

The Tyranny of Arm-Wrestling Methyls on Iron(II) Spin State in Pseudo-Octahedral [Fe(didentate)₃] Complexes.

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Supporting Information

(22 pages)

Table S1. Elemental Analysis of the primary $[\text{Fe}(\text{L5})_3](\text{CF}_3\text{SO}_3)_2 \cdot 1.5\text{H}_2\text{O}$, $[\text{Ni}(\text{L5})_3](\text{BF}_4)_2 \cdot 1.5\text{H}_2\text{O} \cdot 1.5\text{CH}_3\text{CN}$ and $[\text{Zn}(\text{L5})_3](\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$ complexes.

| Molecular formula, Mw /g·mol ⁻¹ | Elemental analysis |
|---|----------------------------------|
| $[\text{Fe}(\text{L5})_3](\text{CF}_3\text{SO}_3)_2 \cdot 1.5\text{H}_2\text{O}$ | 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 |
| $[\text{Ni}(\text{L5})_3](\text{BF}_4)_2 \cdot 1.5\text{H}_2\text{O} \cdot 1.5\text{CH}_3\text{CN}$ | 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 |
| $[\text{Zn}(\text{L5})_3](\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$ | 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 | <i>P</i> 2 ₁ / <i>c</i> |
| Unit cell dimensions | <i>a</i> = 19.8873(10) Å |
| | <i>b</i> = 3.90974(16) Å |
| | <i>c</i> = 14.8924(7) Å |
| | α = 90° |
| | β = 107.876(5)° |
| | γ = 90° |
| Volume | 1102.04(9) Å ³ |
| <i>Z</i> | 4 |
| Density (calculated) | 1.352 Mg/m ³ |
| Absorption coefficient | 0.678 mm ⁻¹ |
| <i>F</i> (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 ≤ <i>h</i> ≤ 23, -4 ≤ <i>k</i> ≤ 4, -8 ≤ <i>l</i> ≤ 17 |
| Reflections collected | 3876 |
| Independent reflections | 2010 [<i>R</i> (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 <i>F</i> ² |
| Data / restraints / parameters | 2010 / 0 / 156 |
| Goodness-of-fit on <i>F</i> ² | 1.086 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> 1 = 0.0385, w <i>R</i> 2 = 0.0987 |
| <i>R</i> indices (all data) | <i>R</i> 1 = 0.0424, w <i>R</i> 2 = 0.1010 |
| Largest diff. peak and hole | 0.209 and -0.186 e.Å ⁻³ |

Table S3 Crystal data and structure refinement for [Fe(L5)₃](ClO₄)₂ (I) and [Ni(L5)₃](ClO₄)₂ (II).

| | I | II |
|---|--|--|
| CCDC numbers | 1988657 | 1988659 |
| Empirical formula | C ₃₉ H ₃₆ Cl ₂ FeN ₁₂ O ₈ | C ₃₉ H ₃₆ Cl ₂ NiN ₁₂ O ₈ |
| Formula Unit | C ₃₉ H ₃₆ Cl ₂ FeN ₁₂ O ₈ | C ₃₉ H ₃₆ Cl ₂ NiN ₁₂ O 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 | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>c</i> |
| | <i>a</i> = 8.2485(3) Å | <i>a</i> = 8.27280(10) Å |
| | <i>b</i> = 38.5553(14) Å | <i>b</i> = 38.2659(6) Å |
| Unit cell dimensions | <i>c</i> = 13.0716(5) Å | <i>c</i> = 12.9930(2) Å |
| | α = 90° | α = 90° |
| | β = 104.291(4)° | β = 104.434(2)° |
| | γ = 90° | γ = 90° |
| Volume | 4028.5(3) Å ³ | 3983.31(11) Å ³ |
| <i>Z</i> | 4 | 4 |
| Density (calculated) | 1.529 Mg/m ³ | 1.551 Mg/m ³ |
| Absorption coefficient | 4.818 mm ⁻¹ | 2.538 mm ⁻¹ |
| <i>F</i> (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 ≤ <i>h</i> ≤ 9, -45 ≤ <i>k</i> ≤ 46, -15 ≤ <i>l</i> ≤ 15 | -9 ≤ <i>h</i> ≤ 7, -46 ≤ <i>k</i> ≤ 32, -15 ≤ <i>l</i> ≤ 15 |
| Reflections collected | 17901 | 16391 |
| Independent reflections | 7364 [<i>R</i> (int) = 0.0243] | 7483 [<i>R</i> (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 <i>F</i> ² | Full-matrix least-squares on <i>F</i> ² |
| Data / restraints / parameters | 7364 / 158 / 582 | 7483 / 0 / 565 |
| Goodness-of-fit on <i>F</i> ² | 1.032 | 1.094 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> 1 = 0.0390, w <i>R</i> 2 = 0.0934 | <i>R</i> 1 = 0.0563, w <i>R</i> 2 = 0.1408 |
| <i>R</i> indices (all data) | <i>R</i> 1 = 0.0435, w <i>R</i> 2 = 0.0964 | <i>R</i> 1 = 0.0657, w <i>R</i> 2 = 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 $[\text{Ni}(\text{L5})_3](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (III) and $[\text{Zn}(\text{L5})_3](\text{ClO}_4)_2$ (IV).

| | III | IV |
|--|---|---|
| CCDC number | 1988656 | 1988657 |
| Empirical formula | $\text{C}_{78}\text{H}_{76}\text{B}_4\text{F}_{16}\text{N}_{24}\text{Ni}_2\text{O}_2$ | $\text{C}_{39}\text{H}_{36}\text{Cl}_2\text{N}_{12}\text{O}_8\text{Zn}$ |
| Formula Unit | $\text{C}_{39}\text{H}_{36}\text{B}_2\text{F}_8\text{N}_{12}\text{Ni} + \text{H}_2\text{O}$ | $\text{C}_{39}\text{H}_{36}\text{Cl}_2\text{N}_{12}\text{O}_8\text{Zn}$ |
| 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 | $a = 8.2559(3)$ Å |
| | $b = 23.1612(5)$ Å | $b = 38.5861(9)$ Å |
| | $c = 15.8218(2)$ Å | $c = 13.0163(3)$ Å |
| | $\alpha = 90^\circ$ | $\alpha = 90^\circ$ |
| | $\beta = 99.1601(14)^\circ$ | $\beta = 104.250(3)^\circ$ |
| | $\gamma = 90^\circ$ | $\gamma = 90^\circ$ |
| 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 | $-25 \leq h \leq 30$, $-30 \leq k \leq 28$, $-20 \leq l \leq 20$ | $-9 \leq h \leq 9$, $-30 \leq k \leq 46$, $-15 \leq l \leq 10$ |
| Reflections collected | 42210 | 17094 |
| Independent reflections | 17452 [$R(\text{int}) = 0.0306$] | 7341 [$R(\text{int}) = 0.0261$] |
| 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 [$I > 2\sigma(I)$] | $R1 = 0.0476$, $wR2 = 0.1151$ | $R1 = 0.0348$, $wR2 = 0.0847$ |
| R indices (all data) | $R1 = 0.0668$, $wR2 = 0.1287$ | $R1 = 0.0475$, $wR2 = 0.0918$ |
| Largest diff. peak and hole | 0.789 and -0.541 e.Å ⁻³ | 0.444 and -0.351 e.Å ⁻³ |

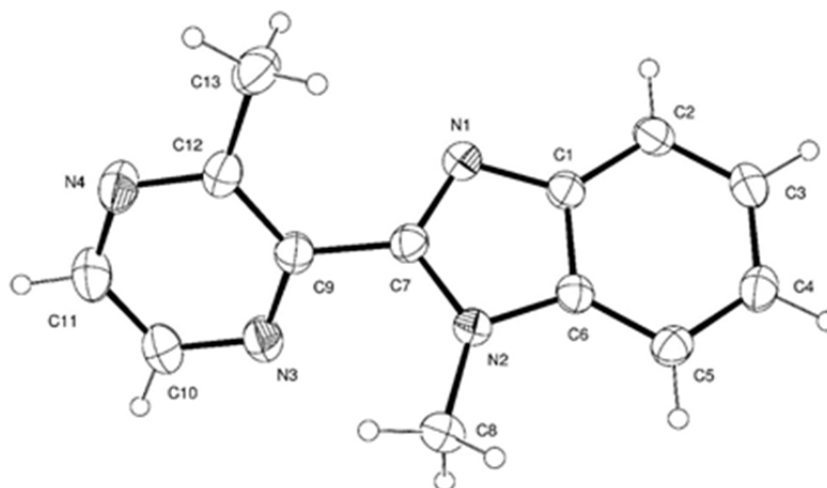


Figure S1 ORTEP view of the ligand **L5** (ellipsoids are drawn at 50% probability) with numbering scheme.

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) | |

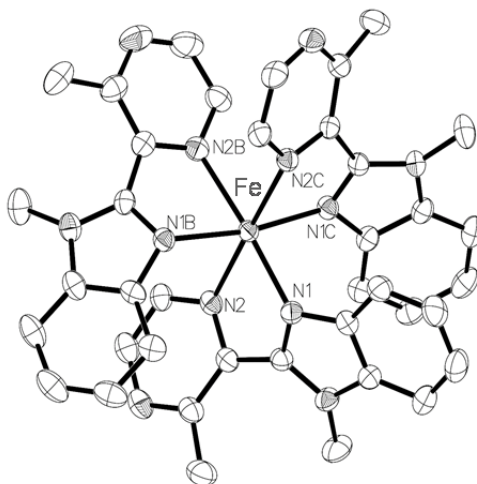


Figure S2 ORTEP view of *mer*-[Fe(L5)₃]²⁺ in the crystal structure of [Fe(L5)₃](ClO₄)₂ (**I**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and ClO₄⁻ counter anions are omitted for clarity.

Table S7 Selected bond distances (Å) and bond angles (°) for [Fe(L5)₃](ClO₄)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 $[\text{Fe}(\text{L5})_3](\text{ClO}_4)_2$ (**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) | |

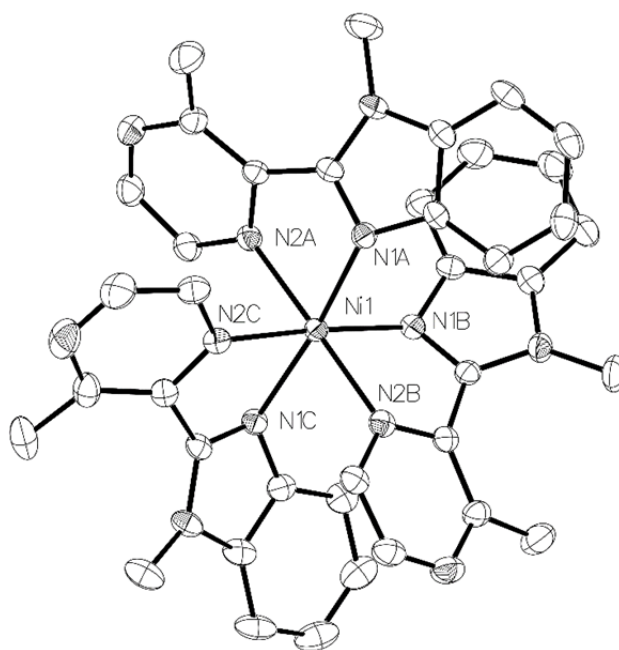
**Figure S3** ORTEP view of $mer\text{-}[\text{Ni}(\text{L5})_3]^{2+}$ in the crystal structure of $[\text{Ni}(\text{L5})_3](\text{ClO}_4)_2$ (**II**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and ClO_4^- counter anions are omitted for clarity.

Table S9 Selected bond distances (Å) and bond angles (°) for [Ni(L5)₃](ClO₄)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(L5)₃](ClO₄)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) | |

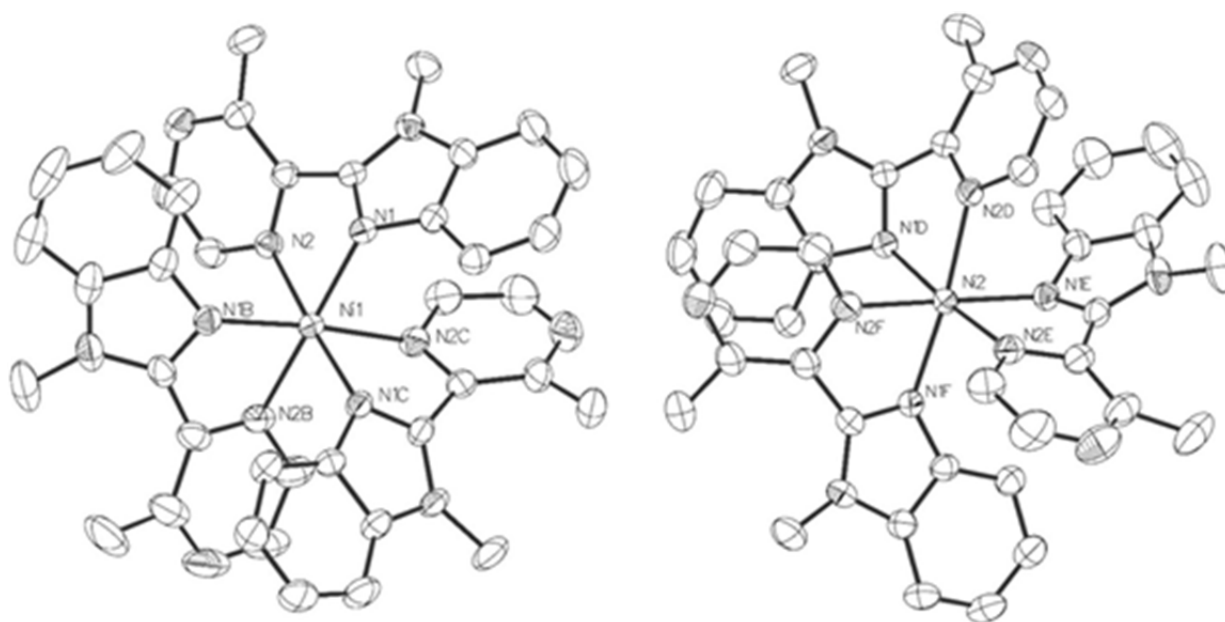


Figure S4 ORTEP view of the two different fac - $[\text{Ni}(\text{L5})_3]^{2+}$ cations in the asymmetric unit of the crystal structure of $[\text{Ni}(\text{L5})_3](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (**III**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and BF_4^- counter anions are omitted for clarity.

Table S11 Selected bond distances (Å) and bond angles (°) for $[\text{Ni}(\text{L5})_3](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (**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 $[\text{Ni}(\text{L5})_3](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (**III**).

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

Unit 2

| Least Squares Planes Description | Max. Deviation (Å) | Dihedral Angle (°) |
|--|--------------------|--------------------|
| Benzimidazole 1 C8D N1D C1D C2D C3D C4D C5D C6D N3D | 0.009 | <u>40.8</u> |
| 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 | |

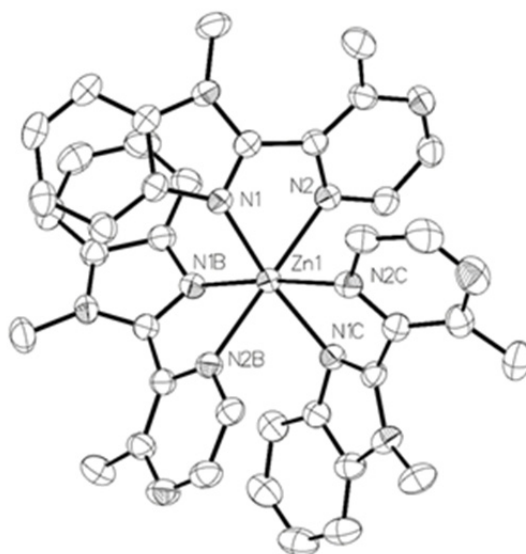


Figure S5 ORTEP view of *mer*-[Zn(L5)₃]²⁺ cation in the crystal structure of [Zn(L5)₃](ClO₄)₂ (**IV**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and ClO₄⁻ counter anions are omitted for clarity.

Table S13 Selected bond distances (Å) and bond angles (°) for [Zn(L5)₃](ClO₄)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(L5)₃](ClO₄)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) | <u>40.5</u> |
| 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(L5)₃](BF₄)₂·1.75CH₃CN (V) and [Zn(L5)₃](BF₄)₂·1.5CH₃CN (VI).

| | V | VI |
|---|---|--|
| Empirical formula | C _{42.50} H _{41.25} B ₂ F ₈ N _{13.75} Ni | C ₄₂ H _{40.50} B ₂ F ₈ N _{13.50} Zn |
| Formula Unit | C ₃₉ H ₃₆ B ₂ F ₈ N ₁₂ Ni + (CH ₃ CN) _{1.75} | C ₃₉ H ₃₆ B ₂ F ₈ N ₁₂ Ni + (CH ₃ CN) _{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 | <i>P3c1</i> | <i>P3c1</i> |
| Unit cell dimensions | <i>a</i> = 20.8028(3) Å | <i>a</i> = 21.05979(9) Å |
| | <i>b</i> = 20.8028(3) Å | <i>b</i> = 21.05979(9) Å |
| | <i>c</i> = 29.5237(4) Å | <i>c</i> = 29.40349(14) Å |
| | $\alpha = 90^\circ$ | $\alpha = 90^\circ$ |
| | $\beta = 90^\circ$ | $\beta = 90^\circ$ |
| | $\gamma = 120^\circ$ | $\gamma = 120^\circ$ |
| Volume | 11064.8(3) Å ³ | 11293.73(11) Å ³ |
| <i>Z</i> | 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 |
| <i>F</i> (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 ≤ <i>h</i> ≤ 26, -27 ≤ <i>k</i> ≤ 26, -38 ≤ <i>l</i> ≤ 38 | -25 ≤ <i>h</i> ≤ 25, -25 ≤ <i>k</i> ≤ 25, -35 ≤ <i>l</i> ≤ 35 |
| Reflections collected | 115787 | 175735 |
| Independent reflections | 16823 [<i>R</i> (int) = 0.0438] | 13967 [<i>R</i> (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 <i>F</i> ² | Full-matrix least-squares on <i>F</i> ² |
| Data / restraints / parameters | 16823 / 156 / 1043 | 13967 / 93 / 1034 |
| Goodness-of-fit on <i>F</i> ² | 1.031 | 1.036 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> 1 = 0.0526, w <i>R</i> 2 = 0.1295 | <i>R</i> 1 = 0.0534, w <i>R</i> 2 = 0.1508 |
| <i>R</i> indices (all data) | <i>R</i> 1 = 0.0815, w <i>R</i> 2 = 0.1496 | <i>R</i> 1 = 0.0564, w <i>R</i> 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) |

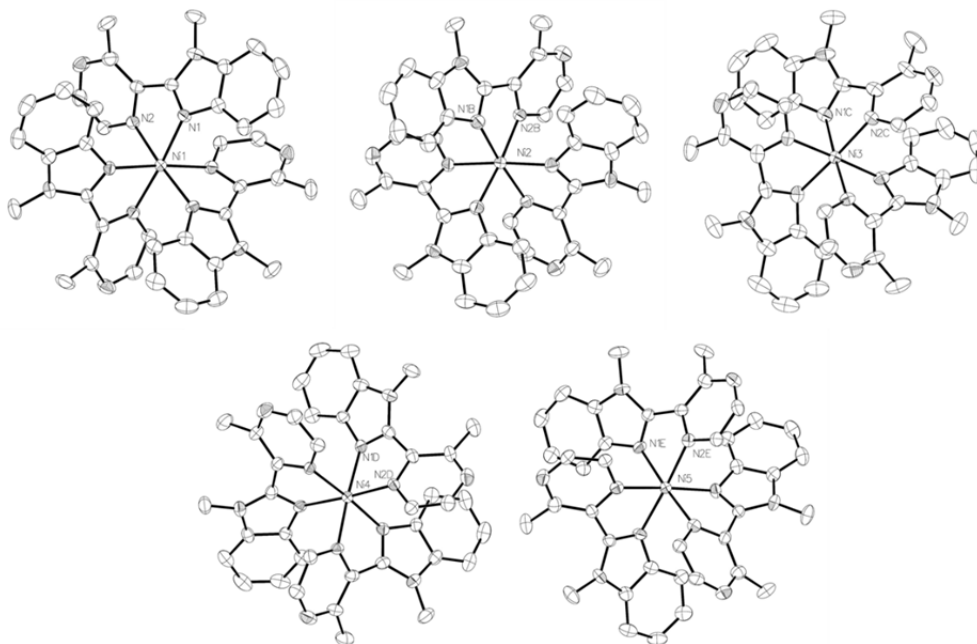


Figure S6 ORTEP view of the five different *fac*-[Ni(L5)₃]²⁺ cations in the asymmetric unit of the crystal structure of [Ni(L5)₃](BF₄)₂·1.75CH₃CN (**V**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and BF₄⁻ counter anions are omitted for clarity.

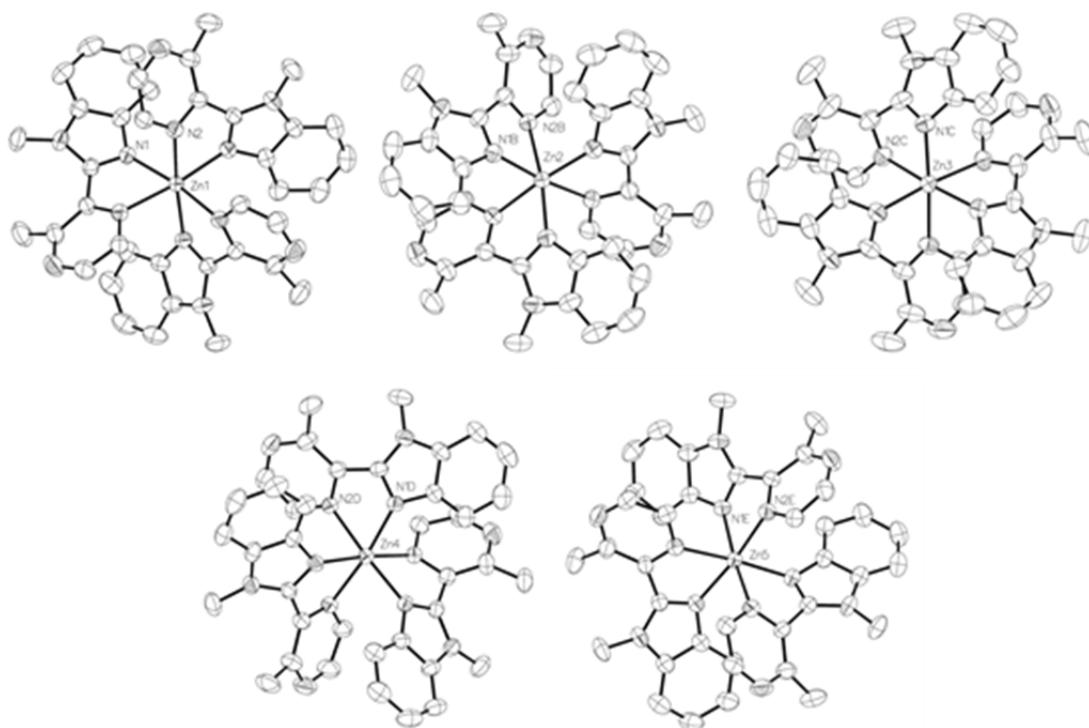


Figure S7 ORTEP view of the five different *fac*-[Zn(L5)₃]²⁺ cations in the asymmetric unit of the crystal structure of [Zn(L5)₃](BF₄)₂·1.5CH₃CN (**VI**) with partial numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and BF₄⁻ counter anions are omitted for clarity.

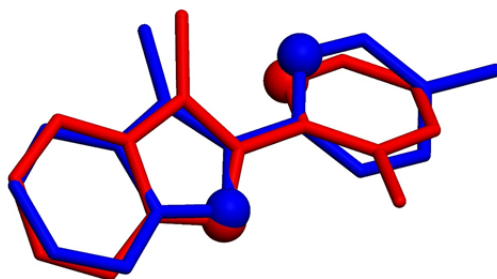


Figure S8. Optimized superimposition of the molecular structures of **L2** (blue) and **L5** (red) in their respective crystal structures. The nitrogen donor atoms of the α,α' -diimine chelate units are highlighted as spheres to show the anti-conformation.

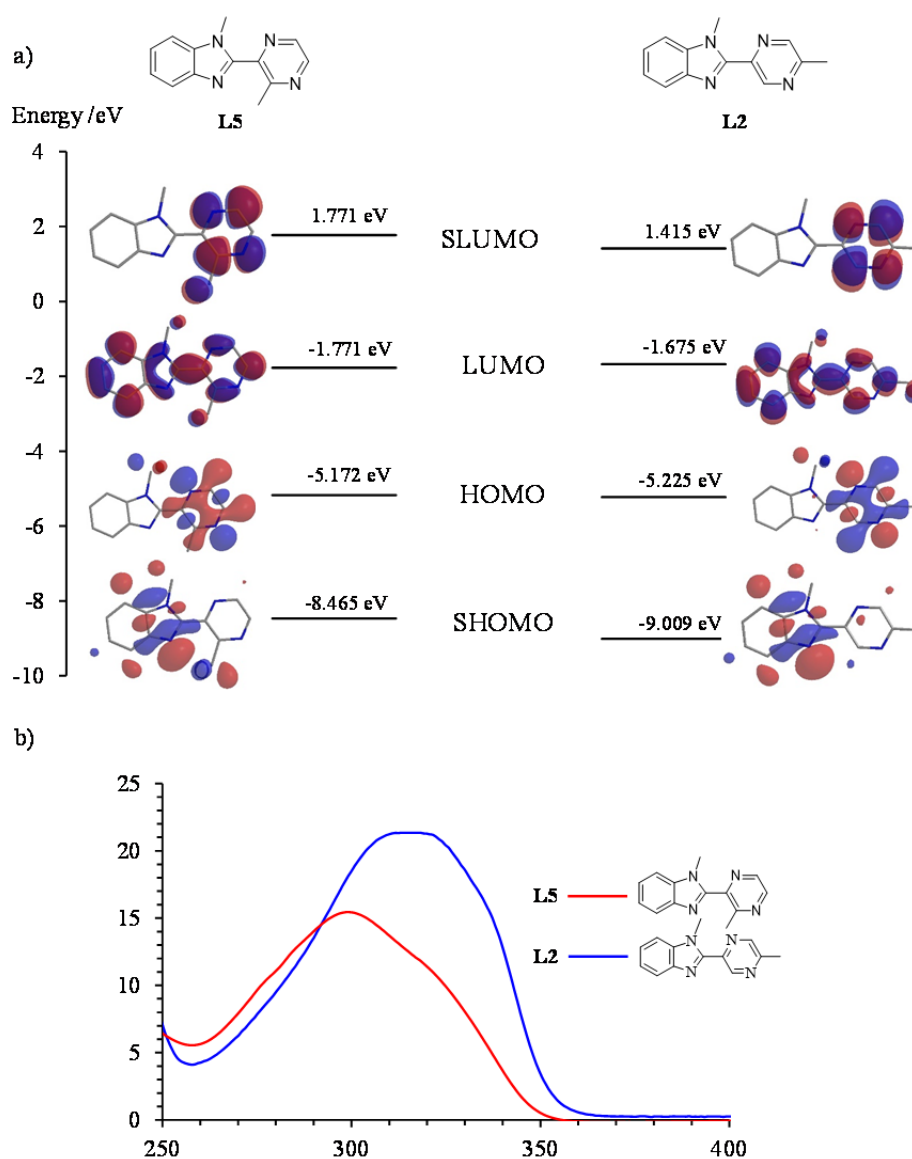


Figure S9. a) Extended Hückel frontier orbitals computed from gas-phase geometries optimized at the MM2 level and b) experimental electronic absorption spectra for ligands **L2** and **L5** in acetonitrile at 293 K.

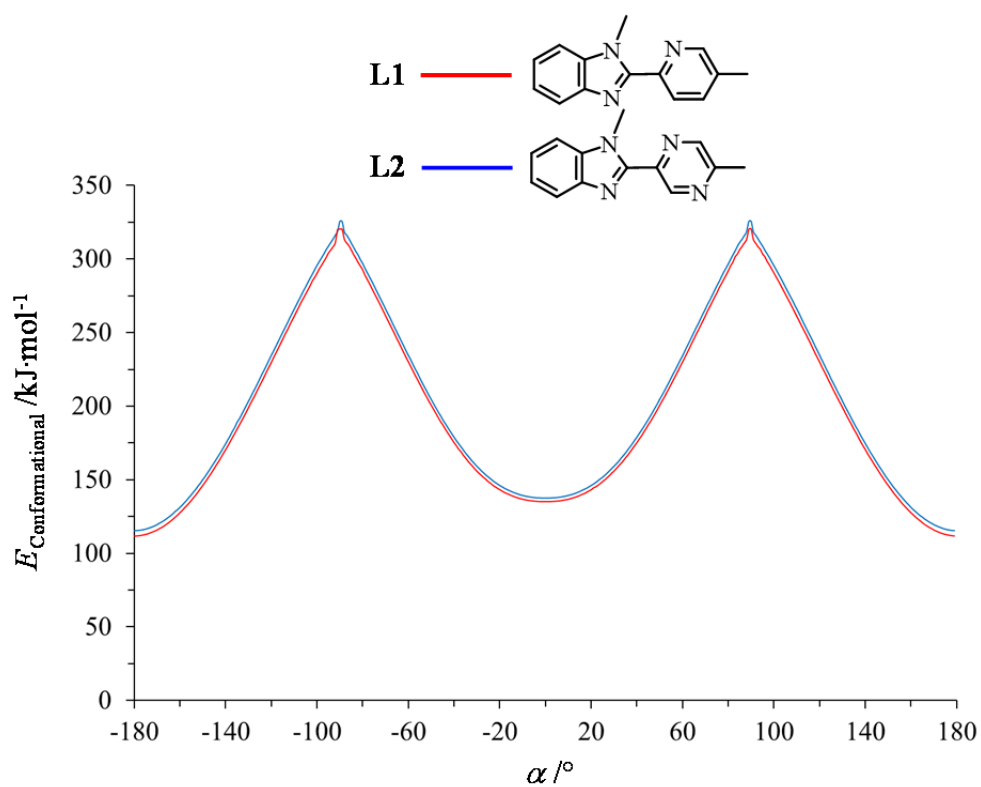


Figure S10. Gas-phase energies computed for **L1** and **L2** at the MM2 level using Chem3D as a function of the interplanar angle α [61].

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 $[\text{Ni}(\mathbf{L5})_3](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (**III**) in the solid state and in 0.1 M acetonitrile solution at 298K.

| | $[\text{Ni}(\mathbf{L5})_3](\text{BF}_4)_2$ (solid) | $[\text{Ni}(\mathbf{L5})_3]^{2+}$ (0.1 M CH_3CN) |
|--|---|---|
| $\tilde{\nu}({}^3\text{T}_2 \leftarrow {}^3\text{A}_2)/\text{cm}^{-1}$ | 10672(3) [0.7] ^b | 10777(3) [5.8] ^c |
| $\tilde{\nu}({}^1\text{E} \leftarrow {}^3\text{A}_2)/\text{cm}^{-1}$ | 12584(6) [0.52] ^b | 12470(8) [3.2] ^c |
| $\tilde{\nu}({}^3\text{T}_1 \leftarrow {}^3\text{A}_2)/\text{cm}^{-1}$ | 16763(3) [0.97] ^b | 17561(2) [10.5] ^c |
| $\Delta_{\text{oct}}/\text{cm}^{-1}$ | 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 $\beta = B/B^0$ using $B^0 = 1042 \text{ cm}^{-1}$ for free Ni^{2+} ion [77]. ^b Absorbance are given between square brackets. ^c Extinction coefficients in $\text{M}^{-1} \cdot \text{cm}^{-1}$ are given between square brackets.

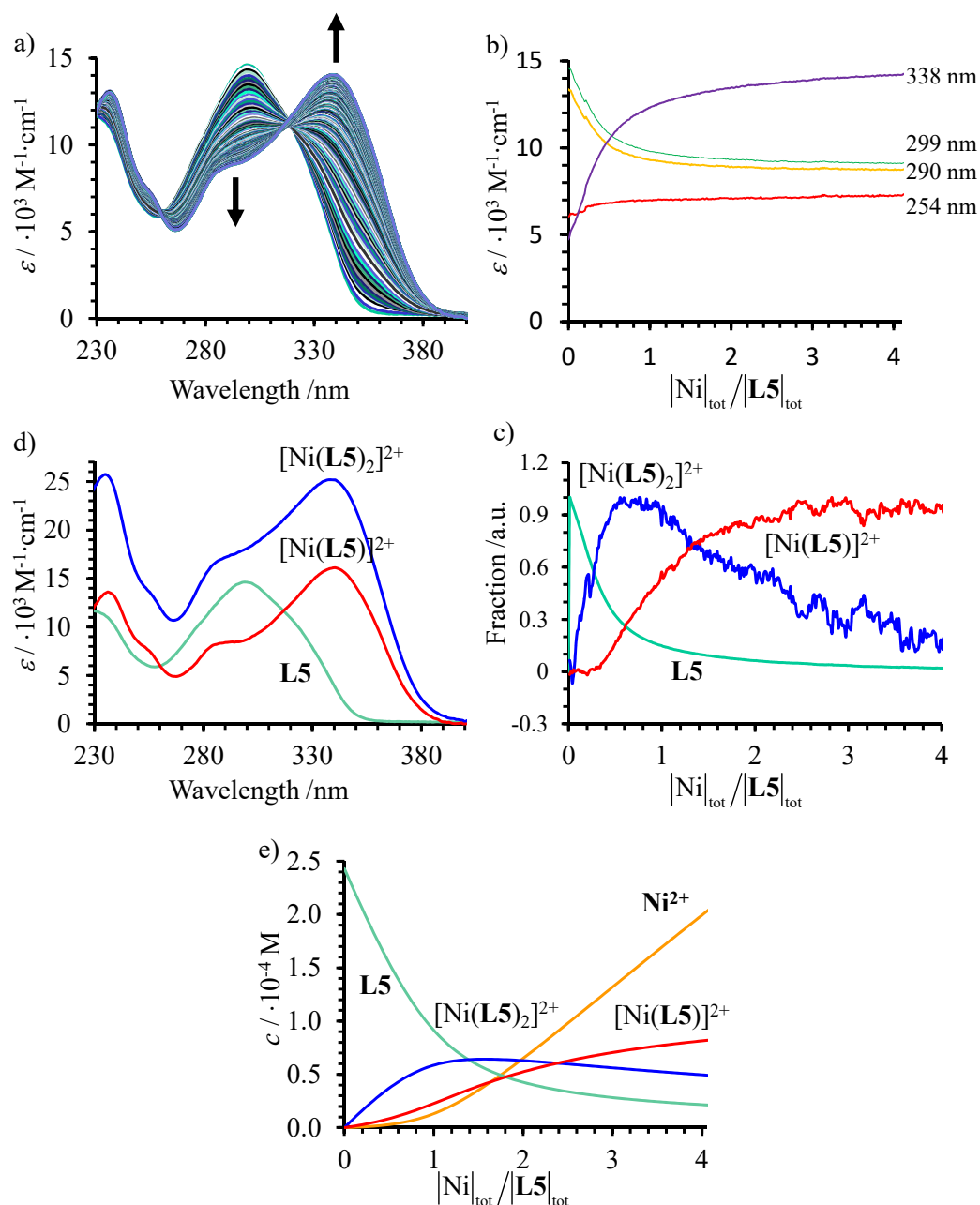


Figure S11. a) Variation of absorption spectra and b) corresponding variation of observed molar extinctions at different wavelengths recorded for the spectrophotometric titration of **L5** with $\text{Ni}(\text{CF}_3\text{SO}_3)_2$ (total ligand concentration: $2.4 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ 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].

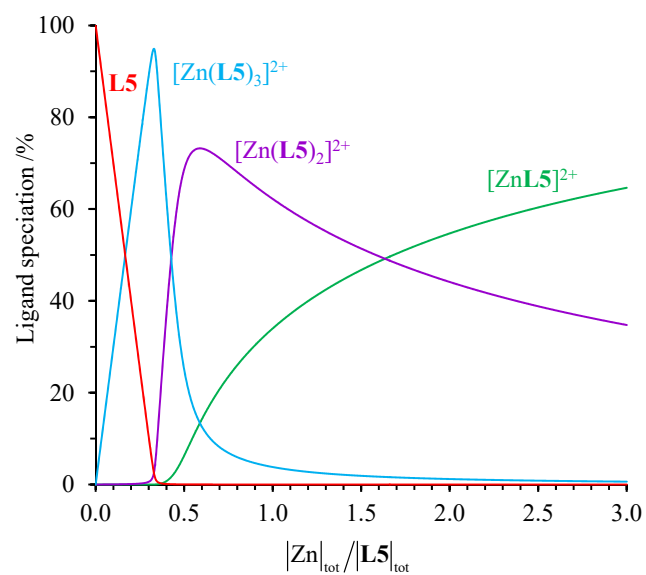


Figure S12. Ligand speciation computed with HySS2009 for the complex species $[\text{Zn}(\text{L5})_n]^{2+}$ at a total ligand concentration of 1 M and using the stability constants collected in Table 3. [81].

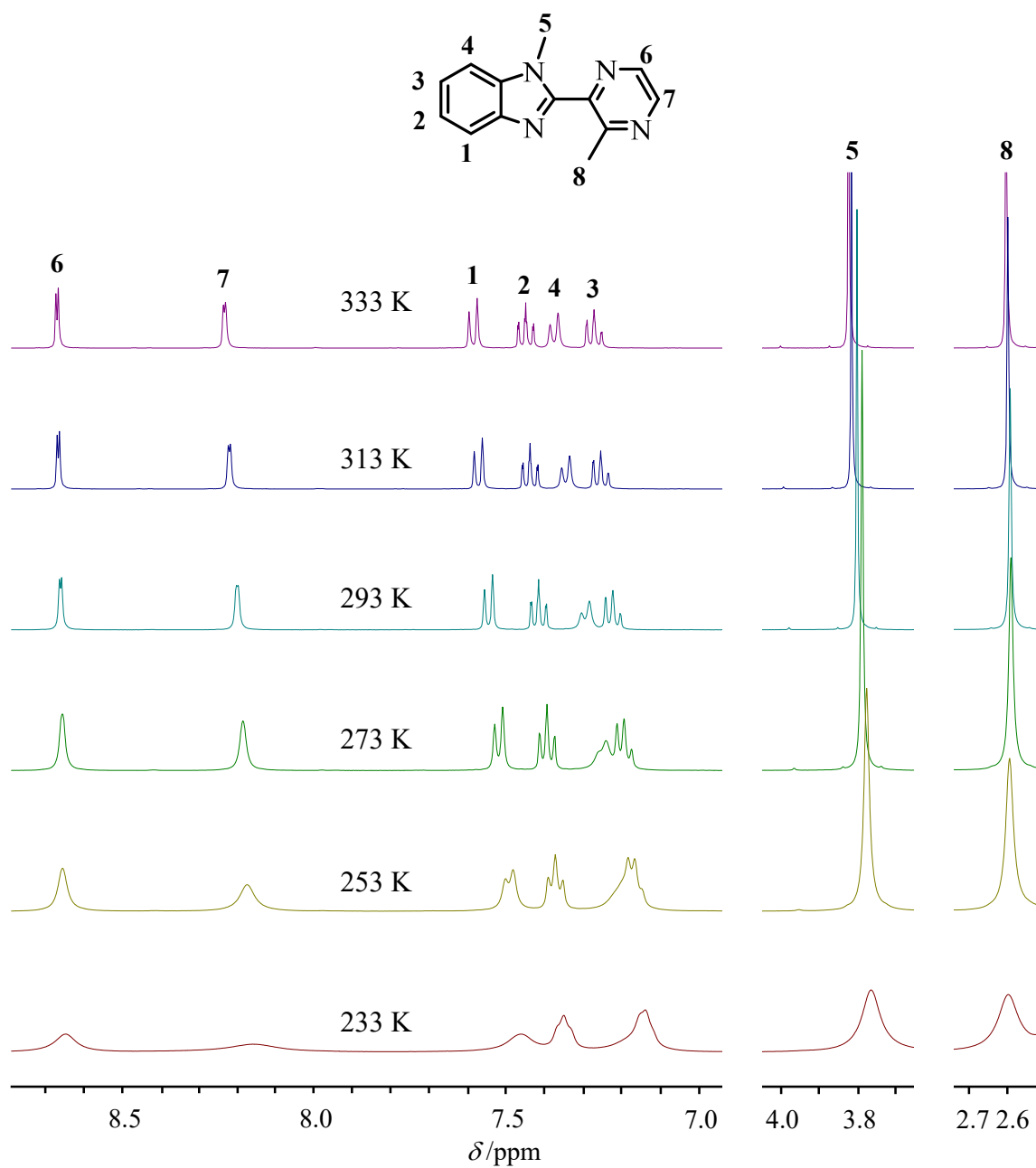


Figure S13. Variable temperature $^1\text{H-NMR}$ spectra of the complex $[\text{Zn}(\text{L5})_3]^{2+}$ in CD_3CN (233 K-333 K) with ligand numbering scheme.