	1.352 Mg/m^3
Absorption coefficient	0.678 mm^{-1}
F(000)	472
Crystal size	0.27 x 0.107 x 0.071 mm^3
Theta range for data collection	2.334 to 69.013°
Index ranges	$-23 \le h \le 23$, $-4 \le k \le 4$, $-8 \le l \le 17$
Reflections collected	3876
Independent reflections	2010 [R(int) = 0.0146]
Completeness to theta = 67.500°	99.50%
Absorption correction	Analytical
Max. and min. transmission	0.955 and 0.872
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2010 / 0 / 156
Goodness-of-fit on F^2	1.086
Final R indices [I>2sigma(I)]	$R1$ = 0.0385, w$R2$ = 0.0987
R indices (all data)	$R1$ = 0.0424, w$R2$ = 0.1010
Largest diff. peak and hole	0.209 and -0.186 e.Å^{-3}

Table S3 Crystal data and structure refinement for $[Fe(\mathbf{L5})_3](ClO_4)_2$ (**I**) and $[Ni(\mathbf{L5})_3](ClO_4)_2$ (**II**).

	I	**II**
CCDC numbers	1988657	1988659
Empirical formula	$C_{39}H_{36}Cl_2FeN_{12}O_8$	$C_{39}H_{36}Cl_2N_{12}NiO_8$
Formula Unit	$C_{39}H_{36}Cl_2FeN_{12}O_8$	$C_{39}H_{36}Cl_2N_{12}NiO_8$
Formula weight	927.55	930.41
Temperature	180 K	180 K
Wavelength	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 8.2485(3) Å b = 38.5553(14) Å c = 13.0716(5) Å α = 90° β = 104.291(4)° γ = 90°	a = 8.27280(10) Å b = 38.2659(6) Å c = 12.9930(2) Å α = 90° β = 104.434(2)° γ = 90°
Volume	4028.5(3) Å^3	3983.31(11) Å^3
Z	4	4
Density (calculated)	1.529 Mg/m^3	1.551 Mg/m^3
Absorption coefficient	4.818 mm^{-1}	2.538 mm^{-1}
F(000)	1912	1920
Crystal size	0.245 x 0.173 x 0.047 mm^3	0.273 x 0.132 x 0.056 mm^3
Theta range for data collection	2.292 to 68.768°	2.309 to 70.759°
Index ranges	$-8 \le h \le 9$, $-45 \le k \le 46$, $-15 \le l \le 15$	$-9 \le h \le 7$, $-46 \le k \le 32$, $-15 \le l \le 15$
Reflections collected	17901	16391
Independent reflections	7364 [R(int) = 0.0243]	7483[R(int) = 0.0382]
Completeness to theta	(67.684°) 99.8%	(67.684°) 99.7%
Absorption correction	Analytical	Gaussian
Max. and min. transmission	0.801 and 0.489	1.000 and 0.732
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7364 / 158 / 582	7483 / 0 / 565
Goodness-of-fit on F^2	1.032	1.094
Final R indices [I>2sigma(I)]	$R1$ = 0.0390, w$R2$ = 0.0934	$R1$ = 0.0563, w$R2$ = 0.1408
R indices (all data)	$R1$ = 0.0435, w$R2$ = 0.0964	$R1$ = 0.0657, w$R2$ = 0.1451
Largest diff. peak and hole	0.466 and -0.371 e.Å^{-3}	0.600 and -0.830 e.Å^{-3}

Table S4 Crystal data and structure refinement for $[Ni(\mathbf{L5})_3](BF_4)_2 \cdot H_2O$ (**III**) and $[Zn(\mathbf{L5})_3](ClO_4)_2$ (**IV**).

	III	**IV**
CCDC number	1988656	1988657
Empirical formula	$C_{78}H_{76}B_4F_{16}N_{24}Ni_2O_2$	$C_{39}H_{36}Cl_2N_{12}O_8Zn$
Formula Unit	$C_{39}H_{36}B_2F_8N_{12}Ni + H_2O$	$C_{39}H_{36}Cl_2N_{12}O_8Zn$
Formula weight	1846.28	937.07
Temperature	180 K	180 K
Wavelength	0.71073 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 23.0916(4) Å b = 23.1612(5) Å c = 15.8218(2) Å α = 90° β = 99.1601(14)° γ = 90°	a = 8.2559(3) Å b = 38.5861(9) Å c = 13.0163(3) Å α = 90° β = 104.250(3)° γ = 90°
Volume	8354.0(3) Å^3	4018.9(2) Å^3
Z	4	4
Density (calculated)	1.468 Mg/m^3	1.549 Mg/m^3
Absorption coefficient	0.549 mm^{-1}	2.668 mm^{-1}
F(000)	3792	1928
Crystal size	0.44 x 0.32 x 0.238 mm^3	0.192 x 0.09 x 0.028 mm^3
Theta range for data collection	1.787 to 28.156°	2.290 to 68.857°
Index ranges	$-25 \le h \le 30$, $-30 \le k \le 28$, $-20 \le l \le 20$	$-9 \le h \le 9$, $-30 \le k \le 46$, $-15 \le l \le 10$
Reflections collected	42210	17094
Independent reflections	17452[R(int) = 0.0306]	7341[R(int) = 0.0261]
Completeness to theta	(25.242°) 99.7%	(67.684°) 99.7%
Absorption correction	Gaussian	Gaussian
Max. and min. transmission	1.000 and 0.344	1.000 and 0.728
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	17452 / 225 / 1187	7341 / 124 / 611
Goodness-of-fit on F^2	1.034	1.019
Final R indices [I>2sigma(I)]	$R1$ = 0.0476, w$R2$ = 0.1151	$R1$ = 0.0348, w$R2$ = 0.0847
R indices (all data)	$R1$ = 0.0668, w$R2$ = 0.1287	$R1$ = 0.0475, w$R2$ = 0.0918
Largest diff. peak and hole	0.789 and -0.541 e.Å^{-3}	0.444 and -0.351 e.Å^{-3}

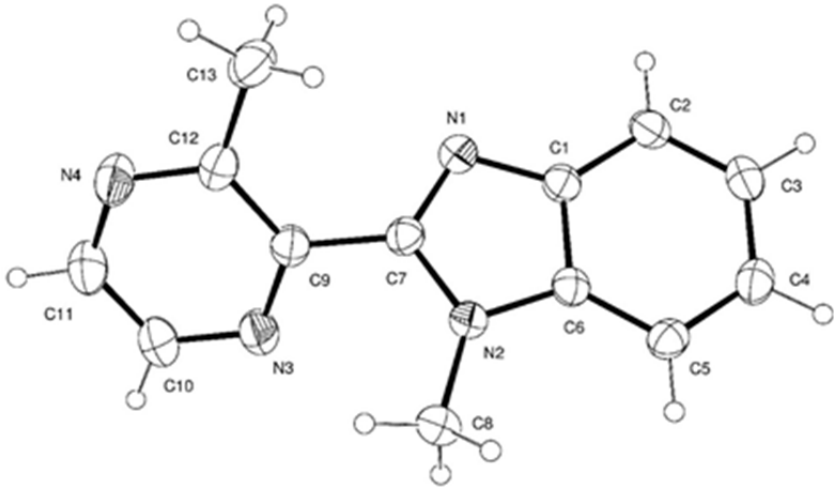

Figure S1 ORTEP view of the ligand **L5** (ellipsoids are drawn at 50% probability) with numbering scheme.

Table S5: Selected bond distances (Å) and bond angles (°) for ligand **L5**.

Bond distances (Å)			
N(1)-C(1)	1.3862(17)	C(1)-C(6)	1.4012(19)
N(1)-C(7)	1.3163(18)	C(2)-C(3)	1.381(2)
N(2)-C(6)	1.3775(17)	C(3)-C(4)	1.399(2)
N(2)-C(7)	1.3755(17)	C(4)-C(5)	1.379(2)
N(2)-C(8)	1.4518(17)	C(5)-C(6)	1.3914(19)
N(3)-C(9)	1.3397(19)	C(7)-C(9)	1.4769(18)
N(3)-C(10)	1.3326(19)	C(9)-C(12)	1.403(2)
N(4)-C(11)	1.333(2)	C(10)-C(11)	1.377(2)
N(4)-C(12)	1.3409(19)	C(12)-C(13)	1.496(2)
C(1)-C(2)	1.3940(19)		

Bond angles (°)			
C(7)-N(1)-C(1)	104.67(11)	N(2)-C(6)-C(5)	131.55(13)
C(6)-N(2)-C(8)	124.58(11)	C(5)-C(6)-C(1)	122.77(12)
C(7)-N(2)-C(6)	106.18(11)	N(1)-C(7)-N(2)	113.37(11)
C(7)-N(2)-C(8)	129.16(11)	N(1)-C(7)-C(9)	124.45(12)
C(10)-N(3)-C(9)	116.95(13)	N(2)-C(7)-C(9)	121.87(12)
C(11)-N(4)-C(12)	117.56(13)	N(3)-C(9)-C(7)	114.84(12)
N(1)-C(1)-C(2)	130.00(13)	N(3)-C(9)-C(12)	122.19(13)
N(1)-C(1)-C(6)	110.10(11)	C(12)-C(9)-C(7)	122.94(13)
C(2)-C(1)-C(6)	119.89(12)	N(3)-C(10)-C(11)	121.20(15)
C(3)-C(2)-C(1)	117.59(13)	N(4)-C(11)-C(10)	122.42(14)
C(2)-C(3)-C(4)	121.73(13)	N(4)-C(12)-C(9)	119.69(14)
C(5)-C(4)-C(3)	121.68(13)	N(4)-C(12)-C(13)	117.37(13)
C(4)-C(5)-C(6)	116.34(13)	C(9)-C(12)-C(13)	122.94(13)
N(2)-C(6)-C(1)	105.67(11)		

Table S6: Selected least-squares planes data for Ligand **L5**

Least Squares Planes Description	Mean Deviation (Å)	Max. Deviation (Å) and atom	Dihedral Angle (°)
Pyrazine 1 C9 N3 C10 C11 N4 C12	0.002	0.03 (N3)	35.2
Benzimidazole 1 C7 N2 C6 C5 C4 C3 C2 C1 N1	0.012	0.020 (C7)	

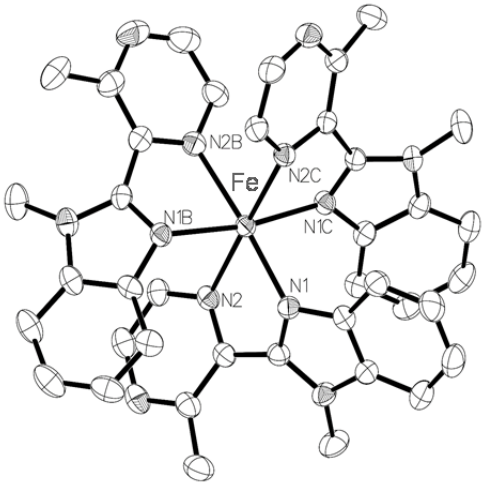

Figure S2 ORTEP view of *mer*-$[Fe(\mathbf{L5})_3]^{2+}$ in the crystal structure of $[Fe(\mathbf{L5})_3](ClO_4)_2$ (**I**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and ClO_4^- counter anions are omitted for clarity.

Table S7 Selected bond distances (Å) and bond angles (°) for $[Fe(\mathbf{L5})_3](ClO_4)_2$ (**I**).

Bond distances (Å)			
Fe(1)-N(2C)	2.2074(18)	Fe(1)-N(2B)	2.2757(19)
Fe(1)-N(1B)	2.1609(18)	Fe(1)-N(1)	2.1327(18)
Fe(1)-N(1C)	2.1343(18)	Fe(1)-N(2)	2.2427(19)

Bond angles (°)			
N(2C)-Fe(1)-N(2B)	81.33(7)	N(1C)-Fe(1)-N(2)	101.46(7)
N(2C)-Fe(1)-N(2)	178.12(6)	N(1)-Fe(1)-N(2C)	102.85(7)
N(1B)-Fe(1)-N(2C)	99.07(7)	N(1)-Fe(1)-N(1B)	101.92(7)
N(1B)-Fe(1)-N(2B)	75.86(7)	N(1)-Fe(1)-N(1C)	87.22(7)
N(1B)-Fe(1)-N(2)	82.72(7)	N(1)-Fe(1)-N(2B)	175.60(7)
N(1C)-Fe(1)-N(2C)	76.69(7)	N(1)-Fe(1)-N(2)	77.27(7)
N(1C)-Fe(1)-N(1B)	170.64(7)	N(2)-Fe(1)-N(2B)	98.60(7)
N(1C)-Fe(1)-N(2B)	95.15(7)		

Table S8 Selected least-squares planes data for complex for $[Fe(\mathbf{L5})_3](ClO_4)_2$ (**I**).

Least Squares Planes Description	Mean Deviation (Å)	Max. Deviation (Å) and atom	Dihedral Angle (°)
Pyrazine 1 N2 C13 C12 N4 C10 C9	0.017	0.025 (C9A)	40.4
Benzimidazole 1 N1 C8 N3 C6 C5 C4 C3 C2 C1	0.004	0.006 (N3A)	
Pyrazine 2 N2B C13B C12B N4B C10B C9B	0.022	0.033 (C9B)	40.2
Benzimidazole 2 C8B N1B C1B C2B C3B C4B C5B C6B N3B	0.028	0.040 (C6B)	
Pyrazine 3 N2C C13C C12C N4C C10C C9C	0.036	0.054 (C9C)	34.9
Benzimidazole 3 C8C N3C C6C C5C C4C C3C C2C C1C N1C	0.02	0.027 (C8C)	

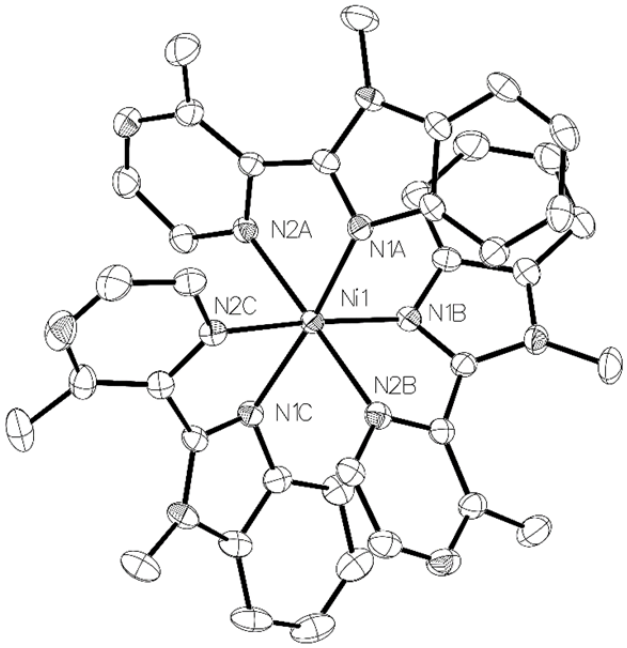

Figure S3 ORTEP view of *mer*-$[Ni(\mathbf{L5})_3]^{2+}$ in the crystal structure of $[Ni(\mathbf{L5})_3](ClO_4)_2$ (**II**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and ClO_4^- counter anions are omitted for clarity.

Table S9 Selected bond distances (Å) and bond angles (°) for $[Ni(\mathbf{L5})_3](ClO_4)_2$ (**II**).

Bond distances (Å)			
Ni(1)-N(1A)	2.069(3)	Ni(1)-N(2A)	2.117(3)
Ni(1)-N(1B)	2.070(3)	Ni(1)-N(2B)	2.142(3)
Ni(1)-N(1C)	2.114(3)	Ni(1)-N(2C)	2.162(3)

Bond angles (°)			
N(1A)-Ni(1)-N(1B)	86.25(11)	N(1B)-Ni(1)-N(2C)	176.17(11)
N(1A)-Ni(1)-N(1C)	173.50(11)	N(1C)-Ni(1)-N(2A)	97.34(10)
N(1A)-Ni(1)-N(2A)	78.94(10)	N(1C)-Ni(1)-N(2B)	81.94(10)
N(1A)-Ni(1)-N(2B)	101.75(10)	N(1C)-Ni(1)-N(2C)	78.27(10)
N(1A)-Ni(1)-N(2C)	95.87(11)	N(2A)-Ni(1)-N(2B)	179.18(10)
N(1B)-Ni(1)-N(1C)	99.76(11)	N(2A)-Ni(1)-N(2C)	82.33(10)
N(1B)-Ni(1)-N(2A)	101.24(10)	N(2B)-Ni(1)-N(2C)	97.14(10)
N(1B)-Ni(1)-N(2B)	79.28(11)		

Table S10 Selected least-squares planes data for complex $[Ni(\mathbf{L5})_3](ClO_4)_2$ (**II**)

Least Squares Planes Description	Mean Deviation (Å)	Max. Deviation (Å) and atom	Dihedral Angle (°)
Benzimidazole 1 N2A C13A C12A N4A C10A C9A	0.04	0.061 (C9A)	33.6
Pyrazine 1 C8A N1A C1A C2A C3A C4A C5A C6A N3A	0.019	0.027 (C3A)	
Benzimidazole 2 C13B C12B N4B C10B C9B N2B	0.022	0.034 (C9B)	38
Pyrazine 2 C8B N1B C1B C2B C3B C4B C5B C6B N3B	0.005	0.008 (C5B)	
Benzimidazole 3 N2C C9C C10C N4C C12C C13C	0.024	0.037 (C9C)	39.7
Pyrazine 3 C8C N1C C1C C2C C3C C4C C5C C6C N3C	0.034	0.053 (C6C)	

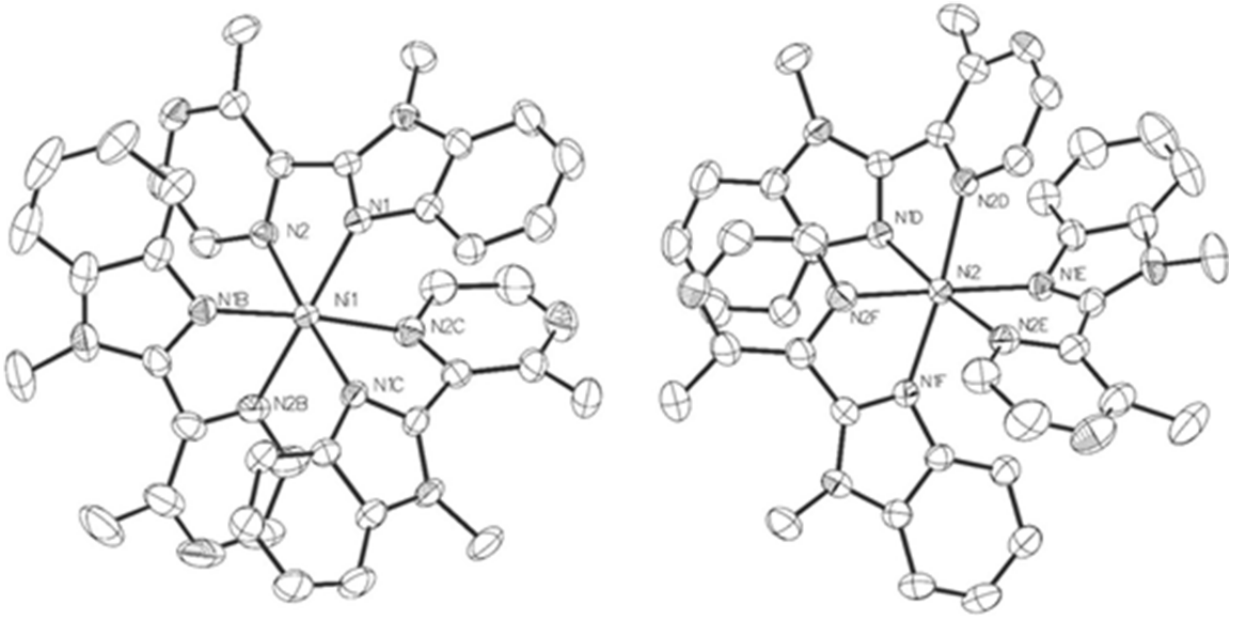

Figure S4 ORTEP view of the two different *fac*-$[Ni(\mathbf{L5})_3]^{2+}$ cations in the asymmetric unit of the crystal structure of $[Ni(\mathbf{L5})_3](BF_4)_2{\cdot}H_2O$ (**III**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and BF_4^- counter anions are omitted for clarity.

Table S11 Selected bond distances (Å) and bond angles (°) for $[Ni(\mathbf{L5})_3](BF_4)_2{\cdot}H_2O$ (**III**).

Bond distances (Å)			
Ni(1)-N(1)	2.101(2)	Ni(2)-N(2E)	2.108(2)
Ni(1)-N(1B)	2.067(2)	Ni(2)-N(1F)	2.059(2)
Ni(1)-N(2)	2.1199(19)	Ni(2)-N(2D)	2.147(2)
Ni(1)-N(1C)	2.0756(19)	Ni(2)-N(1D)	2.084(2)
Ni(1)-N(2C)	2.138(2)	Ni(2)-N(1E)	2.094(2)
Ni(1)-N(2B)	2.122(2)	Ni(2)-N(2F)	2.127(2)

Bond angles (°)			
N(1)-Ni(1)-N(2)	79.73(8)	N(2E)-Ni(2)-N(2D)	96.02(8)
N(1)-Ni(1)-N(2C)	83.30(8)	N(2E)-Ni(2)-N(2F)	96.36(9)
N(1)-Ni(1)-N(2B)	176.06(8)	N(1F)-Ni(2)-N(2E)	86.11(8)
N(1B)-Ni(1)-N(1)	102.44(8)	N(1F)-Ni(2)-N(2D)	174.08(8)
N(1B)-Ni(1)-N(2)	84.56(8)	N(1F)-Ni(2)-N(1D)	98.99(8)
N(1B)-Ni(1)-N(1C)	99.30(8)	N(1F)-Ni(2)-N(1E)	102.97(8)
N(1B)-Ni(1)-N(2C)	174.27(8)	N(1F)-Ni(2)-N(2F)	78.28(8)
N(1B)-Ni(1)-N(2B)	78.98(8)	N(1D)-Ni(2)-N(2E)	174.86(8)
N(2)-Ni(1)-N(2C)	96.78(8)	N(1D)-Ni(2)-N(2D)	78.84(8)
N(2)-Ni(1)-N(2B)	96.81(8)	N(1D)-Ni(2)-N(1E)	99.74(8)
N(1C)-Ni(1)-N(1)	99.00(8)	N(1D)-Ni(2)-N(2F)	84.19(8)
N(1C)-Ni(1)-N(2)	176.13(8)	N(1E)-Ni(2)-N(2E)	79.54(8)
N(1C)-Ni(1)-N(2C)	79.42(8)	N(1E)-Ni(2)-N(2D)	82.87(8)
N(1C)-Ni(1)-N(2B)	84.33(8)	N(1E)-Ni(2)-N(2F)	175.57(8)
N(2B)-Ni(1)-N(2C)	95.32(8)	N(2F)-Ni(2)-N(2D)	95.97(8)

Table S12 Selected least-squares planes data for complex $[Ni(\mathbf{L5})_3](BF_4)_2 \cdot H_2O$ (**III**).

Unit 1

Least Squares Planes Description	Max. Deviation (Å)	Dihedral Angle (°)
Benzimidazole 1 N1 C8 N3 C6 C5 C4 C3 C2 C1	0.01	43.86
Pyrazine 1 N2 C13 C12 N4 C10 C9	0.029	
Benzimidazole 2 C8B N3B N1B C1B C6B C5B C4B C3B C2B	0.009	36.1
Pyrazine 2 C9B C10B N4B C12B C13B N2B	0.026	
Benzimidazole 3 C8C N3C C6C C1C N1C C5C C4C C3C C2C	0.008	40.8
Pyrazine 3 N4C C10C C9C N2C C13C C12C	0.029	

Unit 2

Least Squares Planes Description	Max. Deviation (Å)	Dihedral Angle (°)
Benzimidazole 1 C8D N1D C1D C2D C3D C4D C5D C6D N3D	0.009	40.8
Pyrazine 1 C9D N2D C13D C12D N4D C10D	0.032	
Benzimidazole 2 N1E C8E N3E C6E C1E C2E C3E C4E C5E	0.011	38.3
Pyrazine 2 C9E N2E C13E C12E N4E C10E	0.032	
Benzimidazole 3 N1F C1F C2F C3F C4F C5F C6F N3F C8F	0.007	35.52
Pyrazine 3 C9F N2F C13F C12F N4F C10F	0.029	

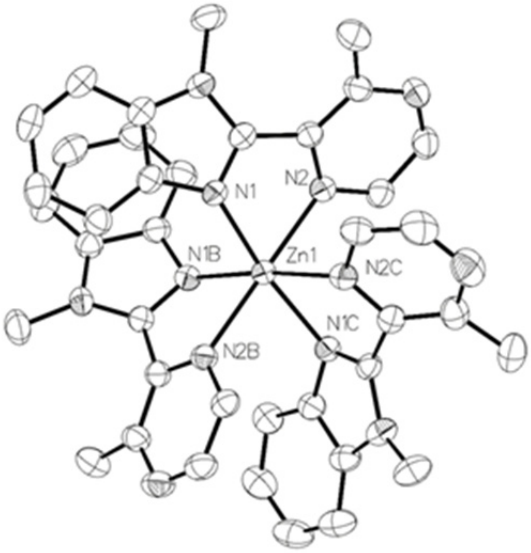

Figure S5 ORTEP view of *mer*-$[Zn(\mathbf{L5})_3]^{2+}$ cation in the crystal structure of $[Zn(\mathbf{L5})_3](ClO_4)_2$ (**IV**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and ClO_4^- counter anions are omitted for clarity.

Table S13 Selected bond distances (Å) and bond angles (°) for $[Zn(\mathbf{L5})_3](ClO_4)_2$ (**IV**).

Bond distances (Å)			
Zn(1)-N(2)	2.1901(18)	Zn(1)-N(1B)	2.0992(18)
Zn(1)-N(1C)	2.1369(17)	Zn(1)-N(2C)	2.3130(19)
Zn(1)-N(1)	2.1081(17)	Zn(1)-N(2B)	2.2554(18)

Bond angles (°)			
N(2)-Zn(1)-N(2C)	81.53(7)	N(1)-Zn(1)-N(2B)	101.22(7)
N(2)-Zn(1)-N(2B)	177.47(7)	N(1B)-Zn(1)-N(2)	104.37(7)
N(1C)-Zn(1)-N(2)	98.46(7)	N(1B)-Zn(1)-N(1C)	102.17(7)
N(1C)-Zn(1)-N(2C)	75.73(7)	N(1B)-Zn(1)-N(1)	88.61(7)
N(1C)-Zn(1)-N(2B)	82.19(7)	N(1B)-Zn(1)-N(2C)	174.03(7)
N(1)-Zn(1)-N(2)	77.70(7)	N(1B)-Zn(1)-N(2B)	77.83(7)
N(1)-Zn(1)-N(1C)	169.18(7)	N(2B)-Zn(1)-N(2C)	96.29(7)
N(1)-Zn(1)-N(2C)	93.62(7)		

Table S14 Selected least-squares planes data for complex $[Zn(\mathbf{L5})_3](ClO_4)_2$ (**IV**).

Least Squares Planes Description	Mean Deviation (Å)	Max. Deviation (Å) and atom	Dihedral Angle (°)
Pyrazine 1 N2 C13 C12 N4 C10 C9	0.037	0.056 (C9)	35.2
Benzimidazole 1 C8 N1 C0AA C6 N3 C5 C4 C3 C2	0.019	0.028 (C8)	
Pyrazine 2 N2B C13B C12B N4B C10B C9B	0.018	0.028 (C9B)	40.5
Benzimidazole 2 C8B N1B C1B C2B C3B C4B C5B C6B N3B	0.005	0.009 (C8B)	
Pyrazine 3 C9C C10C N4C C12C C13C N2C	0.02	0.031 (C9C)	41.3
Benzimidazole 3 C8C N3C C6C C5C C4C C3C C2C C1C N1C	0.029	0.042 (C6C)	

Table S15 Crystal data and structure refinement for $[Ni(\mathbf{L5})_3](BF_4)_2 \cdot 1.75CH_3CN$ (**V**) and $[Zn(\mathbf{L5})_3](BF_4)_2 \cdot 1.5CH_3CN$ (**VI**).

	V	**VI**
Empirical formula	$C_{42.50}H_{41.25}B_2F_8N_{13.75}Ni$	$C_{42}H_{40.50}B_2F_8N_{13.50}Zn$
Formula Unit	$C_{39}H_{36}B_2F_8N_{12}Ni + (CH_3CN)_{1.75}$	$C_{39}H_{36}B_2F_8N_{12}Ni + (CH_3CN)_{1.5}$
Formula weight	976.84	973.35
Temperature	180.15 K	180.01(10) K
Wavelength	0.71073 Å	1.54184 Å
Crystal system	Trigonal	Trigonal
Space group	*P*3*c*1	*P*3*c*1
Unit cell dimensions	*a* = 20.8028(3) Å *b* = 20.8028(3) Å *c* = 29.5237(4) Å $\alpha = 90°$ $\beta = 90°$ $\gamma = 120°$	*a* = 21.05979(9) Å *b* = 21.05979(9) Å *c* = 29.40349(14) Å $\alpha = 90°$ $\beta = 90°$ $\gamma = 120°$
Volume	11064.8(3) $Å^3$	11293.73(11) $Å^3$
Z	10.00002	10.0002
Density (calculated)	1.466 Mg/m^3	1.431 Mg/m^3
Absorption coefficient	0.522 mm^{-1}	1.461 mm^{-1}
F(000)	5024	4990
Crystal size	0.293 x 0.275 x 0.21 mm^3	0.293 x 0.275 x 0.21 mm^3
Theta range for data collection	2.076 to 28.169°	3.862 to 68.937°
Index ranges	$-27 \le h \le 26, -27 \le k \le 26, -38 \le l \le 38$	$-25 \le h \le 25, -25 \le k \le 25, -35 \le l \le 35$
Reflections collected	115787	175735
Independent reflections	16823[*R*(int) = 0.0438]	13967 [*R*(int) = 0.0323]
Completeness to theta	(25.242°) 99.90%	(67.684°) 100%
Absorption correction	Gaussian	Gaussian
Max. and min. transmission	1.000 and 0.332	1.000 and 0.670
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	16823 / 156 / 1043	13967 / 93 / 1034
Goodness-of-fit on F^2	1.031	1.036
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0526, w*R*2 = 0.1295	*R*1 = 0.0534, w*R*2 = 0.1508
R indices (all data)	*R*1 = 0.0815, w*R*2 = 0.1496	*R*1 = 0.0564, w*R*2 = 0.1558
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	1.679 and -0.687 e.$Å^{-3}$	1.608 and -0.434 e.$Å^{-3}$
Absolute structure parameter	0.50(2)	0.12(3)

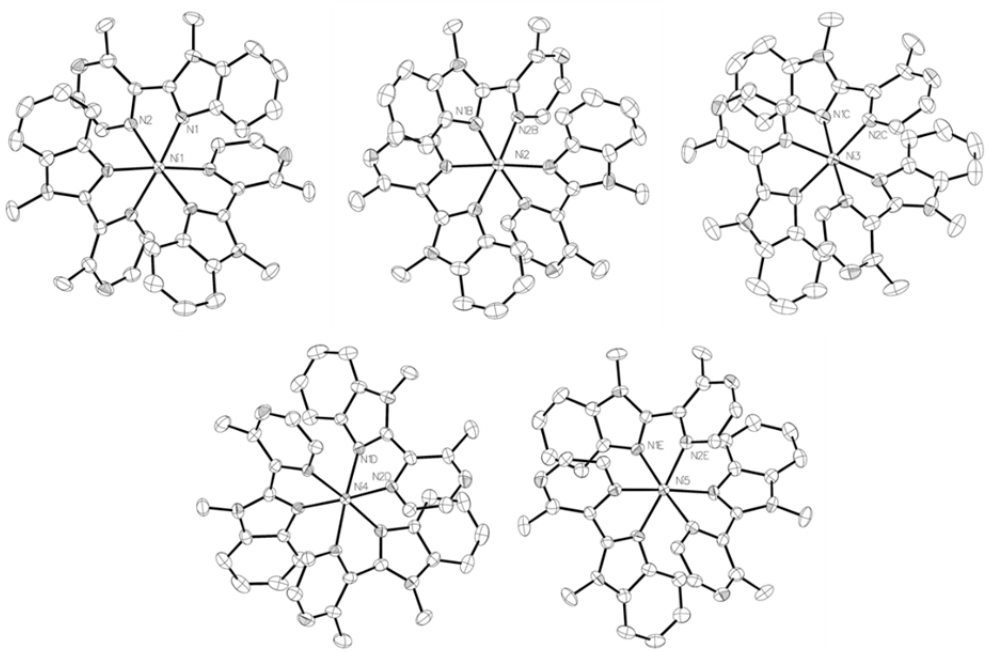

Figure S6 ORTEP view of the five different *fac*-$[Ni(\mathbf{L5})_3]^{2+}$ cations in the asymmetric unit of the crystal structure of $[Ni(\mathbf{L5})_3](BF_4)_2 \cdot 1.75CH_3CN$ (**V**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and BF_4^- counter anions are omitted for clarity.

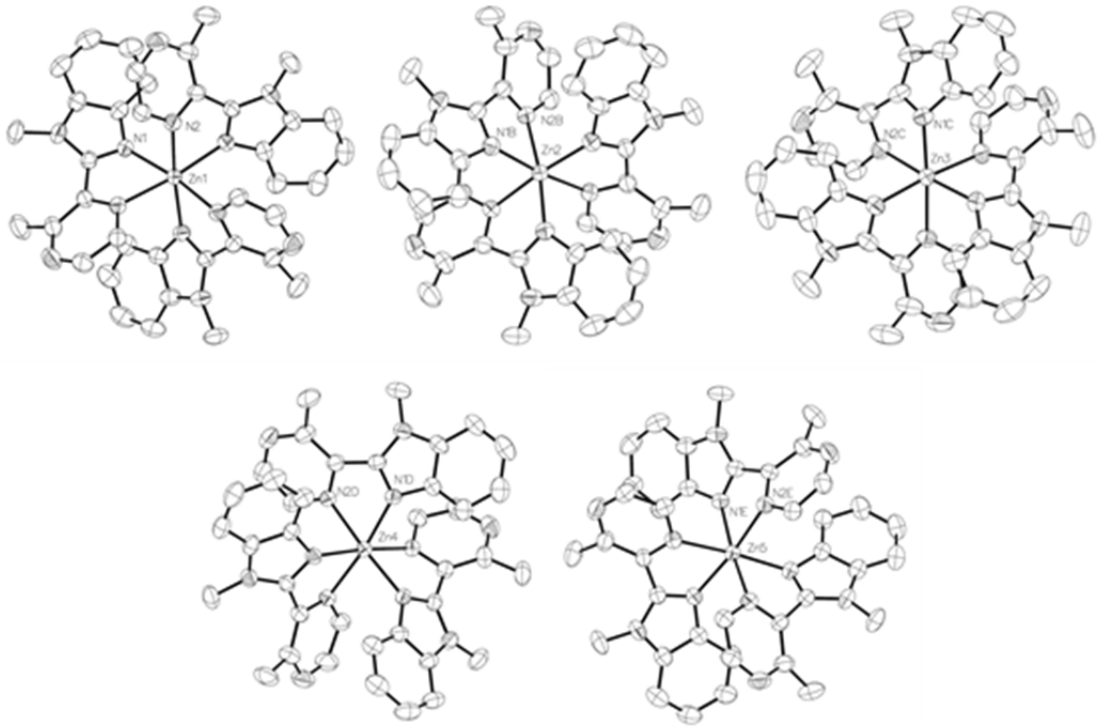

Figure S7 ORTEP view of the five different *fac*-$[Zn(\mathbf{L5})_3]^{2+}$ cations in the asymmetric unit of the crystal structure of $[Zn(\mathbf{L5})_3](BF_4)_2 \cdot 1.5CH_3CN$ (**VI**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and BF_4^- counter anions are omitted for clarity.

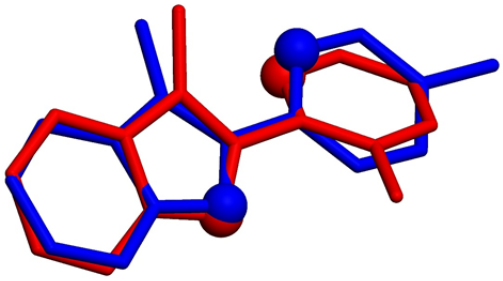

Figure S8. Optimized superimposition of the molecular structures of **L2** (blue) and **L5** (red) in their respective crystal structures. The nitrogen donor atoms of the α,α'-diimine chelate units are highlighted as spheres to show the anti-conformation.

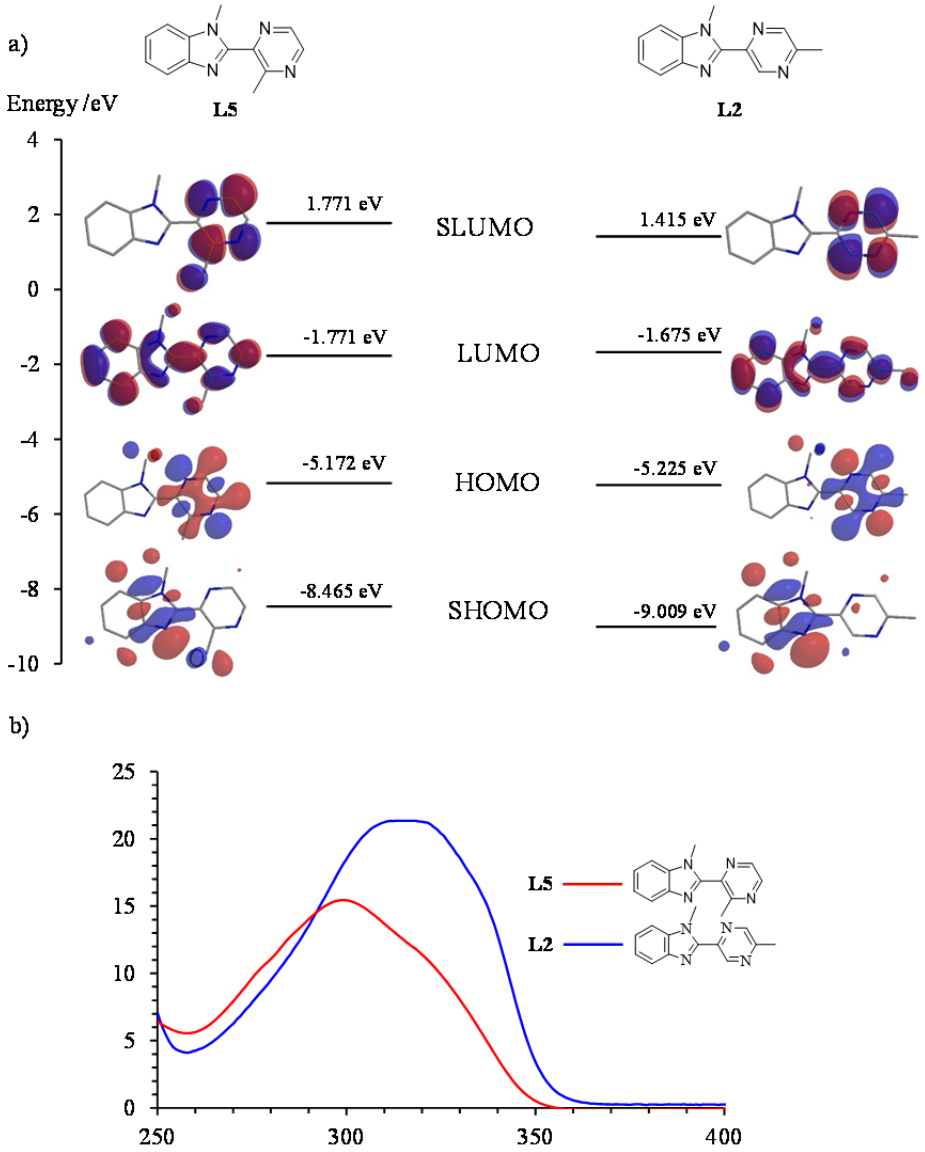

Figure S9. a) Extended Hückel frontier orbitals computed from gas-phase geometries optimized at the MM2 level and b) experimental electronic absorption spectra for ligands **L2** and **L5** in acetonitrile at 293 K.

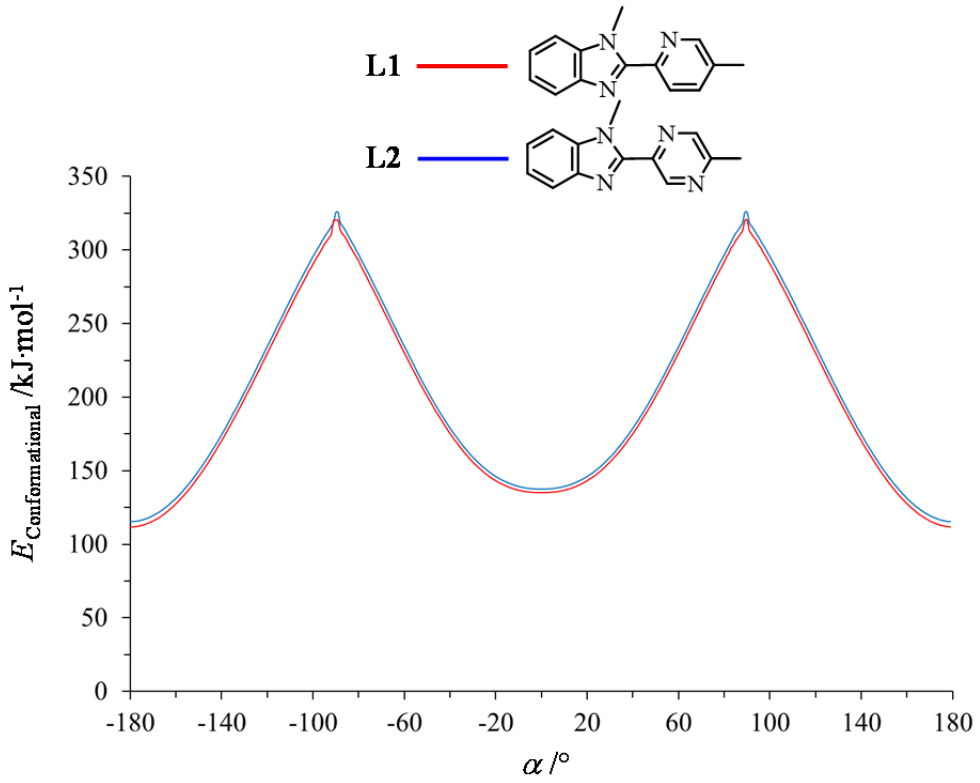

Figure S10. Gas-phase energies computed for **L1** and **L2** at the MM2 level using Chem3D as a function of the interplanar angle α [61].

Table S16: Energies of the intrashell d-d transitions, ligand-field strengths (Δ_{oct}) and Racah parameters (B, C) computed with eqns (10)-(13) for $[Ni(\mathbf{L5})_3](BF_4)_2 \cdot H_2O$ (**III**) in the solid state and in 0.1 M acetonitrile solution at 298K.

	$[Ni(\mathbf{L5})_3](BF_4)_2$ (solid)	$[Ni(\mathbf{L5})_3]^{2+}$ (0.1 M CH_3CN)
$\tilde{\nu}\left({}^3T_2 \leftarrow {}^3A_2\right)/cm^{-1}$	10672(3) [0.7][b]	10777(3) [5.8][c]
$\tilde{\nu}\left({}^1E \leftarrow {}^3A_2\right)/cm^{-1}$	12584(6) [0.52][b]	12470(8) [3.2][c]
$\tilde{\nu}\left({}^3T_1 \leftarrow {}^3A_2\right)/cm^{-1}$	16763(3) [0.97][b]	17561(2) [10.5][c]
Δ_{oct} /cm^{-1}	10672	10777
B /cm^{-1}	760	983
C /cm^{-1}	3413	2573
Δ_{oct}/B	14.04	10.97
C/B	4.49	2.62
β[a]	0.73	0.94

[a] Nephelauxetic parameter $\beta = B/B^o$ using B^o = 1042 cm^{-1} for free Ni^{2+} ion [77]. [b] Absorbance are given between square brackets. [c] Extinction coefficients in M^{-1}·cm^{-1} are given between square brackets.

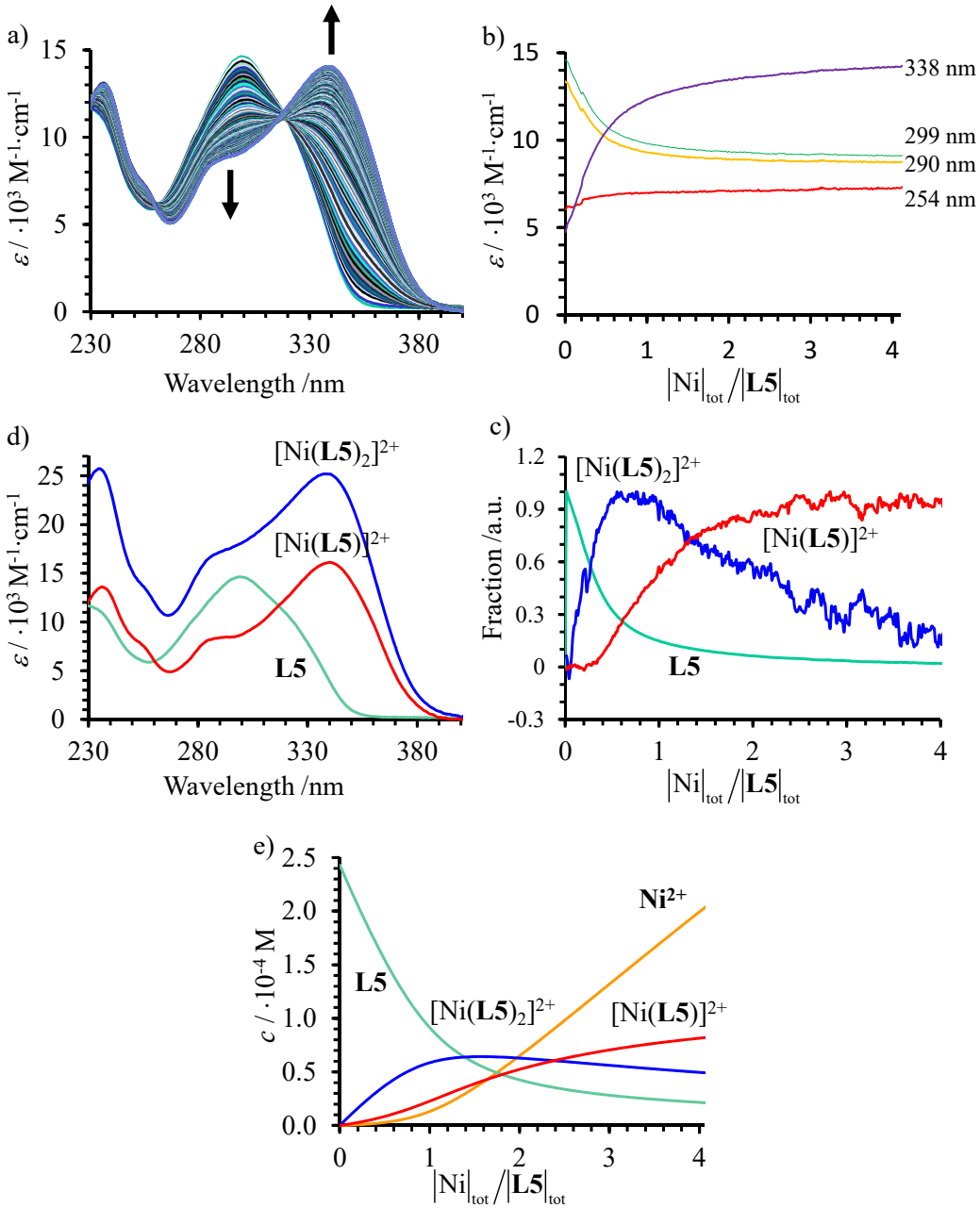

Figure S11. a) Variation of absorption spectra and b) corresponding variation of observed molar extinctions at different wavelengths recorded for the spectrophotometric titration of **L5** with $Ni(CF_3SO_3)_2$ (total ligand concentration: $2.4 \cdot 10^{-4}$ mol·dm^{-3} in acetonitrile, 298 K). c) Evolving factor analysis using four absorbing eigenvectors [48-50], d) re-constructed individual electronic absorption spectra [51-53] and e) associated computed speciation [81].

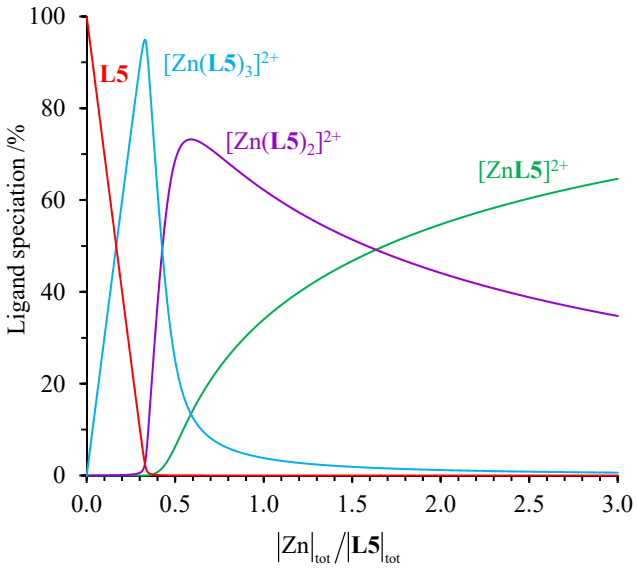

Figure S12. Ligand speciation computed with HySS2009 for the complex species $[Zn(\mathbf{L5})_n]^{2+}$ at a total ligand concentration of 1 M and using the stability constants collected in Table 3. [81].

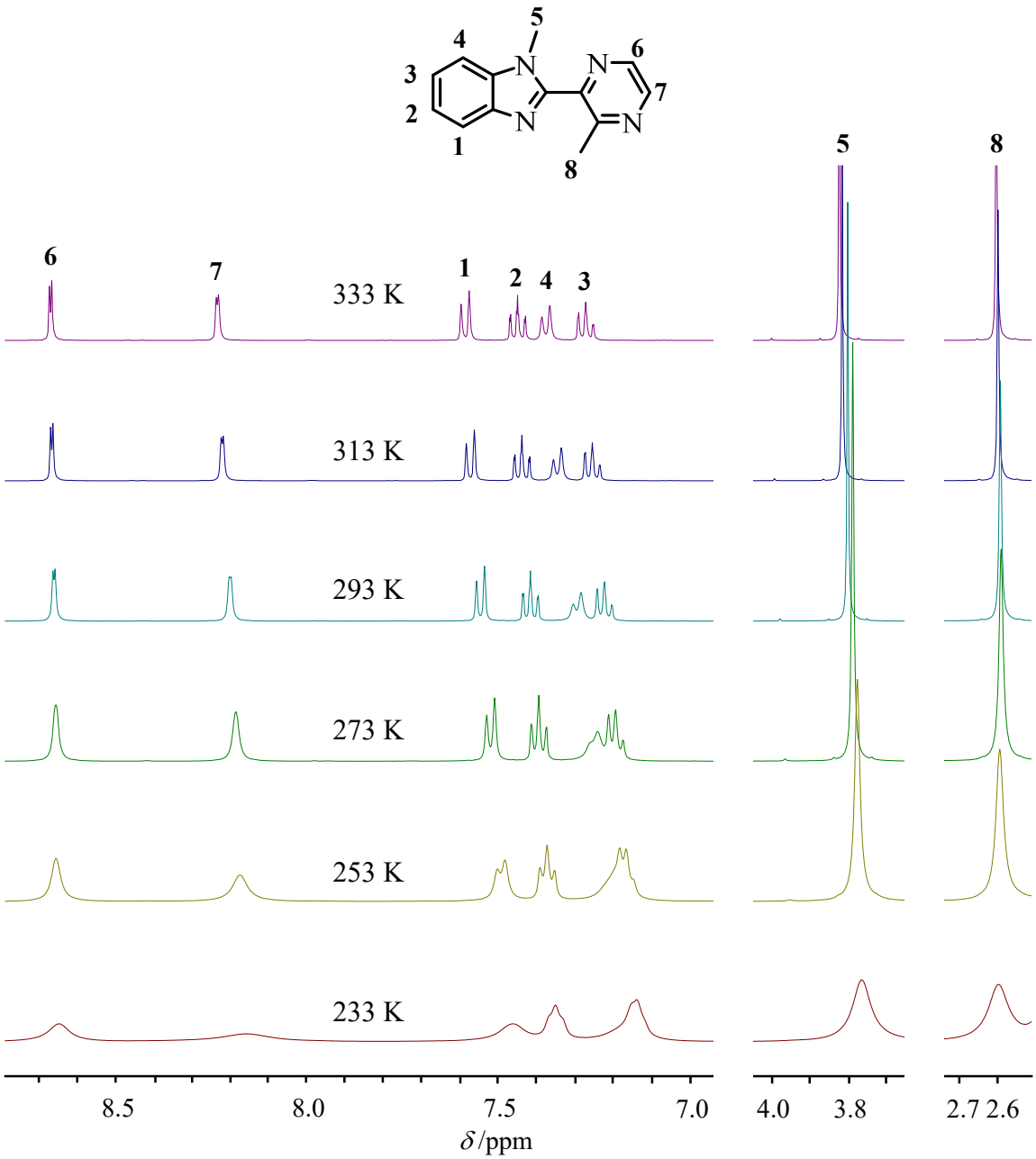

Figure S13. Variable temperature ^{1}H-NMR spectra of the complex $[Zn(\mathbf{L5})_3]^{2+}$ in CD_3CN (233 K-333 K) with ligand numbering scheme.