Tuning spin-crossover transition temperatures in non-symmetrical homoleptic meridional/facial \( \text{[Fe(didentate)\textsubscript{3}]\textsuperscript{2+}} \) complexes: what for and who cares about it?

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Supporting Information

(90 pages)
Appendix 1: Derivation of eq. 18.61

The general expression of the Curie law for a mixture containing high-spin and low spin complexes is

$$\chi_M T = x_{hs} \cdot (C_{hs} + T \cdot TIP_{hs}) + x_{ls} \cdot (C_{ls} + T \cdot TIP_{ls})$$  \hspace{1cm} (16)$$

The introduction of the mass balance depicted in eq. (A1-1) into eq. (19) gives eq. (A1-2)

$$x_{hs} + x_{ls} = 1$$  \hspace{1cm} (A1-1)$$

$$\chi_M T = x_{ls} \cdot (C_{ls} - C_{hs} + T \cdot (TIP_{ls} - TIP_{hs})) + C_{hs} + T \cdot TIP_{hs}$$  \hspace{1cm} (A1-2)$$

Taking into account the spin crossover equilibria

$$K_{sco} = x_{ls}/x_{hs} = (1-x_{ls})/x_{hs}$$

provides

$$x_{ls} = 1/(1 + K_{sco})$$. Introduction into eq. (A1-2) yields

$$\chi_M T = \frac{(C_{ls} - C_{hs} + T \cdot (TIP_{ls} - TIP_{hs}))}{1 + K_{sco}} + C_{hs} + T \cdot TIP_{hs}$$  \hspace{1cm} (A1-3)$$

Finally, the introduction of the van’t Hoff relationship

$$\Delta H_{sco} - T \Delta S_{sco} = -RT \ln(K_{sco})$$

yields

$$\chi_M T = \frac{(C_{ls} - C_{hs} + T \cdot (TIP_{ls} - TIP_{hs}))}{1 + \exp \left( \frac{1}{R} \left( \Delta S_{sco} - \frac{\Delta H_{sco}}{T} \right) \right)} + C_{hs} + T \cdot TIP_{hs}$$  \hspace{1cm} (18)$$

In order to locate pertinent minima, the linear least-square fits of the magnetic data collected for [Fe(L6)_3]^{2+} and [Fe(L7)_3]^{2+} complexes in CD₃CN were initiated by setting $C_{ls} = 0$ cm³·K·mol⁻¹ and TIP₃₀ = 351·10⁻⁶ cm³·mol⁻¹ found for [Fe(bipy)_3]^{2+}, and $C_{hs} = 3.44$ cm³·K·mol⁻¹ and TIP₃₀ = 358·10⁻⁶ cm³·mol⁻¹ found for [Fe(L2)_3]^{2+} while fitting $\Delta H_{sco}$ and $\Delta S_{sco}$. Then, a second non-linear fitting process with the simultaneous optimization of five parameters ($C_{ls} = 0$ cm³·K·mol⁻¹) lead to the data collected in Table 3, entries 5-6.
Appendix 2: Derivation of eq. 20.61

For mononuclear homoleptic tris-diimine Fe II complexes existing as a mixture of meridional and facial isomers, each displaying specific thermodynamic spin state equilibria but analogous (i.e. taken as identical) Curie constants ($C_{hs}$ and $C_{ls}$) and temperature-independent parameters (TIP$_{hs}$ and TIP$_{ls}$), Eq. (16) transforms into

$$\chi_M^T = (x_{hs}^{\text{fac}} + x_{hs}^{\text{mer}}) \cdot (C_{hs} + T \cdot \text{TIP}_{hs}) + (x_{ls}^{\text{fac}} + x_{ls}^{\text{mer}}) \cdot (C_{ls} + T \cdot \text{TIP}_{ls})$$

The various mole fractions are correlated by mass balance (eq. A2-1) and by thermodynamic constants (eqs A2-2 to A2-4).

$$x_{hs}^{\text{fac}} + x_{hs}^{\text{fac}} + x_{hs}^{\text{mer}} + x_{hs}^{\text{mer}} = 1$$ (A2-1)

$$K_{\text{Fe,La} \rightarrow \text{fac}} = \frac{x_{hs}^{\text{fac}}}{x_{hs}^{\text{mer}} + x_{hs}^{\text{mer}}}$$ (A2-2)

$$K_{\text{ SCO}} = \frac{x_{hs}^{\text{fac}}}{x_{hs}^{\text{fac}}}$$ (A2-3)

$$K_{\text{SCO}} = \frac{x_{hs}^{\text{mer}}}{x_{hs}^{\text{mer}}}$$ (A2-4)

Straightforward mathematical manipulations yield

$$x_{hs}^{\text{mer}} = \frac{1}{(1 + K_{\text{Fe,La} \rightarrow \text{fac}})(1 + K_{\text{mer} \rightarrow \text{fac}}(\text{La}))}$$ (A2-5)

$$x_{hs}^{\text{mer}} = \frac{K_{\text{mer} \rightarrow \text{fac}}}{{(1 + K_{\text{Fe,La} \rightarrow \text{fac}})(1 + K_{\text{SCO}})}}$$ (A2-6)

$$x_{hs}^{\text{fac}} = \frac{K_{\text{Fe,La} \rightarrow \text{fac}}}{(1 + K_{\text{mer} \rightarrow \text{fac}})(1 + K_{\text{SCO}})}$$ (A2-7)

$$x_{hs}^{\text{fac}} = \frac{K_{\text{SCO}}}{(1 + K_{\text{mer} \rightarrow \text{fac}})(1 + K_{\text{SCO}})}$$ (A2-8)

Finally, the introduction of eqs (A2-5)-(A2-8) into eq. (22) yields
\[ \lambda_M^\text{para} T = \left( \frac{K_{\text{SCO}}^{\text{fac-Fe}(Lk)_3} K_{\text{mer-\text{fac}}}^{\text{Fe, Lk}_3}}{(1 + K_{\text{mer-\text{fac}}}^{\text{fac-Fe}(Lk)_3})(1 + K_{\text{mer-\text{fac}}}^{\text{ SCO}})} + \frac{K_{\text{SCO}}^{\text{mer-Fe}(Lk)_3}}{1 + K_{\text{mer-\text{fac}}}^{\text{ SCO}}}) \right) (C_{\text{ls}} + T \cdot \text{TIP}_{\text{ls}}) \]

\[ + \left( \frac{K_{\text{mer-\text{fac}}}^{\text{fac-Fe}(Lk)_3}}{(1 + K_{\text{mer-\text{fac}}}^{\text{fac-Fe}(Lk)_3})(1 + K_{\text{mer-\text{fac}}}^{\text{ SCO}})} + \frac{1}{1 + K_{\text{mer-\text{fac}}}^{\text{ SCO}}}) \right) (C_{\text{ls}} + T \cdot \text{TIP}_{\text{ls}}) \]  

Eq. (20) was used for the fits of \( \lambda_M^\text{para} T \) products collected for \([\text{Fe(L6)}]^{2+}\) in acetonitrile (Figure 7) with the help of the van’t Hoff laws collected in eqs (A2-9)-(A2-11).

\[ K_{\text{mer-\text{fac}}}^{\text{fac-Fe}(Lk)_3} = \exp \left( \frac{1}{R} \left( \frac{\Delta S_{\text{mer-\text{fac}}}^{\text{fac-Fe}(Lk)_3}}{T} - \frac{\Delta H_{\text{mer-\text{fac}}}^{\text{fac-Fe}(Lk)_3}}{T} \right) \right) \]  

(A2-9)

\[ K_{\text{SCO}}^{\text{fac-Fe}(Lk)_3} = \exp \left( \frac{1}{R} \left( \frac{\Delta S_{\text{SCO}}^{\text{fac-Fe}(Lk)_3}}{T} - \frac{\Delta H_{\text{SCO}}^{\text{fac-Fe}(Lk)_3}}{T} \right) \right) \]  

(A2-10)

\[ K_{\text{SCO}}^{\text{mer-Fe}(Lk)_3} = \exp \left( \frac{1}{R} \left( \frac{\Delta S_{\text{SCO}}^{\text{mer-Fe}(Lk)_3}}{T} - \frac{\Delta H_{\text{SCO}}^{\text{mer-Fe}(Lk)_3}}{T} \right) \right) \]  

(A2-11)
Figure S1 $^1$H-NMR of the ligand 1-methyl-2-(pyrimidin-2-yl)-1H-benzo[d]imidazole (L6, CD$_3$CN, 298 K).

Figure S2 $^1$H-NMR of the ligand 1-methyl-2-(pyrimidin-2-yl)-1H-benzo[d]imidazole (L6, CD$_3$CN, 298 K) highlighting the aromatic part.
**Figure S3** $^{13}$C-NMR of the ligand 1-methyl-2-(pyrimidin-2-yl)-1H-benzo[d]imidazole ($L_6$, CD$_3$CN, 298 K).

**Figure S4** 2D-{$^1$H,$^1$H}-COSY NMR of the ligand 1-methyl-2-(pyrimidin-2-yl)-1H-benzo[d]imidazole ($L_6$, CD$_3$CN, 298 K).
Figure S5 2D-$\text{H}^1\text{H}$-NOESY NMR of the ligand 1-methyl-2-(pyrimidin-2-y1)-1H-benzo[d]imidazole (L6, CD$_3$CN, 298 K).

Figure S6 2D-$\text{H}^1\text{N}$-HMBC NMR of the ligand 1-methyl-2-(pyrimidin-2-y1)-1H-benzo[d]imidazole (L6, CD$_2$Cl$_2$, 298 K).
Figure S7 $^1$H-NMR of the ligand 1-methyl-2-(pyrimidin-4-yl)-1H-benzo[d]imidazole (L7, CD$_3$CN, 298 K).

Figure S8 $^1$H-NMR of the ligand 1-methyl-2-(pyrimidin-4-yl)-1H-benzo[d]imidazole (L7, CD$_3$CN, 298 K) highlighting the aromatic part.
Figure S9  $^{13}$C-NMR of the ligand 1-methyl-2-(pyrimidin-4-yl)-1H-benzo[d]imidazole ($L_7$, CD$_3$CN, 298 K).

Figure S10  2D-$^{1}H,^{1}H$-COSY NMR of the ligand 1-methyl-2-(pyrimidin-2-yl)-1H-benzo[d]imidazole ($L_7$, CD$_3$CN, 298 K).
Figure S11 2D-$\{^{1}\text{H},^{1}\text{H}\}$-NOESY NMR of the ligand 1-methyl-2-(pyrimidin-4-yl)-1H-benzo[d]imidazole (L7, CD$_3$CN, 298 K).

Figure S12 2D-$\{^{1}\text{H},^{15}\text{N}\}$-HMBC NMR of the ligand 1-methyl-2-(pyrimidin-4-yl)-1H-benzo[d]imidazole (L7, CD$_2$Cl$_2$, 298 K).
Figure S13  Gas-phase computed energies of ligands L1 (red), L4 (blue), L6 (green) and L7 (yellow) as a function of the interplanar angle measured between the N-heterocyclic azine ring plane and the benzimidazole ring plane.
Figure S14 a) Extended Hückel computed frontier orbitals (optimized gas-phase models) and b) computed charges (in electrostatic units) borne by the nitrogen donor atoms for the didentate ligands L1, L4, L6 and L7 (Perkin Elmer Chem3D Pro, version 16.0.1.4, Perkin Elmer Informatics, Inc. 1998-2017. https://www.perkinelmer.com/product/chemoffice-professional-chemofficepro).
Table S1  Crystal data and structure refinement for L6.

| Compound                  | L6                                                        |
|---------------------------|-----------------------------------------------------------|
| Empirical formula         | C$_{12}$H$_{10}$N$_{4}$                                   |
| Formula weight            | 210.24                                                    |
| Temperature               | 180.01(10) K                                             |
| Wavelength                | 1.54184 Å                                                 |
| Crystal system            | Orthorhombic                                              |
| Space group               | Pbca                                                      |
| Unit cell dimensions      |                                                          |
| $a$                       | 16.9371(3) Å                                             |
| $b$                       | 9.58870(10) Å                                            |
| $c$                       | 25.1582(4) Å                                             |
| $\alpha$                  | 90°                                                       |
| $\beta$                   | 90°                                                       |
| $\gamma$                  | 90°                                                       |
| Volume                    | 4085.81(11) Å                                            |
| $Z$                       | 16                                                        |
| Density (calculated)      | 1.367 Mg/m$^3$                                            |
| Absorption coefficient    | 0.696 mm$^{-1}$                                           |
| $F(000)$                  | 1760                                                      |
| Crystal size              | 0.192 x 0.085 x 0.018 mm$^3$                             |
| Theta range for data collection | 3.514 to 70.689°                                   |
| Index ranges              | -16≤h≤20, -11≤k≤8, -30≤l≤25                              |
| Reflections collected     | 15128                                                     |
| Independent reflections   | 3894 [R(int) = 0.0259]                                    |
| Completeness to theta = 67.684° | 100.00%                                      |
| Absorption correction     | Gaussian                                                  |
| Max. and min. transmission| 1.000 and 0.838                                           |
| Refinement method         | Full-matrix least-squares on $F^2$                       |
| Data / restraints / parameters | 3894 / 0 / 291                                |
| Goodness-of-fit on $F^2$  | 1.063                                                     |
| Final $R$ indices [$I>2\sigma(I)$] | $R1 = 0.0402$, $wR2 = 0.0964$                      |
| $R$ indices (all data)    | $R1 = 0.0518$, $wR2 = 0.1061$                           |
| Extinction coefficient    | n/a                                                       |
| Largest diff. peak and hole | 0.136 and -0.236 e.Å$^{-3}$                          |
Figure S15 ORTEP view of the two different ligand molecules in the crystal structure of L6 (ellipsoids are drawn at 40% probability) with numbering scheme. Hydrogen atoms are omitted for clarity.

Table S2  Selected bond distances (Å) and bond angles (°) for ligand L6.

| Bond Distances (Å) | Bond Distances (Å) | Bond Distances (Å) |
|------------------|------------------|------------------|
| C11 - N2         | 1.4637(17)       | C36 - N24        | 1.343(2)       |
| N1 - C12         | 1.3180(18)       | C36 - C35        | 1.340(2)       |
| N1 - C5          | 1.3758(18)       | N21 - C32        | 1.3180(19)     |
| C12 - N2         | 1.3736(17)       | N21 - C25        | 1.3815(19)     |
| C12 - C13        | 1.4781(19)       | C32 - N22        | 1.3761(18)     |
| C5 - C6          | 1.395(2)         | C32 - C33        | 1.4804(19)     |
| C5 - C10         | 1.4035(19)       | C25 - C26        | 1.398(2)       |
| N2 - C10         | 1.3821(18)       | C25 - C30        | 1.393(2)       |
| C13 - N4         | 1.3313(19)       | N22 - C30        | 1.3798(19)     |
| C13 - N3         | 1.3401(19)       | N22 - C31        | 1.460(2)       |
| C6 - C7          | 1.372(2)         | C33 - N24        | 1.319(2)       |
| C10 - C9         | 1.392(2)         | C33 - N23        | 1.320(2)       |
| N4 - C16         | 1.335(2)         | C26 - C27        | 1.376(3)       |
| N3 - C14         | 1.335(2)         | C30 - C29        | 1.395(2)       |
| C7 - C8          | 1.399(2)         | N23 - C34        | 1.334(2)       |
| C9 - C8          | 1.376(2)         | C27 - C28        | 1.392(3)       |
| C16 - C15        | 1.366(3)         | C29 - C28        | 1.380(3)       |
| C14 - C15        | 1.385(3)         | C34 - C35        | 1.360(3)       |
| Bond Angles (°)          |       |       |       |
|--------------------------|-------|-------|-------|
| C12-N1-C5                | 105.11(11) | C35-C36-N24 | 123.36(17) |
| N1-C12-N2                | 113.16(12) | C32-N21-C25 | 104.70(12) |
| N1-C12-C13               | 122.01(12) | N21-C32-N22 | 113.28(12) |
| N2-C12-C13               | 124.83(12) | N21-C32-C33 | 122.46(13) |
| N1-C5-C6                 | 129.64(13) | N22-C32-C33 | 124.25(12) |
| N1-C5-C10                | 110.08(12) | N21-C25-C26 | 129.43(15) |
| C6-C5-C10                | 120.27(13) | N21-C25-C30 | 110.25(13) |
| C12-N2-C11               | 129.84(12) | C30-C25-C26 | 120.32(14) |
| C12-N2-C10               | 106.08(11) | C32-N22-C30 | 105.83(12) |
| C10-N2-C11               | 124.06(11) | C32-N22-C31 | 130.48(12) |
| N4-C13-C12               | 118.02(12) | C30-N22-C31 | 123.62(12) |
| N4-C13-N3                | 126.43(13) | N24-C33-C32 | 117.80(13) |
| N3-C13-C12               | 115.55(13) | N24-C33-N23 | 125.92(14) |
| C7-C6-C5                 | 118.03(14) | N23-C33-C32 | 116.28(13) |
| N2-C10-C5                | 105.55(12) | C27-C26-C25 | 117.48(18) |
| N2-C10-C9                | 132.68(13) | C25-C30-C29 | 122.23(15) |
| C9-C10-C5                | 121.76(13) | N22-C30-C25 | 105.94(12) |
| C13-N4-C16               | 116.00(14) | N22-C30-C29 | 131.83(15) |
| C14-N3-C13               | 115.75(14) | C33-N24-C36 | 115.93(15) |
| C6-C7-C8                 | 121.00(15) | C33-N23-C34 | 115.30(15) |
| C8-C9-C10                | 116.66(14) | C26-C27-C28 | 121.67(17) |
| N4-C16-C15               | 122.76(16) | C28-C29-C30 | 116.44(17) |
| N3-C14-C15               | 122.34(17) | N23-C34-C35 | 123.91(16) |
| C9-C8-C7                 | 122.25(14) | C29-C28-C27 | 121.85(16) |
| C16-C15-C14              | 116.73(15) | C36-C35-C34 | 115.58(15) |
**Table S3**  Selected least-squares planes data for ligand L6.

| Least-squares planes description | Max. deviation (Å) | Atom | Dihedral Angle (°) |
|----------------------------------|--------------------|------|--------------------|
| Benzimidazole 1                  | 0.010              | C12  | 5.93(5)            |
| for N1 C5 C6 C7 C8 C9 C10 N2 C12 |                    |      |                    |
| Pyrimidine 1                     | 0.005              | N3   |                    |
| N3 C14 C15 C16 N4 C13            |                    |      |                    |
| Benzimidazole 2                  | 0.006              | C26-C28 | 9.71(5)        |
| N21 C25 C26 C27 C28 C29 C30 N22  |                    |      |                    |
| Pyrimidine 2                     | 0.004              | C33C35C34 |            |
| N23 C34 C35 C36 N24 C33          |                    |      |                    |

**Figure S16**  Intermolecular stacking between molecules of ligand L6 (molecule 1 in red and molecule 2 in blue). Arrows show the normals to planes and grey dotted lines the centroid-centroid distances (Å).
Figure S17 View of the molecular packing along $a$ axis (left) and along $b$ axis (right).
Table S4  Crystal data and structure refinement for ligand L7.

| Compound | L7 |
|----------|----|
| Empirical formula | $\text{C}_{12}\text{H}_{10}\text{N}_4$ |
| Formula weight | 210.24 |
| Temperature/K | 180.15 |
| Crystal system | monoclinic |
| Space group | $\text{P}2_1/c$ |
| $a$/Å | 7.7949(3) |
| $b$/Å | 11.6274(5) |
| $c$/Å | 22.4728(10) |
| $\alpha$/° | 90 |
| $\beta$/° | 99.254(4) |
| $\gamma$/° | 90 |
| Volume/Å³ | 2010.29(14) |
| $Z$ | 8 |
| $\rho$ calc/g·cm⁻³ | 1.389 |
| $\mu$/mm⁻¹ | 0.707 |
| $F(000)$ | 880.0 |
| Crystal size/mm³ | $0.407 \times 0.263 \times 0.224$ |
| Radiation | CuKα ($\lambda = 1.54184$) |
| $2\Theta$ range for data collection/° | 8.586 to 141.53 |
| Index ranges | $-9 \leq h \leq 9$, $-14 \leq k \leq 14$, $-27 \leq l \leq 26$ |
| Reflections collected | 8262 |
| Independent reflections | 8262 [$R_{\text{sigma}} = 0.0270$] |
| Data/restraints/parameters | 8262/0/292 |
| Goodness-of-fit on $F^2$ | 1.065 |
| Final $R$ indexes [$I \geq 2\sigma (I)$] | $R_1 = 0.0521$, $wR_2 = 0.1511$ |
| Final $R$ indexes [all data] | $R_1 = 0.0595$, $wR_2 = 0.1592$ |
| Largest diff. peak/hole / e Å⁻³ | 0.33/-0.26 |
Figure S18 ORTEP view of the two different ligand molecules in its crystal structure of L7 (ellipsoids are drawn at 50% probability) with numbering scheme.

Table S5  Selected bond distances (Å) and bond angles (°) for ligand L7.

| Bond Length (Å) | N1-C5    | N1-C12   | N2-C10   | N2-C11   | N2-C12   | N3-C15   | N3-C16   | N4-C13   | N4-C16   | C5-C6    | C5-C10   | C6-C7    | C7-C8    | C8-C9    | C9-C10   | C12-C13  | C13-C14  | C14-C15  |
|----------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|                | 1.382(3) | 1.320(2) | 1.384(3) | 1.459(2) | 1.374(2) | 1.335(3) | 1.319(3) | 1.349(3) | 1.338(3) | 1.394(3) | 1.400(3) | 1.381(3) | 1.407(3) | 1.379(3) | 1.393(3) | 1.467(3) | 1.390(3) | 1.368(3) |
|                | N21-C25  | N21-C32  | N22-C30  | N22-C31  | N22-C32  | N23-C35  | N23-C36  | N24-C33  | N24-C36  | C25-C26  | C25-C30  | C26-C27  | C27-C28  | C28-C29  | C29-C30  | C32-C33  | C33-C34  | C34-C35  |
|                | 1.318(2) | 1.380(3) | 1.461(2) | 1.375(2) | 1.338(3) | 1.320(3) | 1.345(3) | 1.338(3) | 1.398(3) | 1.403(3) | 1.378(3) | 1.415(4) | 1.377(3) | 1.394(3) | 1.468(3) | 1.397(3) | 1.375(3) | 1.318(2) |
| Bond Angles (°)                          |          |          |          |
|----------------------------------------|----------|----------|----------|
| C12-N1-C5                              | 104.83(15) | C32-N21-C25  | 104.82(15) |
| C10-N2-C11                             | 123.41(16) | C30-N22-C31  | 123.40(16) |
| C12-N2-C10                             | 105.83(15) | C32-N22-C30  | 105.88(15) |
| C12-N2-C11                             | 130.73(17) | C32-N22-C31  | 130.71(16) |
| C16-N3-C15                             | 114.66(19) | C36-N23-C35  | 114.69(19) |
| C16-N4-C13                             | 115.22(19) | C36-N24-C33  | 115.53(19) |
| N1-C5-C6                               | 129.57(18) | N21-C25-C26  | 129.87(18) |
| N1-C5-C10                              | 110.02(17) | N21-C25-C30  | 110.03(17) |
| C6-C5-C10                              | 120.41(19) | C26-C25-C30  | 120.10(18) |
| C7-C6-C5                               | 117.8(2)  | C27-C26-C25  | 118.1(2)   |
| C6-C7-C8                               | 121.0(2)  | C26-C27-C28  | 121.1(2)   |
| C9-C8-C7                               | 122.0(2)  | C29-C28-C27  | 121.5(2)   |
| C8-C9-C10                              | 116.57(19) | C28-C29-C30  | 117.0(2)   |
| N2-C10-C5                              | 105.87(16) | N22-C30-C25  | 105.82(16) |
| N2-C10-C9                              | 131.93(18) | N22-C30-C29  | 131.99(19) |
| C9-C10-C5                              | 122.20(19) | C29-C30-C25  | 122.20(19) |
| N1-C12-N2                              | 113.44(17) | N21-C32-N22  | 113.45(17) |
| N1-C12-C13                             | 120.67(16) | N21-C32-C33  | 120.43(16) |
| N2-C12-C13                             | 125.88(17) | N22-C32-C33  | 126.12(16) |
| N4-C13-C12                             | 119.30(17) | N24-C33-C32  | 119.64(17) |
| N4-C13-C14                             | 120.91(18) | N24-C33-C34  | 120.92(19) |
| C14-C13-C12                            | 119.76(18) | C34-C33-C32  | 119.43(17) |
| C15-C14-C13                            | 117.48(19) | C35-C34-C33  | 117.24(19) |
| N3-C15-C14                             | 123.1(2)  | N23-C35-C34  | 123.1(2)   |
| N3-C16-N4                              | 128.6(2)  | N23-C36-N24  | 128.6(2)   |
Table S6  Selected least-squares planes data for ligand L7.

| Least-squares planes description | Max. deviation (Å) | Atom | Dihedral Angle (°) |
|---------------------------------|--------------------|------|--------------------|
| Benzimidazole 1                 | 0.010              | N2   | 12.966)            |
| N1 C5 C6 C7 C8 C9 C10 N2 C12    |                    |      |                    |
| Pyrimidine 1                    | 0.005              | C13  |                    |
| N3 C14 C15 C16 N4 C13           |                    |      |                    |
| Benzimidazole 2                 | 0.006              | N22  | 7.58(6)            |
| N21 C25 C26 C27 C28 C29 C30 N22 C32 |                |      |                    |
| Pyrimidine 2                    | 0.005              | N24  |                    |
| N23 C34 C35 C36 N24 C33         |                    |      |                    |

Figure S19  Intermolecular stacking in ligand L7. The grey dotted lines show the the centroid-centroid distances (in Å).
Figure S20 View of the molecular packing along $a$ axis (left) and along $c$ axis (right) showing the one-dimensional $\pi$–$\pi$ stacking along $a$ direction.
Figure S21 a) Variation of absorption spectra and b) corresponding variation of observed molar extinctions at different wavelengths recorded for the spectrophotometric titration of L6 with Zn(CF₃SO₃)₂ (total ligand concentration: 2.1·10⁻⁴ mol.dm⁻³ in acetonitrile, 298 K). c) Evolving factor analysis using four absorbing eigenvectors and d) re-constructed individual electronic absorption spectra. e) Speciation for [L₆]ₜₖₖ = 2·10⁻⁴ M computed by using the stability constants obtained by non-linear least-square fits (Table 1).
Figure S22 a) Variation of absorption spectra and b) corresponding variation of observed molar extinctions at different wavelengths recorded for the spectrophotometric titration of \( \text{L}_7 \) with \( \text{Zn} (\text{CF}_3\text{SO}_3)_2 \) (total ligand concentration: \( 2.1 \cdot 10^{-4} \text{ mol.dm}^{-3} \) in acetonitrile, 298 K). c) Evolving factor analysis using four absorbing eigenvectors and d) re-constructed individual electronic absorption spectra. e) Speciation computed for \( [\text{L}_7]_{\text{tot}} = 2 \cdot 10^{-4} \text{ M} \) by using the stability constants obtained by non-linear least-square fits (Table 1).
Figure S23 a) Variation of absorption spectra and b) corresponding variation of observed molar extinctions at different wavelengths recorded for the spectrophotometric titration of \[\text{L6}\] with \[\text{Fe(CF}_3\text{SO}_3)_2\] (total ligand concentration: \(2.1 \cdot 10^{-4}\ \text{mol dm}^{-3}\) in acetonitrile, 298 K). c) Evolving factor analysis using four absorbing eigenvectors and d) re-constructed individual electronic absorption spectra. e) Speciation for \([\text{L6}]_\text{tot} = 2 \cdot 10^{-4}\ \text{M}\) computed by using the stability constants obtained by non-linear least-square fits (Table 1).
**Figure S24** a) Variation of absorption spectra and b) corresponding variation of observed molar extinctions at different wavelengths recorded for the spectrophotometric titration of \( L_7 \) with \( \text{Ni(BF}_4\text{)}_2 \) (total ligand concentration: \( 9.4 \times 10^{-5} \text{ mol.dm}^{-3} \) in acetonitrile, 298 K).  
c) Evolving factor analysis using four absorbing eigenvectors and d) re-constructed individual electronic absorption spectra.  
e) Speciation for \([L_7]_{tot} = 9.4 \times 10^{-5} \text{ M} \) computed by using the stability constants obtained by non-linear least-square fits (Table 1).
Table S7 Stability constants for the successive formation of \([M(Lk)_n]^{2+}\) (\(M = \text{Zn, Ni, Fe}\), \(Lk = L1, L4, n = 1, 2, 3\), non-coordinating anions: \(\text{ClO}_4^-, \text{CF}_3\text{SO}_3^-\) or \(\text{BF}_4^-\)) in acetonitrile (293 K), metal-ligand interaction parameter \((f^{M,Lk})\) and inter-ligand interaction parameter \((u^{Lk,Lk})\), and associated energies \(\Delta G_{\text{affinity}} = -RT\ln(f^{M,Lk})\) and \(\Delta E_{\text{interaction}} = -RT\ln(u^{Lk,Lk})\).

|        | \(\log(f^{M,Lk})\) | \(\Delta G_{\text{affinity}}/\text{kJ} \cdot \text{mol}^{-1}\) | \(\log(u^{Lk,Lk})\) | \(\Delta E_{\text{interaction}}/\text{kJ} \cdot \text{mol}^{-1}\) |
|--------|---------------------|-------------------------------------------------|-----------------|-----------------|
| \([\text{Zn}(L4)_n]^{2+}\)^\(^a\) | 6.89(3) | 5.46(6) | -31.1(3) | -0.18(7) | 1.1(4) |
|        | \(\log(\beta_{1,1}) = 6.89(3)\)^\(^a\) | | | | |
|        | \(\log(\beta_{1,2}) = 12.76(5)\)^\(^a\) | | | | |
|        | \(\log(\beta_{1,3}) = 17.64(5)\)^\(^a\) | | | | |
| \([\text{Zn}(L1)_n]^{2+}\)^\(^a\) | 7.7(7) | 6.32(5) | -36.0(3) | 0.40(5) | -2.3(3) |
|        | \(\log(\beta_{1,1}) = 7.7(7)\)^\(^a\) | | | | |
|        | \(\log(\beta_{1,2}) = 15.0(4)\)^\(^a\) | | | | |
|        | \(\log(\beta_{1,3}) = 21.9(6)\)^\(^a\) | | | | |
| \([\text{Fe}(L4)_n]^{2+}\)^\(^b\) | 6.05(9) | 4.5(1) | -25.9(8) | 0.5(2) | -2.7(9) |
|        | \(\log(\beta_{1,1}) = 6.045(9)\)^\(^b\) | | | | |
|        | \(\log(\beta_{1,2}) = 11.49(2)\)^\(^b\) | | | | |
|        | \(\log(\beta_{1,3}) = 16.82(2)\)^\(^b\) | | | | |
| \([\text{Fe}(L1)_n]^{2+}\)^\(^b\) | 7.0(1) | 5.8(1) | -32.9(8) | 1.0(2) | -5(1) |
|        | \(\log(\beta_{1,1}) = 7.0(1)\)^\(^b\) | | | | |
|        | \(\log(\beta_{1,2}) = 14.7(2)\)^\(^b\) | | | | |
|        | \(\log(\beta_{1,3}) = 21.9(4)\)^\(^b\) | | | | |

\(^a\) Reference 74. \(^b\) Reference 61
Figure S25 Microspecies and associated microscopic formation constants considered for the complexes a) [Zn(Lk)(CH$_3$CN)$_4$]$^{2+}$, b) [Zn(Lk)$_2$(CH$_3$CN)$_2$]$^{2+}$ and c) [Zn(Lk)$_3$]$^{2+}$. For [Zn(Lk)$_2$(CH$_3$CN)$_2$]$^{2+}$, we use the cis/trans terminology for describing the relative orientation of the two solvent molecules, whereas the additional mer/fac designation refers to the relative orientation of the two unsymmetrical ligands as defined in the saturated [Zn(Lk)$_3$]$^{2+}$ complex, i.e. a trans NA-Zn-NA arrangement is noted merA, a trans NB-Zn-NB is noted merB and a trans NA-Zn-NB is noted fac.
Figure S26 Concentration profiles obtained using HySS2009 simulation\textsuperscript{73} and the formation constants collected in Table 1 for the complex species $[\text{Fe(II)\text{L}_{6}}]^{2+}$ at a) $[\text{L}_{6}]_{\text{tot}} = 10$ mM, and b) $[\text{L}_{6}]_{\text{tot}} = 100$ mM (acetonitrile, 293 K).
Figure S27 Concentration profiles obtained using HySS2009 simulation\textsuperscript{73} and the formation constants collected in Table 1 for the complex species [Ni(L7)\textsubscript{n}]\textsuperscript{2+} at a) [L7]\textsubscript{tot} = 10 mM, and b) [L7]\textsubscript{tot} = 100 mM (acetonitrile, 293 K).
Figure S28 a) Room and b) variable temperature $^1$H NMR spectra recorded for $[\text{Zn(L6)}_3]^{2+}$ using $[\text{L6}]_{\text{tot}} = 10 \text{ mM}$ in CD$_3$CN ($f = \text{facial}, m = \text{meridional}$).
Figure S29 a) Room and b) variable temperature $^1$H NMR spectra recorded for $[\text{Zn(L7)}_3]^{2+}$ using $[\text{L7}]_{\text{tot}} = 0.1$ M in CD$_3$OD ($f$ = facial, $m$ = meridional).
Figure S30 Van’t Hoff plots of \( \ln(K_{\text{mer-fac}}) \) vs. \( 1/T \) (equilibrium 14) for a solution of a) 10 mM \( [\text{Zn(L6)}_3]^{2+} \) in CD$_3$CN (233–253 K), b) 10 mM \( [\text{Zn(L6)}_3]^{2+} \) in CD$_3$OD (210–238 K) and c) 100 mM \( [\text{Zn(L7)}_3]^{2+} \) in CD$_3$OD (208–228 K).
Table S8 Thermodynamic enthalpic ($\Delta H_{\text{mer}\rightarrow \text{fac}}^{\text{Zn,Lk}}$) and entropic ($\Delta S_{\text{mer}\rightarrow \text{fac}}^{\text{Zn,Lk}}$) contributions to equilibrium (14) in solution.

| Complex          | Solvent   | $\varepsilon$ a | $\Delta H_{\text{mer}\rightarrow \text{fac}}^{\text{Zn,Lk}}$ /kJ⋅mol$^{-1}$ | $\Delta S_{\text{mer}\rightarrow \text{fac}}^{\text{Zn,Lk}}$ /J⋅mol$^{-1}$.K$^{-1}$ | $\Delta G_{\text{mer}\rightarrow \text{fac}}^{\text{Zn,Lk}}$ b /kJ⋅mol$^{-1}$ | $T_{1/2}$ /K | Ref. |
|------------------|-----------|-----------------|---------------------------------|---------------------------------|---------------------------------|-------------|------|
| [Zn(1L)3]$^{2+}$ | CD$_3$CN  | 37.5            | -1.7(1)                         | -14(1)                          | 2.5(3)                          | 121(11)     | 74   |
|                  | CD$_3$NO$_2$ | 35.9            | -7.4(3)                         | -39(1)                          | 4.2(4)                          | 190(9)      | 74   |
| [Zn(4L)3]$^{2+}$ | CD$_3$CN  | 37.5            | -4(1)                           | -16(4)                          | 0.8(1.6)                        | 250(88)     | 74   |
|                  | CD$_3$NO$_2$ | 35.9            | -11(1)                          | -45(4)                          | 2.4(1.5)                        | 244(31)     | 74   |

a Relative dielectric constants. b $\Delta G_{\text{mer}\rightarrow \text{fac}}^{\text{Zn,Lk}}$ are calculated at $T = 298$ K.

Figure S31 Absorption spectrum of [Ni(6L)$_3$]$^{2+}$ in acetonitrile (0.1 M, 298 K, red trace, left axis) and solid-state absorption spectrum of [Ni(6L)$_3$(BF$_4$)$_2$] (298 K, green trace, right axis) with the d-d transitions labelled on the graph.
Figure S32 Absorption spectrum of [Ni(L7)3]2+ in acetonitrile (0.1 M, 298 K, red trace, left axis) and solid-state absorption spectrum of [Ni(L7)3](BF4)2 (298 K, green trace, right axis) with the d-d transitions labelled on the graph.

Table S9 Ligand-field strengths (\(\Delta_{\text{oct}}\)) and Racah parameters (\(B, C\)) computed\(^{61}\) for [Ni(Lk)3]^{2+} in 0.1 M acetonitrile solution at 298 K.

|          | [Ni(L1)3]^{2+} | [Ni(L4)3]^{2+} | [Ni(L6)3]^{2+} | [Ni(L7)3]^{2+} |
|----------|----------------|----------------|----------------|----------------|
| \(\Delta_{\text{oct}}/\text{cm}^{-1}\) | 11423          | 11476          | 11605          | 11385          |
| \(B/\text{cm}^{-1}\)     | 889            | 866            | 865            | 870            |
| \(C/\text{cm}^{-1}\)     | 3096           | 3149           | 2995           | 3068           |
| \(\Delta_{\text{oct}}/B\) | 12.9           | 13.3           | 13.4           | 13.1           |
| \(C/B\)                | 3.48           | 3.64           | 3.46           | 3.52           |
| \(\beta^a\)            | 0.85           | 0.83           | 0.83           | 0.83           |

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\(^{a}\) Nephelauxetic parameter \(\beta = B/B^0\) using \(B^0 = 1042 \text{ cm}^{-1}\) for free Ni^{2+} ion.\(^{88}\)
**Figure S33** Variable temperature $^1$H-NMR spectra recorded for 10 mM [Fe(L6)$_3$]$^{2+}$ in CD$_3$CN.

**Figure S34** Shift of the $^1$H-NMR signal of tert-butanol outside the coaxial tube ($\delta_{\text{ref}}$) to higher frequencies with respect to the signal of tert-butanol used as the reference ($\delta_{\text{int}}$) in the coaxial tube at temperatures between 233 K – 333 K for the paramagnetic complex [Fe(L6)$_3$]$^{2+}$ in solution (10.2 mM in CD$_3$CN).
Empirical linear $H/S$ compensation observed for the spin crossover equilibria observed in $[\text{Fe(}Lk\text{)}_3]^{2+}$ in CD$_3$CN ($Lk = L1, L4, L6$ and $L7$).

**Figure S35** Empirical linear $H/S$ compensation observed for the spin crossover equilibria observed in $[\text{Fe(}Lk\text{)}_3]^{2+}$ in CD$_3$CN ($Lk = L1, L4, L6$ and $L7$).
Table S10 Elemental analysis of the primary [Ni(L6)3](BF4)2·1.55CH3CN·0.4H2O, [Zn(L6)3](CF3SO3)2·0.6H2O, [Fe(L6)3](BF4)2·0.15CH3CN·1.2H2O, [Ni(L7)3](BF4)2·0.85H2O, [Zn(L7)3](PF6)2·1.25H2O and [Fe(L7)3](PF6)1.76(BF4)0.24·0.6H2O complexes.

| Complex                                      | %C  | %H  | %N  | Mol. Wt. |
|----------------------------------------------|-----|-----|-----|----------|
| [Ni(L6)3](BF4)2·1.55CH3CN·0.4H2O             | 50.29 | 3.83 | 20.32 | 933.865  |
| η = 66%                                      |     |     |     |          |
| Calculated                                   |     |     |     |          |
| Found                                        | 50.19 | 3.7  | 20.46 |          |
| Deviation                                    | 0.1  | 0.13| 0.14 |          |
| [Zn(L6)3](CF3SO3)2·0.6H2O                   | 45.41 | 3.13 | 16.72 | 1005.42 |
| η = 72%                                      |     |     |     |          |
| Calculated                                   |     |     |     |          |
| Found                                        | 45.38 | 3.07 | 16.76 |          |
| Deviation                                    | 0.03 | 0.06| 0.04 |          |
| [Fe(L6)3](BF4)2·0.15CH3CN·1.2H2O            | 49.1 | 3.73 | 19.17 | 887.951 |
| η = 79%                                      |     |     |     |          |
| Calculated                                   |     |     |     |          |
| Found                                        | 49.17 | 3.82 | 19.54 |          |
| Deviation                                    | 0.07 | 0.09| 0.08 |          |
| [Ni(L7)3](BF4)2·0.85H2O                     | 49.23 | 3.64 | 19.14 | 878.32  |
| η = 52%                                      |     |     |     |          |
| Calculated                                   |     |     |     |          |
| Found                                        | 49.05 | 3.41 | 18.93 |          |
| Deviation                                    | 0.18 | 0.23| 0.21 |          |
| [Zn(L7)3](PF6)2·1.25H2O                     | 42.87 | 3.25 | 16.67 | 1008.52 |
| η = 51%                                      |     |     |     |          |
| Calculated                                   |     |     |     |          |
| Found                                        | 42.78 | 3.16 | 16.76 |          |
| Deviation                                    | 0.09 | 0.09| 0.09 |          |
| [Fe(L7)3](PF6)1.76(BF4)0.24·0.6H2O          | 44.42 | 3.23 | 17.27 | 973.34  |
| η = 46%                                      |     |     |     |          |
| Calculated                                   |     |     |     |          |
| Found                                        | 44.09 | 3.25 | 17.06 |          |
| Deviation                                    | 0.33 | 0.02| 0.21 |          |
### Table S11: Crystal data and structure refinement for [Zn(L6)]\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2}(C\textsubscript{2}H\textsubscript{3}N)\textsubscript{2.5} (1), [Zn(L6)]\textsubscript{3}(BF\textsubscript{4})\textsubscript{2}(CH\textsubscript{3}CN)\textsubscript{2} (2), [Ni(L6)]\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2} (3) and [Ni(L6)]\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2}·CH\textsubscript{3}CN (4).

|                  | [Zn(L6)]\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2}(CH\textsubscript{3}CN)\textsubscript{2.5} (1) | [Zn(L6)]\textsubscript{3}(BF\textsubscript{4})\textsubscript{2}(CH\textsubscript{3}CN)\textsubscript{2} (2) | [Ni(L6)]\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2} (3) | [Ni(L6)]\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2}·CH\textsubscript{3}CN (4) |
|------------------|--------------------------------------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Empirical formula| C\textsubscript{41}H\textsubscript{37.5}Cl\textsubscript{2}N\textsubscript{14.5}O\textsubscript{8}Zn | C\textsubscript{40}H\textsubscript{36}B\textsubscript{2}F\textsubscript{8}N\textsubscript{12}Zn  | C\textsubscript{36}H\textsubscript{30}Cl\textsubscript{2}N\textsubscript{12}NiO\textsubscript{8} | C\textsubscript{36}H\textsubscript{30}Cl\textsubscript{2}N\textsubscript{13}NiO\textsubscript{8} |
| Formula Unit     | C\textsubscript{36}H\textsubscript{30}Cl\textsubscript{2}N\textsubscript{12}Zn·(C\textsubscript{2}H\textsubscript{3}N)\textsubscript{2} | C\textsubscript{36}H\textsubscript{30}Cl\textsubscript{2}N\textsubscript{12}Zn·(C\textsubscript{2}H\textsubscript{3}N)\textsubscript{2} | C\textsubscript{36}H\textsubscript{30}Cl\textsubscript{2}N\textsubscript{12}NiO\textsubscript{8}·C\textsubscript{2}H\textsubscript{3}N | C\textsubscript{36}H\textsubscript{30}Cl\textsubscript{2}N\textsubscript{13}NiO\textsubscript{8}·C\textsubscript{2}H\textsubscript{3}N |
| Formula weight   | 997.69                                                                 | 951.82                                                                 | 888.33                                                                 | 929.38                                                                 |
| Temperature      | 180.00(10) K                                                               | 180.01(10) K                                                               | 100.00(10) K                                                               | 180.00(10) K                                                               |
| Wavelength       | 1.54184 Å                                                                   | 1.54184 Å                                                                   | 1.54184 Å                                                                   | 1.54184 Å                                                                   |
| Crystal system   | Triclinic                                                                   | Triclinic                                                                   | Triclinic                                                                   | Monoclinic                                                                   |
| Space group      | P-1                                                                         | P-1                                                                         | P-1                                                                         | P12\textsubslash/c1                                                        |
| a                | a = 12.7622(7) Å                                                           | a = 11.8497(5) Å                                                           | a = 14.6645(6) Å                                                           | a = 9.51580(10) Å                                                         |
| b                | b = 14.6333(6) Å                                                           | b = 13.0576(5) Å                                                           | b = 14.5548(6) Å                                                           | b = 22.5839(2) Å                                                          |
| c                | c = 14.8701(5) Å                                                           | c = 14.6652(5) Å                                                           | c = 17.0631(6) Å                                                           | c = 19.1174(2) Å                                                         |
| Unit cell dimensions | \(\alpha = 62.805(4)°\)                                                  | \(\alpha = 77.910(3)°\)                                                  | \(\alpha = 90.232(3)°\)                                                  | \(\alpha = 90°\)                                                          |
| \(\beta\)       | \(\beta = 69.432(4)°\)                                                 | \(\beta = 83.652(3)°\)                                                 | \(\beta = 93.788(3)°\)                                                 | \(\beta = 96.5810(10)°\)                                                |
| \(\gamma\)      | \(\gamma = 70.165(4)°\)                                                 | \(\gamma = 73.048(4)°\)                                                 | \(\gamma = 90.093(3)°\)                                                 | \(\gamma = 90°\)                                                          |
| Volume           | 2258.7(2) Å\(^3\)                                                         | 2119.42(15) Å\(^3\)                                                      | 3634.0(2) Å\(^3\)                                                        | 4081.33(7) Å\(^3\)                                                      |
| Z                | 2                                                                           | 2                                                                           | 4                                                                           | 4                                                                           |
| Density (calculated) | 1.467 Mg/m\(^3\)                                                       | 1.491 Mg/m\(^3\)                                                         | 1.624 Mg/m\(^3\)                                                         | 1.513 Mg/m\(^3\)                                                        |
| Absorption coefficient | 2.428 mm\(^{-1}\)                                                        | 1.547 mm\(^{-1}\)                                                        | 2.752 mm\(^{-1}\)                                                        | 2.485 mm\(^{-1}\)                                                        |
| F(000)           | 1026                                                                         | 972                                                                         | 1824                                                                        | 1912                                                                        |
| Crystal size     | 0.354 x 0.281 x 0.232 mm\(^3\)                                               | 0.495 x 0.162 x 0.127 mm\(^3\)                                              | 0.186 x 0.114 x 0.076 mm\(^3\)                                              | 0.234 x 0.218 x 0.18 mm\(^3\)                                              |
| Theta range for data collection | 3.477 to 68.893°.                                                        | 3.602 to 68.837°.                                                        | 2.595 to 68.975°.                                                        | 3.040 to 68.897°.                                                        |
Index ranges | -15≤h≤15, -17≤k≤16, -17≤l≤13 | -14≤h≤14, -15≤k≤15, -16≤l≤17 | -17≤h≤15, -17≤k≤17, -19≤l≤20 | -11≤h≤10, -27≤k≤27, -17≤l≤23 |
---|---|---|---|---|
Reflections collected | 17217 | 16019 | 32057 | 33472 |
Independent reflections | 8247 [R(int) = 0.0154] | 7730 [R(int) = 0.0312] | 13338 [R(int) = 0.0420] | 7537 [R(int) = 0.0197] |
Completeness to theta (67.5°) | 99.70% | 99.80% | 99.90% | 100.00% |
Absorption correction | Gaussian | Analytical | Analytical | Analytical |
Max. and min. transmission | 1.000 and 0.470 | 0.883 and 0.679 | 0.868 and 0.726 | 0.699 and 0.638 |
Refinement method | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 |
Data / restraints / parameters | 8245 / 10 / 610 | 7730 / 0 / 535 | 13338 / 254 / 1247 | 7537 / 62 / 609 |
Goodness-of-fit on F2 | 1.053 | 1.048 | 1.110 | 1.044 |
Final R indices [I>2sigma(I)] | R1 = 0.0689, wR2 = 0.1910 | R1 = 0.0564, wR2 = 0.1545 | R1 = 0.0841, wR2 = 0.1817 | R1 = 0.0468, wR2 = 0.1301 |
R indices (all data) | R1 = 0.0751, wR2 = 0.1970 | R1 = 0.0686, wR2 = 0.1657 | R1 = 0.0905, wR2 = 0.1860 | R1 = 0.0484, wR2 = 0.1316 |
Extinction coefficient | n/a | n/a | n/a | n/a |
Largest diff. peak and hole | 0.710 and -0.821 e.Å\(^{-3}\) | 0.933 and -0.559 e.Å\(^{-3}\) | 0.646 and -0.881 e.Å\(^{-3}\) | 0.821 and -0.669 e.Å\(^{-3}\) |

**Comments on the models:**

[Zn(L6)\(_3\)](BF\(_4\))\(_2\)∙(CH\(_3\)CN)\(_2\) (2): The acetonitrile solvent molecules were found to be highly disordered in voids (V=387 Å\(^3\)) and their contribution to the scattering was masked using the solvent-masking routine smtbx.mask in OLEX2 [B. Rees, L. Jenner and M. Yusupov, *Acta Cryst. D*, 2005, 61, 1299-1301.]. The electron count and voids volume correspond to about two acetonitrile molecules per formula unit, which were added in the given chemical formula and other crystal data.

[Ni(L6)\(_3\)](ClO\(_4\))\(_2\) (3): The structure is based on twinned data and refined with two components of ratio 0.664/0.336 and twin law -1 0 0 0 1 0 0 0 -1.
Table S12 Crystal data and structure refinement for [Ni(L\textsubscript{6})\textsubscript{3}](BF\textsubscript{4})\textsubscript{2}:C\textsubscript{2}H\textsubscript{3}N (5), [Fe(L\textsubscript{6})\textsubscript{3}](ClO\textsubscript{4})\textsubscript{2} (6), and [Fe(L\textsubscript{6})\textsubscript{3}](BF\textsubscript{4})\textsubscript{2}:(C\textsubscript{5}H\textsubscript{12}O)\textsubscript{0.5} (7).

|                  | [Ni(L\textsubscript{6})\textsubscript{3}](BF\textsubscript{4})\textsubscript{2}:CH\textsubscript{3}CN | [Fe(L\textsubscript{6})\textsubscript{3}](ClO\textsubscript{4})\textsubscript{2} | [Fe(L\textsubscript{6})\textsubscript{3}](BF\textsubscript{4})\textsubscript{2}:(C\textsubscript{5}H\textsubscript{12}O)\textsubscript{0.5} |
|------------------|------------------------------------------------|---------------------------------|------------------------------------------------|
| **Empirical formula** | C\textsubscript{38}H\textsubscript{33}B\textsubscript{2}F\textsubscript{8}N\textsubscript{13}Ni | C\textsubscript{36}H\textsubscript{30}Cl\textsubscript{2}FeN\textsubscript{12}O\textsubscript{8} | C\textsubscript{39.50}H\textsubscript{36.6}B\textsubscript{2}F\textsubscript{8}FeN\textsubscript{12}O\textsubscript{0.5} |
| **Formula Unit** | C\textsubscript{36}H\textsubscript{30}B\textsubscript{2}F\textsubscript{8}N\textsubscript{12}Ni, C\textsubscript{2}H\textsubscript{3}N | C\textsubscript{36}H\textsubscript{30}Cl\textsubscript{2}FeN\textsubscript{12}O\textsubscript{8} | C\textsubscript{36}H\textsubscript{30}B\textsubscript{3}F\textsubscript{8}FeN\textsubscript{12}:(C\textsubscript{5}H\textsubscript{12}O)\textsubscript{0.5}(C\textsubscript{2}H\textsubscript{3}N)\textsubscript{0.5} |
| **Formula weight** | 904.1 | 885.47 | 923.88 |
| **Temperature** | 180.00(10) K | 100.01(10) K | 180.00(10) K |
| **Wavelength** | 1.54184 Å | 1.54184 Å | 1.54184 Å |
| **Crystal system** | Monoclinic | Monoclinic | Triclinic |
| **Space group** | P\textsubscript{12}/c\textsubscript{1} | P\textsubscript{12}/c\textsubscript{1} | P\textsubscript{1} |
| **a** = 9.42950(10) Å | a = 14.8236(2) Å | a = 11.8247(6) Å |
| **b** = 22.5937(3) Å | b = 14.3119(2) Å | b = 12.9758(6) Å |
| **c** = 18.8708(2) Å | c = 16.9607(3) Å | c = 14.7202(6) Å |
| **α** = 90° | α = 90° | α = 77.760(4)° |
| **β** = 94.9100(10)° | β = 94.4286(13)° | β = 83.510(4)° |
| **γ** = 90° | γ = 90° | γ = 74.276(4)° |
| **Volume** | 4005.62(8) Å\textsuperscript{3} | 3587.54(10) Å\textsuperscript{3} | 2120.94(17) Å\textsuperscript{3} |
| **Z** | 4 | 4 | 2 |
| **Density (calculated)** | 1.499 Mg/m\textsuperscript{3} | 1.639 Mg/m\textsuperscript{3} | 1.447 Mg/m\textsuperscript{3} |
| **Absorption coefficient** | 1.449 mm\textsuperscript{-1} | 5.379 mm\textsuperscript{-1} | 3.579 mm\textsuperscript{-1} |
| **F(000)** | 1848 | 1816 | 946 |
| **Crystal size** | 0.308 x 0.215 x 0.172 mm\textsuperscript{3} | 0.265 x 0.199 x 0.077 mm\textsuperscript{3} | 0.329 x 0.128 x 0.051 mm\textsuperscript{3} |
| **Theta range for data collection** | 3.058 to 68.802° | 2.990 to 68.807° | 3.077 to 69.825° |
| Index ranges         | -11 ≤ h ≤ 11, -23 ≤ k ≤ 27, -15 ≤ l ≤ 22 | -12 ≤ h ≤ 17, -17 ≤ k ≤ 16, -20 ≤ l ≤ 20 | -14 ≤ h ≤ 14, -12 ≤ k ≤ 15, -17 ≤ l ≤ 17 |
|---------------------|------------------------------------------|---------------------------------------------|--------------------------------------------|
| Reflections collected | 17683                                    | 16165                                       | 16085                                      |
| Independent reflections | 7352 [R(int) = 0.0170]                 | 6553 [R(int) = 0.0190]                     | 7746 [R(int) = 0.0291]                    |
| Completeness to theta = 67.500° | 99.80%                                   | 99.80%                                      | 99.70%                                     |
| Absorption correction | Analytical                               | Analytical                                 | Analytical                                |
| Max. and min. transmission | 0.830 and 0.746                         | 0.681 and 0.392                            | 0.852 and 0.558                           |
| Refinement method    | Full-matrix least-squares on F^2         | Full-matrix least-squares on F^2           | Full-matrix least-squares on F^2          |
| Data / restraints / parameters | 7352 / 75 / 637                        | 6553 / 42 / 581                            | 7746 / 14 / 624                           |
| Goodness-of-fit on F2 | 1.056                                    | 1.033                                       | 1.028                                      |
| Final R indices [I>2σ(I)] | R1 = 0.0413, wR2 = 0.1084              | R1 = 0.0372, wR2 = 0.0964                  | R1 = 0.0590, wR2 = 0.1660                 |
| R indices (all data) | R1 = 0.0452, wR2 = 0.1109               | R1 = 0.0411, wR2 = 0.0992                  | R1 = 0.0724, wR2 = 0.1819                 |
| Extinction coefficient | n/a                                      | n/a                                         | n/a                                        |
| Largest diff. peak and hole | 0.652 and -0.567 eÅ⁻³                 | 0.715 and -0.570 eÅ⁻³                      | 0.502 and -0.396 eÅ⁻³                     |
Table S13 Crystal data and structure refinement for [Zn(L7)_3](ClO_4)_2 (8) [Zn(L7)_3](PF_6)_2 (9) and [Ni(L7)_3](ClO_4)_1.48(PF_6)_0.52 (10).

|                          | [Zn(L7)_3](ClO_4)_2 (8) | [Zn(L7)_3](PF_6)_2 (9) | [Ni(L7)_3](PF_6)_0.52(ClO_4)_1.48 (10) |
|--------------------------|-------------------------|------------------------|----------------------------------------|
| Empirical formula        | C_{36}H_{30}Cl_{2}N_{12}O_{8}Zn | C_{36}H_{30}F_{12}N_{12}P_{2}Zn | C_{72}H_{60}Cl_{12.96}F_{6.24}N_{24}Ni_{11.82}P_{1.04} |
| Formula Unit             | C_{36}H_{30}Cl_{2}N_{12}O_{8}Zn | C_{36}H_{30}F_{12}N_{12}P_{2}Zn | (C_{36}H_{30}N_{12}NiO_{5.92}Cl_{6.48}F_{3.12}P_{0.52})_{2} |
| Formula weight           | 894.99                  | 986.03                 | 1824                                   |
| Temperature              | 180.00(10) K            | 149.99(10) K           | 120.01(12) K                           |
| Wavelength               | 1.54184 Å               | 1.54184 Å              | 1.54184 Å                              |
| Crystal system           | Trigonal                | Monoclinic             | Monoclinic                             |
| Space group              | P-3c1                   | P12/c1                 | P12/c1                                 |
| Unit cell dimensions     |                         |                        |                                        |
|                         | α = 90°                 | α = 90°                | α = 90°                                |
|                         | β = 90°                 | β = 91.9320(9)°        | β = 98.5966(14)°                       |
|                         | γ = 120°                | γ = 90°                | γ = 90°                                |
| Volume                   | 1806.86(14) Å^3         | 3929.78(7) Å^3         | 7688.46(19) Å^3                       |
| Z                        | 2                       | 4                      | 4                                      |
| Density (calculated)     | 1.645 Mg/m^3            | 1.667 Mg/m^3           | 1.576 Mg/m^3                           |
| Absorption coefficient   | 2.937 mm^{-1}           | 2.581 mm^{-1}          | 2.570 mm^{-1}                          |
| F(000)                   | 916                     | 1992                   | 3731                                   |
| Crystal size             | 0.126 x 0.102 x 0.063 mm^3 | 0.236 x 0.062 x 0.059 mm^3 | 0.092 x 0.073 x 0.043 mm^3             |
| Theta range for data collection | 4.400 to 68.876°          | 3.255 to 74.472°         | 3.071 to 71.738°                      |
| Index ranges | -12≤h≤11, -12≤k≤12, -24≤l≤23 | -16≤h≤14, -13≤k≤13, -33≤l≤33 | -23≤h≤19, -25≤k≤26, -21≤l≤23 |
|-------------|-----------------------------|-----------------------------|-----------------------------|
| Reflections collected | 6333 | 52508 | 67327 |
| Independent reflections | 1125 [R(int) = 0.0250] | 8009 [R(int) = 0.0299] | 14753 [R(int) = 0.0279] |
| Completeness to theta = 67.500° | 100.00% | 99.90% | 99.90% |
| Absorption correction | Analytical | Gaussian | Gaussian |
| Max. and min. transmission | 0.856 and 0.787 | 1.000 and 0.384 | 1.000 and 0.729 |
| Refinement method | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 1125 / 0 / 164 | 8008 / 806 / 724 | 14753 / 980 / 1219 |
| Goodness-of-fit on F^2 | 1.125 | 1.058 | 1.048 |
| R1 = 0.0658, | R1 = 0.0505, | R1 = 0.0536, |
| wR2 = 0.1578 | wR2 = 0.1400 | wR2 = 0.1396 |
| R1 = 0.0708, | R1 = 0.0539, | R1 = 0.0635, |
| wR2 = 0.1609 | wR2 = 0.1429 | wR2 = 0.1454 |

Largest diff. peak and hole 0.490 and -0.798 e.Å⁻³ 0.92 and -0.75 e.Å⁻³ 1.121 and -0.697 e.Å⁻³

Comments on the models:

[Zn(L7)₃](ClO₄)₂ (8): Zn atom is located onto a 3-fold axis and nearby a 2-fold axis perpendicular to it. There is only 1/3 of the complex in the asymmetric unit which is disordered around the 2-fold axis (occupancies fixed to 0.5).

[Zn(L7)₃](PF₆)₂ (9): Two disordered hexafluorophosphate anion were refined using two components. Restraints were used on P-F and F-F distances as well as on anisotropic displacement parameters. The displacement parameters of the phosphor atoms were constrained to be identical. One part of the ligand is also disordered and was refined using 2 components and restrains on the geometry (FLAT and SADI) and on the displacement parameters (RIGU SIMU). EADP restraints were used on very close atoms.

[Ni(L7)₃](PF₆)₀.₅₂(ClO₄)₁.₄₈ (10): Two of the counterions were disordered and could not be satisfactorily modelled using only hexafluorophosphate. Since perchlorate were also present in the solution, a mixed perchlorate and hexafluoroborate model were used. One other counterion was fitted using two perchlorate molecules. Restraints were used on distances and displacement parameters. The displacement parameters of some central atoms were constrained to be identical. Finally, a disordered solvent molecule could not be fitted properly in our hands. The squeeze/bypass method was used. The R before applying the solvent correction were R1=0.0751 and wR2 0.2194. Four holes were located per unit-cell containing each about 24 electrons. This is almost the electron count of an acetonitrile molecule.
Table S14 Crystal data and structure refinement for Ni(L7)3(BF4)2·CH3OH·(CH3CN)0.5 (11), [Fe(L7)3](PF6)(BF4)·CH3OH (12) and [Fe(L7)3](PF6)1.72(ClO4)0.28·CH3OH (13).

|                      | [Ni(L7)3](BF4)2·CH3OH·(CH3CN)0.5 (11) | [Fe(L7)3](PF6)1.25(BF4)·CH3OH (12) | [Fe(L7)3](PF6)1.72(ClO4)0.28·CH3OH (13) |
|----------------------|---------------------------------------|-----------------------------------|--------------------------------------|
| **Empirical formula**| C38H35.50B2F8N12.50NiO (C36H30N12NiB2F8) | C73H64B2.5F19Fe2N24OP1.5 (C36H30N12FeB1.25P0.75F9)2 | C73H64Cl0.56F20.63Fe2N24O3.25P3.44 (C36H30N12Fe2Cl0.28F10.36O1.12P1.72)2 |
| **Formula Unit**     | (CH3OH)(CH3CN)0.5                     | (CH3OH)                           | (CH3OH)                             |
| **Formula weight**   | 915.62                                | 1839.80                           | 1959.46                             |
| **Temperature**      | 150.00(10) K                          | 150.00(10) K                      | 150.15 K                            |
| **Wavelength**       | 1.54184 Å                             | 1.54184 Å                         | 1.54184 Å                           |
| **Crystal system**   | Triclinic                             | Monoclinic                        | Monoclinic                          |
| **Space group**      | P-1                                   | P12/n1                            | P12/n1                              |
| **a**                | a = 11.6311(2) Å                      | a = 18.82600(10) Å                | a = 19.0452(4) Å                    |
| **b**                | b = 12.8430(2) Å                      | b = 21.23850(10) Å                | b = 21.4963(4) Å                    |
| **c**                | c = 14.99232(18) Å                    | c = 18.88290(10) Å                | c = 19.0632(5) Å                    |
| **α**                | α= 94.6407(12)°                       | α= 90°                            | α= 90°                              |
| **β**                | β= 100.7070(12)°                      | β= 98.0140(10)°                   | β= 98.075(2)°                       |
| **γ**                | γ= 113.7978(17)°                      | γ= 90°                            | γ= 90°                              |
| **Volume**           | 1982.93(6) Å³                        | 7476.33(7) Å³                     | 7727.1(3) Å³                        |
| **Z**                | 2                                     | 4                                 | 4                                    |
| **Density (calculated)** | 1.534 Mg/m³                          | 1.635 Mg/m³                      | 1.684 Mg/m³                        |
| **Absorption coefficient** | 1.486 mm⁻¹                         | 4.412 mm⁻¹                       | 4.911 mm⁻¹                          |
| **F(000)**           | 938                                   | 3800                              | 3979                                 |
Crystal size 0.232 x 0.153 x 0.049 mm³ 0.217 x 0.056 x 0.031 mm³ 0.082 x 0.037 x 0.022 mm³
Theta range for data collection 3.046 to 74.466° 3.105 to 74.447° 3.116 to 70.252°
Index ranges -14≤h≤14, -16≤k≤15,-15≤l≤18 -23≤h≤20, -26≤k≤26, -23≤l≤23 -22≤h≤23, -25≤k≤25, -20≤l≤22
Reflections collected 34638 96589 56784
Independent reflections 7887 [R(int)=0.0360] 14949 [R(int)=0.0268] 14030 [R(int)=0.0572]
Completeness to theta = 67.5° 99.00% 99.20% 97.3%
Absorption correction Analytical Gaussian Gaussian
Max. and min. transmission 0.934 and 0.788 1.000 and 0.429 0.948 and 0.708
Refinement method Full-matrix least-squares on F² Full-matrix least-squares on F² Full-matrix least-squares on F²
Data / restraints / parameters 7887/0/567 14949/395/1253 14030/207/1227
Goodness-of-fit on F² 1.121 1.038 1.035
Final R indices [I>2σ(I)] R₁=0.0506, wR₂=0.1424 R₁=0.0379, wR₂=0.1023 R₁=0.0764, wR₂=0.2007
R indices (all data) R₁=0.0550, wR₂=0.1457 R₁=0.0430, wR₂=0.1056 R₁=0.1190, wR₂=0.2256
Largest diff. peak 0.796 and -0.775 e.Å⁻³ 1.136 and -0.416 e.Å⁻³ 1.204 and -0.710 e.Å⁻³

Comments on the models:
[Fe(L7)3](PF6)(BF4)∙CH3OH (12): One disordered tetrafluoroborate anion was refined using two components. Restraints were used on B-F and F-F distances as well as on anisotropic displacement parameters. The displacement parameters of the boron atoms were constrained to be identical. A disordered solvent methanol molecule was also modelled with two components, using restraints on C-O distances and displacement parameters. Two sites are mixed tetrafluoroborate/ hexafluorophosphate sites and were refined using two components with restraints on the geometry (SADI) and restraints and constraints on the displacement parameters (RIGU and EADP)

[Fe(L7)3](PF6)1.72(ClO4)0.28∙CH3OH (13): One of the counterions was disordered and could not be satisfactorily modelled using only hexafluorophosphate. Since perchlorate were also present in the solution, a mixed perchlorate and hexafluorophosphate model was used, giving a better fit to the electronic density. Restraints were used on distances and displacement parameters. A disordered solvent methanol molecule was also modelled using two components, with restraints on distances and displacement parameters.
Figure S36 ORTEP view of $[\text{Zn}(\text{L6})_3]^{2+}$ in the crystal structure of $[\text{Zn}(\text{L6})_3](\text{ClO}_4)_2\cdot(\text{C}_2\text{H}_3\text{N})_{2.5}$ (1) (a) fac isomer (b) mer isomer (ellipsoids are drawn at 40% probability) with numbering scheme. Hydrogen atoms and ClO$_4^-$ counter anions are omitted for clarity.
Table S15  Selected bond distances (Å) and bond angles (°) for [Zn(L6)3](ClO4)2∙(C2H3N)2.5 (1).

| Bond Distances (Å) |  |
|-------------------|---|
| Zn(1A)-N(1)      | 2.183(4) | Zn(1B)-N(1) | 2.062(4) |
| Zn(1A)-N(3)      | 2.055(4) | Zn(1B)-N(3) | 2.430(4) |
| Zn(1A)-N(5)      | 2.248(4) | Zn(1B)-N(5) | 1.972(4) |
| Zn(1A)-N(7)      | 2.173(4) | Zn(1B)-N(7) | 2.373(4) |
| Zn(1A)-N(9A)     | 2.065(6) | Zn(1B)-N(9B) | 2.111(7) |
| Zn(1A)-N(11A)    | 2.497(7) | Zn(1B)-N(11B) | 2.206(8) |

| Bond Angles (°) |  |
|----------------|---|
| N(1)-Zn(1A)-N(5) | 94.23(14) | N(1)-Zn(1B)-N(3) | 72.36(14) |
| N(1)-Zn(1A)-N(11A) | 102.01(18) | N(1)-Zn(1B)-N(7) | 154.67(17) |
| N(3)-Zn(1A)-N(1) | 77.95(14) | N(1)-Zn(1B)-N(9B) | 96.6(2) |
| N(3)-Zn(1A)-N(5) | 98.28(14) | N(1)-Zn(1B)-N(11B) | 104.5(2) |
| N(3)-Zn(1A)-N(7) | 96.76(15) | N(5)-Zn(1B)-N(1) | 107.21(17) |
| N(3)-Zn(1A)-N(9A) | 153.7(2) | N(5)-Zn(1B)-N(3) | 94.89(15) |
| N(3)-Zn(1A)-N(11A) | 83.41(19) | N(5)-Zn(1B)-N(7) | 75.40(15) |
| N(5)-Zn(1A)-N(11A) | 163.65(18) | N(5)-Zn(1B)-N(9B) | 155.5(2) |
| N(7)-Zn(1A)-N(1) | 166.89(16) | N(5)-Zn(1B)-N(11B) | 92.1(2) |
| N(7)-Zn(1A)-N(5) | 74.50(13) | N(7)-Zn(1B)-N(3) | 82.33(13) |
| N(7)-Zn(1A)-N(11A) | 89.15(17) | N(9B)-Zn(1B)-N(3) | 97.8(2) |
| N(9A)-Zn(1A)-N(1) | 96.47(18) | N(9B)-Zn(1B)-N(7) | 85.6(2) |
| N(9A)-Zn(1A)-N(5) | 107.80(18) | N(9B)-Zn(1B)-N(11B) | 76.1(3) |
| N(9A)-Zn(1A)-N(7) | 93.42(18) | N(11B)-Zn(1B)-N(3) | 173.0(3) |
| N(9A)-Zn(1A)-N(11A) | 72.5(2) | N(11B)-Zn(1B)-N(7) | 100.5(2) |
Table S16 Selected least-squares planes data for [Zn(L6)3](ClO4)2∙(C2H3N)2.5 (1)

| Least-squares planes description | Max. deviation (Å) | Atom | Dihedral Angle (°) |
|----------------------------------|--------------------|------|-------------------|
| Benzimidazole 1                  | 0.016              | C2   | 4.7(2)            |
| N1 C1 C2 C3 C4 C5 C6 N2 C7       |                    |      |                   |
| Pyrimidine 1                     | 0.009              | C11  |                   |
| C9 N3 C12 C11 C10 N4             |                    |      |                   |
| Benzimidazole 2                  | 0.021              | C19  | 11.3(2)           |
| C19 N5 C13 C14 C15 C16 C17 C18 N6 |                   |      |                   |
| Pyrimidine 2                     | 0.008              | N8   |                   |
| C21 N8 C22 C23 C24 N7            |                    |      |                   |
| Benzimidazole 3A                 | 0.055              | C31A | 8.5(2)            |
| C31A N9A C25A C26A C27A C28A C29A|                    |      |                   |
| C30A N10A                        |                    |      |                   |
| Pyrimidine 3A                    | 0.036              | C36A-C34A |           |
| C33A N12A C34A C35A C36A N11A    |                    |      |                   |
| Benzimidazole 3B                 | 0.110              | C27B | 3.1(3)            |
| C31B N9B C25B C26B C27B C28B C29B|                    |      |                   |
| C30B N10B                        |                    |      |                   |
| Pyrimidine 3B                    | 0.041              | C36B |                   |
| C33B N12B C36B C35B C34B N11B    |                    |      |                   |
Figure S37 ORTEP view of $\text{fac-}[\text{Zn(L6)}_3]^{2+}$ in the crystal structure of $[\text{Zn(L6)}_3](\text{BF}_4)_2$. (CH$_3$CN)$_2$ (2) (ellipsoids are drawn at 40% probability) with numbering scheme. Hydrogen atoms and BF$_4^-$ counter anions are omitted for clarity.
### Table S17
Selected bond distances (Å) and bond angles (°) for \([\text{Zn(L6)}_3](\text{BF}_4)_2\cdot(\text{CH}_3\text{CN})_2\) (2).

| Bond Distances (Å) |   |
|--------------------|---|
| Zn(1)-N(1)        | 2.130(3) |
| Zn(1)-N(3)        | 2.248(3) |
| Zn(1)-N(5)        | 2.127(2) |
| Zn(1)-N(7)        | 2.261(3) |
| Zn(1)-N(9)        | 2.069(3) |
| Zn(1)-N(11)       | 2.234(3) |

| Bond Angles (°)    |   |
|--------------------|---|
| N(1)-Zn(1)-N(3)   | 75.46(10) |
| N(1)-Zn(1)-N(7)   | 162.32(10) |
| N(1)-Zn(1)-N(11)  | 93.53(10) |
| N(3)-Zn(1)-N(7)   | 87.61(9) |
| N(5)-Zn(1)-N(1)   | 100.78(10) |
| N(5)-Zn(1)-N(3)   | 94.87(9) |
| N(5)-Zn(1)-N(7)   | 75.32(9) |
| N(5)-Zn(1)-N(11)  | 165.64(10) |

### Table S18
Selected least-squares planes data for \([\text{Zn(L6)}_3](\text{BF}_4)_2\) (2).

| Least-squares planes description | Max. deviation (Å) | Atom | Dihedral Angle (°) |
|---------------------------------|-------------------|------|--------------------|
| Benzimidazole 1                 | 0.016             | C1   | 9.7(1)             |
| N1 C1 C2 C3 C4 C5 C6 N2 C7      |                   |      |                    |
| Pyrimidine 1                    | 0.001             | N4-C9-C11-C12 |  |
| C9 N3 C12 C11 C10 N4            |                   |      |                    |
| Benzimidazole 2                 | 0.032             | C19  | 17.2(1)            |
| C19 N5 C13 C14 C15 C16 C17 C18 N6 |          |      |                    |
| Pyrimidine 2                    | 0.011             | C21  |                    |
| C21 N8 C22 C23 C24 N7           |                   |      |                    |
| Benzimidazole 3                 | 0.014             | N10  | 8.73(14)           |
| C31 N9 C25 C26 C27 C28 C29 C30 N10 |      |      |                    |
| Pyrimidine 3                    | 0.016             | C33  |                    |
| C33 N12 C34 C35 C36 N11         |                   |      |                    |
Figure S38 ORTEP view of the two different mer-[Ni(L6)]$_3^{2+}$ cations in the crystal structure of [Ni(L6)$_3$(ClO$_4$)$_2$] (3) (ellipsoids are drawn at 40% probability) with numbering scheme. Hydrogen atoms, and ClO$_4^-$ counter anions are omitted for clarity.
Table S19 Selected bond distances (Å) and bond angles (°) of [Ni(L6)3](ClO4)2 (3).

| Bond Distances (Å)          | Ni(1)-N(1) 2.073(6) | Ni(2)-N(15) 2.111(6) |
|-----------------------------|----------------------|----------------------|
| Ni(1)-N(3)                  | 2.112(7)             | Ni(2)-N(17) 2.089(7) |
| Ni(1)-N(5)                  | 2.061(6)             | Ni(2)-N(19) 2.110(6) |
| Ni(1)-N(7)                  | 2.188(7)             | Ni(2)-N(21A) 2.010(12) |
| Ni(1)-N(9)                  | 2.079(7)             | Ni(2)-N(23A) 2.250(13) |
| Ni(1)-N(11)                 | 2.088(7)             | Ni(2)-N(21B) 1.895(16) |
| Ni(2)-N(13)                 | 2.072(6)             | Ni(2)-N(23B) 2.264(16) |

| Bond Angles (°)             | N(1)-Ni(1)-N(3) 77.8(3) | N(15)-Ni(2)-N(23A) 87.6(4) |
|-----------------------------|--------------------------|--------------------------|
| N(1)-Ni(1)-N(7)             | 90.0(3)                  | N(15)-Ni(2)-N(23B) 91.3(5) |
| N(1)-Ni(1)-N(11)            | 91.0(3)                  | N(17)-Ni(2)-N(15) 95.6(2) |
| N(3)-Ni(1)-N(7)             | 97.2(3)                  | N(17)-Ni(2)-N(19) 79.0(3) |
| N(5)-Ni(1)-N(1)             | 87.6(3)                  | N(17)-Ni(2)-N(23A) 175.8(4) |
| N(5)-Ni(1)-N(3)             | 163.9(3)                 | N(17)-Ni(2)-N(23B) 87.6(4) |
| N(5)-Ni(1)-N(7)             | 92.2(3)                  | N(19)-Ni(2)-N(15) 172.3(2) |
| N(5)-Ni(1)-N(9)             | 76.9(3)                  | N(19)-Ni(2)-N(23A) 97.6(4) |
| N(5)-Ni(1)-N(11)            | 102.7(3)                 | N(19)-Ni(2)-N(23B) 93.8(5) |
| N(9)-Ni(1)-N(1)             | 94.0(3)                  | N(21A)-Ni(2)-N(13) 162.8(4) |
| N(9)-Ni(1)-N(3)             | 95.6(3)                  | N(21A)-Ni(2)-N(15) 93.2(4) |
| N(9)-Ni(1)-N(7)             | 176.8(2)                 | N(21A)-Ni(2)-N(17) 104.3(4) |
| N(9)-Ni(1)-N(11)            | 77.8(3)                  | N(21A)-Ni(2)-N(19) 93.3(4) |
| N(11)-Ni(1)-N(3)            | 171.8(3)                 | N(21A)-Ni(2)-N(23A) 78.3(5) |
| N(11)-Ni(1)-N(7)            | 99.1(3)                  | N(21B)-Ni(2)-N(13) 102.3(5) |
| N(13)-Ni(2)-N(15)           | 78.3(2)                  | N(21B)-Ni(2)-N(15) 92.4(5) |
| N(13)-Ni(2)-N(17)           | 91.5(2)                  | N(21B)-Ni(2)-N(17) 165.2(5) |
| N(13)-Ni(2)-N(19)           | 96.4(2)                  | N(21B)-Ni(2)-N(19) 94.1(5) |
| N(13)-Ni(2)-N(23A)          | 86.3(4)                  | N(21B)-Ni(2)-N(23B) 79.8(6) |
| N(13)-Ni(2)-N(23B)          | 169.4(5)                 |                         |
Table S20 Selected least-squares planes data for \([\text{Ni}(\text{L6})_3](\text{ClO}_4)_2\) (3).

| Least-squares planes description | Max. deviation (Å) | Atom | Dihedral Angle (°) |
|----------------------------------|--------------------|------|-------------------|
| Benzimidazole 1                  | 0.023              | C2   |                   |
| N1 C1 C2 C3 C4 C5 C6 N2 C7       |                    |      |                   |
| Pyrimidine 1                     | 0.012              | C12  |                   |
| N3 C9 N4 C10 C11 C12             |                    |      |                   |
| Benzimidazole 2                  | 0.027              | C18  |                   |
| N5 C19 N6 C18 C17 C16 C15 C14 C13|                    |      |                   |
| Pyrimidine 2                     | 0.023              | N8   |                   |
| N7 C24 C23 C22 N8 C21            |                    |      |                   |
| Benzimidazole 3                  | 0.028              | C29  |                   |
| N9 C25 C26 C27 C28 C29 C30 N10 C31|                    |      |                   |
| Pyrimidine 3                     | 0.009              | N12  |                   |
| N11 C36 C35 C34 N12 C33          |                    |      |                   |
| Benzimidazole 1’                 | 0.022              | C40  |                   |
| C43 N13 C37 C38 C39 C40 C41 C42 N14|                    |      |                   |
| Pyrimidine 1’                    | 0.010              | N16  |                   |
| N15 C48 C47 C46 N16 C45          |                    |      |                   |
| Benzimidazole 2’                 | 0.018              | C53  |                   |
| N17 C49 C50 C51 C52 C53 C54 N18 C55|                    |      |                   |
| Pyrimidine 2’                    | 0.019              | N19  |                   |
| N19 C57 N20 C58 C59 C60          |                    |      |                   |
| Benzimidazole 3’A                | 0.034              | N21A |                   |
| N21A C67A N22A C66A C65A C64A    |                    |      |                   |
| C63A C62A C61A                    |                    |      |                   |
| Pyrimidine 3’A                   | 0.020              | N24A |                   |
| C69A N24A C70A C71A C72A N23A    |                    |      |                   |
| Benzimidazole 3’B                | 0.091              | C67B |                   |
| N9 C25 C26 C27 C28 C29 C30 N10 C31|                    |      |                   |
| Pyrimidine 3’B                   | 0.026              | N23B-|                   |
| C69B N24B C70B C71B C72B N23B    |                    |      |                   |
Figure S39 ORTEP view of \( \text{fac-[Ni(L6)}_3]^{2+} \) in the crystal structure of \([\text{Ni(L6)}_3](\text{ClO}_4)_2\cdot\text{C}_2\text{H}_3\text{N}\) (4) (ellipsoids are drawn at 40% probability) with numbering scheme. Hydrogen atoms, and ClO\(_4^-\) counter anions are omitted for clarity.
Table S21 Selected bond distances (Å) and bond angles (°) for [Ni(L6)3](ClO4)2∙C2H3N (4).

| Bond Distances (Å) |  |
|--------------------|--|
| Ni(1)-N(1)         | 2.062(2) |
| Ni(1)-N(3)         | 2.140(2) |
| Ni(1)-N(5)         | 2.067(2) |
| Ni(1)-N(7)         | 2.093(2) |
| Ni(1)-N(9)         | 2.077(2) |
| Ni(1)-N(11)        | 2.120(2) |

| Bond Angles (°)    |  |
|--------------------|--|
| N(1)-Ni(1)-N(3)    | 78.27(7)  |
| N(1)-Ni(1)-N(5)    | 99.14(8)  |
| N(1)-Ni(1)-N(7)    | 170.87(8) |
| N(1)-Ni(1)-N(9)    | 100.54(7) |
| N(1)-Ni(1)-N(11)   | 86.60(7)  |
| N(5)-Ni(1)-N(3)    | 87.38(7)  |
| N(5)-Ni(1)-N(7)    | 78.62(8)  |
| N(5)-Ni(1)-N(9)    | 98.43(7)  |
Table S22 Selected least-squares planes data for [Ni(L6)3](ClO4)2$\cdot$C2H3N (4).

| Least-squares planes description | Max. deviation (Å) | Atom   | Dihedral Angle (°) |
|----------------------------------|--------------------|--------|--------------------|
| Benzimidazole 1                  | 0.012              | C3     | 7.39(8)            |
| N1 C1 C2 C3 C4 C5 C6 N2 C7       |                    |        |                    |
| Pyrimidine 1                     | 0.006              | C9-N3  |                    |
| N3 C9 N4 C10 C11 C12             |                    |        |                    |
| Benzimidazole 2                  | 0.042              | C19    | 10.96(8)           |
| 0N5 C13 C14 C15 C16 C17 C18 N6 C19 |                  |        |                    |
| Pyrimidine 2                     | 0.006              | C21-C23|                    |
| N7 C24 C23 C22 N8 C21            |                    |        |                    |
| Benzimidazole 3                  | 0.041              | C31    | 16.34(10)          |
| N9 C25 C26 C27 C28 C29 C30 N10 C31 |                  |        |                    |
| Pyrimidine 3                     | 0.008              | C33    |                    |
| N11 C36 C35 C34 N12 C33          |                    |        |                    |
Figure S40 ORTEP view of fac-[Ni(L6)_3]^{2+} in the crystal structure of [Ni(L6)_3](BF_4)_2·CH_3CN (5) (ellipsoids are drawn at 40% probability) with numbering scheme. Hydrogen atoms, acetonitrile solvent molecules and BF_4-counter anions are omitted for clarity.
Table S23 Selected bond distances (Å) and bond angles (°) for [Ni(L6)3](BF4)2∙CH3CN (5).

| Bond Distances (Å)       |       |
|--------------------------|-------|
| Ni(1)-N(1)               | 2.066(2) |
| Ni(1)-N(3)               | 2.098(2) |
| Ni(1)-N(5)               | 2.075(2) |
| Ni(1)-N(7)               | 2.121(2) |
| Ni(1)-N(9)               | 2.063(2) |
| Ni(1)-N(11)              | 2.135(2) |

| Bond Angles (°)           |       |
|---------------------------|-------|
| N(1)-Ni(1)-N(3)           | 78.61(9) |
| N(1)-Ni(1)-N(5)           | 98.24(6) |
| N(1)-Ni(1)-N(7)           | 173.35(6) |
| N(1)-Ni(1)-N(11)          | 92.76(6) |
| N(1)-Ni(1)-N(1)           | 89.15(6) |
| N(1)-Ni(1)-N(7)           | 78.14(6) |
| N(5)-Ni(1)-N(11)          | 174.13(6) |
| N(5)-Ni(1)-N(13)          | 96.14(6) |
| N(5)-Ni(1)-N(11)          | 99.60(6) |
| N(5)-Ni(1)-N(7)           | 100.05(6) |
| N(5)-Ni(1)-N(11)          | 86.58(6) |
| N(5)-Ni(1)-N(11)          | 78.12(6) |
Table S24 Selected least-squares planes data for [Ni(L6)3](BF4)2·CH3CN (5).

| Least-squares planes description | Max. deviation (Å) | Atom | Dihedral Angle (°) |
|---------------------------------|--------------------|------|-------------------|
| Benzimidazole 1                 | 0.040              | C7   | 10.94(8)          |
| N1 C7 N2 C6 C5 C4 C3 C2 C1      |                    |      |                   |
| Pyrimidine 1                    | 0.008              | N4-C9|                   |
| N3 C12 C11 C10 N4 C9            |                    |      |                   |
| Benzimidazole 2                 | 0.04               | C19  | 16.39(9)          |
| N5 C19 N6 C18 C17 C16 C15 C14 C13|               |      |                   |
| Pyrimidine 2                    | 0.009              | N7-  |                   |
| N7 C24 C23 C22 N8 C21           |                    |      |                   |
| Benzimidazole 3                 | 0.010              | C31  | 7.54(8)           |
| N9 C25 C26 C27 C28 C29 C30 N10 C31|               |      |                   |
| Pyrimidine 3                    | 0.008              | N11  |                   |
| N11 C33 N12 C34 C35 C36         |                    |      |                   |
Figure S41 ORTEP view of the two different *mer-*[Fe(L6)₃]²⁺ cations in the crystal structure of [Fe(L₆)₃](ClO₄)₂ (6) (ellipsoids are drawn at 40% probability) at 180 K with numbering scheme. Hydrogen atoms and counter anions are omitted for clarity.
Table S25 Selected bond distances (Å) and bond angles (°) for [Fe(L6)]3(ClO4)2 (6) at 180 K.

| Bond Distances (Å) |  |
|--------------------|---|
| Fe(1)-N(1)         | 1.989(4) |
| Fe(1)-N(3)         | 2.018(5) |
| Fe(1)-N(5)         | 1.999(4) |
| Fe(1)-N(7)         | 2.003(4) |
| Fe(1)-N(9)         | 2.005(4) |
| Fe(1)-N(11)        | 1.998(4) |
| Fe(1B)-N(1B)       | 2.071(4) |
| Fe(1B)-N(3B)       | 2.164(5) |
| Fe(1B)-N(5B)       | 2.054(4) |
| Fe(1B)-N(7B)       | 2.095(4) |
| Fe(1B)-N(9B)       | 2.078(5) |
| Fe(1B)-N(11B)      | 2.088(5) |

| Bond Angles (°)    |  |
|--------------------|---|
| N(1)-Fe(1)-N(3)   | 80.47(19) |
| N(1)-Fe(1)-N(5)   | 168.95(19) |
| N(1)-Fe(1)-N(7)   | 93.05(17) |
| N(1)-Fe(1)-N(9)   | 99.30(18) |
| N(1)-Fe(1)-N(11)  | 91.77(17) |
| N(1B)-Fe(1B)-N(3B)| 87.81(18) |
| N(1B)-Fe(1B)-N(7B)| 77.52(16) |
| N(1B)-Fe(1B)-N(9B)| 92.04(17) |
| N(1B)-Fe(1B)-N(11B)| 97.32(17) |
| N(5)-Fe(1B)-N(1B) | 162.2(2)  |
| N(5B)-Fe(1B)-N(3B)| 76.9(2)   |
| N(5B)-Fe(1B)-N(7B)| 92.56(17) |
| N(5B)-Fe(1B)-N(9B)| 103.76(19) |
| N(5B)-Fe(1B)-N(11B)| 93.96(17) |
| N(5B)-Fe(1B)-N(3B)| 87.70(18) |
| N(7B)-Fe(1B)-N(3B)| 176.46(17) |
| N(9B)-Fe(1B)-N(7B)| 95.73(18) |
| N(9B)-Fe(1B)-N(11B)| 78.22(19) |
| N(11B)-Fe(1B)-N(3B)| 98.28(19) |
| N(11B)-Fe(1B)-N(7B)| 172.01(17) |
Table S26 Selected least-squares planes data for [Fe(L6)](ClO4)2 (6).

| Least-squares planes description | Max. deviation (Å) | Atom | Dihedral Angle (°) |
|---------------------------------|-------------------|------|-------------------|
| Benzimidazole 1                 | 0.031             | C6   | 8.9(2)            |
| C7 N2 C6 C5 C4 C3 C2 C1 N1      |                   |      |                   |
| Pyrimidine 1                    | 0.017             | C12  |                   |
| C9 N3 C12 C11 C10 N4            |                   |      |                   |
| Benzimidazole 2                 | 0.032             | C18  | 9.9(2)            |
| C19 N5 C13 C14 C15 C16 C17 C18 N6 |                 |      |                   |
| Pyrimidine 2                    | 0.003             | C23  |                   |
| N7 C21 N8 C22 C23 C24           |                   |      |                   |
| Benzimidazole 3                 | 0.020             | C27  | 1.8(2)            |
| N9 C31 N10 C30 C29 C28 C27 C26 C25 |               |      |                   |
| Pyrimidine 3                    | 0.014             | C33  |                   |
| N11 C36 C35 C34 N12 C33         |                   |      |                   |
| Benzimidazole 1B                | 0.028             | C2B  | 11.6(2)           |
| C7B N2B C6B C5B C4B C3B C2B C1B N1B |              |      |                   |
| Pyrimidine 1B                   | 0.009             | C24B |                   |
| N7B C21B N8B C22B C23B C24B     |                   |      |                   |
| Benzimidazole 2B                | 0.034             | C18B | 8.2(2)            |
| C19B N5B C13B C14B C15B C16B C17B |               |      |                   |
| C18B N6B                        |                   |      |                   |
| Pyrimidine 2B                   | 0.018             | C12B |                   |
| C9B N3B C12B C11B C10B N4B      |                   |      |                   |
| Benzimidazole 3B                | 0.024             | C30B | 2.6(2)            |
| N9B C31B N10B C30B C29B C28B C27B |               |      |                   |
| C26B C25B                       |                   |      |                   |
| Pyrimidine 3B                   | 0.020             | C33B |                   |
| N11B C36B C35B C34B N12B C33B   |                   |      |                   |
Figure S42 ORTEP view of \( \text{fac-}[\text{Fe}(\text{L}6)_3]^{2+} \) cations in the crystal structure of \([\text{Fe}(\text{L}6)_3](\text{BF}_4)_2\cdot(\text{C}_5\text{H}_12\text{O})_{0.5}\cdot(\text{C}_2\text{H}_5\text{N})_{0.5} \) (7) (ellipsoids are drawn at 40\% probability) with numbering scheme. Hydrogen atoms and counter anions are omitted for clarity.
Table S27  Selected bond distances (Å) and bond angles (°) for [Fe(L6)_3](BF_4)_2·(C_5H_12O)_{0.5}·(C_2H_5N)_{0.5} (7).

| Bond Distances (Å)          |                |
|-----------------------------|----------------|
| Fe(1)-N(14)                 | 2.101(3)       |
| Fe(1)-N(3)                  | 2.143(3)       |
| Fe(1)-N(5)                  | 2.102(3)       |
| Fe(1)-N(7)                  | 2.150(4)       |
| Fe(1)-N(9)                  | 2.063(4)       |
| Fe(1)-N(11)                 | 2.150(3)       |

| Bond Angles (°)              |                |
|-----------------------------|----------------|
| N(14)-Fe(1)-N(3)            | 76.61(11)      |
| N(1)-Fe(1)-N(7)             | 165.93(11)     |
| N(1)-Fe(1)-N(11)            | 91.15(11)      |
| N(3)-Fe(1)-N(7)             | 90.21(11)      |
| N(3)-Fe(1)-N(11)            | 90.08(11)      |
| N(5)-Fe(1)-N(1)             | 98.56(10)      |
| N(5)-Fe(1)-N(3)             | 93.30(10)      |
| N(5)-Fe(1)-N(7)             | 77.00(10)      |
Table S28 Selected least-squares planes data for [Fe(L6)]_3[(BF_4)_2·(C_5H_12O)_{0.5}·(C_2H_5N)_{0.5} (7).

| Least-squares planes description | Max. deviation (Å) | Atom   | Dihedral Angle (°) |
|----------------------------------|--------------------|--------|--------------------|
| Benzimidazole 1                  | 0.022              | C3     | 8.7(1)             |
| C7 N1 C1 C2 C3 C4 C5 C6 N2       |                    |        |                    |
| Pyrimidine 1                     | 0.009              | C10    |                    |
| N3 C12 C11 C10 N4 C9             |                    |        |                    |
| Benzimidazole 2                  | 0.034              | C19    | 14.5(2)            |
| N5 C13 C14 C15 C16 C17 C18 N6 C19|                    |        |                    |
| Pyrimidine 2                     | 0.009              | C21    |                    |
| N7 C24 C23 C22 N8 C21            |                    |        |                    |
| Benzimidazole 3                  | 0.011              | N9-C30 | 7.6(2)             |
| N9 C25 C26 C27 C28 C29 C30 N10 C31|                    |        |                    |
| Pyrimidine 3                     | 0.013              | C33    |                    |
| N11 C33 N12 C34 C35 C36          |                    |        |                    |
Figure S43 ORTEP view of fac-[Zn(L7)3]2+ cations in the crystal structures of [Zn(L7)3](ClO4)2 (8) (ellipsoids are drawn at 40% probability) with numbering scheme. Hydrogen atoms and counter anions are omitted for clarity. The cation is located on a crystallographic threefold axis and near a twofold axis (therefore all ligands are disordered but the conformation stays facial).

Table S29 Selected bond distances (Å) and bond angles (°) of [Zn(L7)3](ClO4)2 (8).

| Bond Distances (Å) |  |
|--------------------|---|
| Zn(1)-N(1)         | 2.083(6) |
| Zn(1)-N(3)         | 2.307(13) |

| Bond Angles (°)    |  |
|--------------------|---|
| N(1)-Zn(1)-N(3)    | 74.5(5) |

Table S30 Selected least-squares planes data for [Zn(L3)3](ClO4)2 (8).

| Least-squares planes description | Max. deviation (Å) | Atom | Dihedral Angle (°) |
|----------------------------------|--------------------|------|-------------------|
| Benzimidazole 1                  | 0.032              | C1   | 20.2(4)           |
| N1 C1 C2 C3 C4 C5 N2 C6 C7       |                    |      |                   |
| Pyrimidine 1                     | 0.036              | C11  |                   |
| N3 C9 C10 C11 C12 N4             |                    |      |                   |
**Figure S44** ORTEP view of \(\text{fac}-[\text{Zn}(L7)_3]^{2+}\) cations in the crystal structure of \([\text{Zn}(L7)_3](\text{PF}_6)_2\) (8) (ellipsoids are drawn at 40% probability) with numbering scheme. Hydrogen atoms and counter anions are omitted for clarity.
Table S31 Selected bond distances (Å) and bond angles (°) of [Zn(L7)₃](PF₆)₂ (9).

| Bond Distances (Å)          |          | Bond Angles (°)                                      |
|-----------------------------|----------|----------------------------------------------------|
| Zn(1)-N(1)                  | 2.084(2) | Zn(1)-N(2)                                          |
| Zn(1)-N(2)                  | 2.334(2) | Zn(1)-N(3)                                          |
| Zn(1)-N(3)                  | 2.108(2) | Zn(1)-N(4)                                          |
|                             |          | Zn(1)-N(5)                                          |
|                             |          | Zn(1)-N(6)                                          |
|                             |          | 2.241(2)                                            |
|                             |          | 2.110(2)                                            |
|                             |          | 2.156(18) and 2.179(3)                              |

| Bond Angles (°)             |          |                                                   |
|-----------------------------|----------|----------------------------------------------------|
| N(1)-Zn(1)-N(2)             | 74.77(9) | N(3)-Zn(1)-N(6)                                    |
| N(1)-Zn(1)-N(3)             | 96.24(8) | N(4)-Zn(1)-N(2)                                    |
| N(1)-Zn(1)-N(4)             | 163.37(9)| N(5)-Zn(1)-N(2)                                    |
| N(1)-Zn(1)-N(5)             | 101.13(9)| N(5)-Zn(1)-N(4)                                    |
| N(1)-Zn(1)-N(6)             | 97.96(12)and 91.4(9)| N(5)-Zn(1)-N(6)                                    |
| N(3)-Zn(1)-N(2)             | 90.94(8) | N(6)-Zn(1)-N(2)                                    |
| N(3)-Zn(1)-N(4)             | 76.12(8) | N(6)-Zn(1)-N(4)                                    |
| N(3)-Zn(1)-N(5)             | 101.19(8)|                                                   |
|                             |          | 165.79(11) and 172.1(9)                            |
|                             |          | 90.42(8)                                            |
|                             |          | 167.61(8)                                           |
|                             |          | 94.89(9)                                            |
|                             |          | 76.57(12) and 75.5(8)                              |
|                             |          | 92.28(12) and 92.8(8)                              |
|                             |          | 90.01(11) and 96.9(9)                              |
|                             |          |                                                   |

Table S32 Selected least-squares planes data for [Zn(L7)₃](PF₆)₂ (9).

| Least-squares planes description | Max. deviation (Å) | Atom | Dihedral Angle (°) |
|----------------------------------|--------------------|------|--------------------|
| Benzimidazole 1                  | 0.035              | N1   | 5.0(1)             |
| N1 C7 C8 C9 C10 C11 N13 C12 C15 |                    |      | C23-25             |
| Pyrimidine 1                     | 0.027              | N19  |                    |
| N2 C20 N19 C18 C17 C16           |                    |      | 4.68(9)            |
| Benzimidazole 2                  | 0.009              | C23  |                    |
| N3 C21 C22 C23 C24 C25 C26 N27   |                    |      |                    |
| C29                              |                    |      |                    |
| Pyrimidine 2                     | 0.019              | N4   |                    |
| C30 C31 C32 N33 C34 N4           |                    |      |                    |
| Benzimidazole 3                  | 0.02               | C38  | 21.2(1) and 15.8(3)|
| N5 C35 C36 C37 C38 C39 C40 N41   |                    |      |                    |
| C43                              |                    |      |                    |
| Pyrimidine 3                     | 0.03 (N6A)         | N6A  |                    |
| C44 C45 C46 N47 C48 N6           |                    |      |                    |
|                                 | 0.01(N6B)          | C48B |                    |
Figure S45 ORTEP view of mer-[Ni(L7)3]^{2+} cations in the crystal structure of [Ni(L7)3](PF6)_{0.52}(ClO4)_{1.48} (10) (ellipsoids are drawn at 50% probability) with numbering scheme. Hydrogen atoms and counter anions are omitted for clarity.
Table S33 Selected bond distances (Å) and bond angles (°) of [Ni(L7)3](PF6)0.52(ClO4)1.48 (10)

| Bond Distances (Å) |     |     |
|-------------------|-----|-----|
| Ni(1)-N(1)        | 2.047(2) | Ni(1B)-N(1B) | 2.072(2) |
| Ni(1)-N(2)        | 2.119(2) | Ni(1B)-N(2B) | 2.113(2) |
| Ni(1)-N(3)        | 2.064(2) | Ni(1B)-N(3B) | 2.046(2) |
| Ni(1)-N(4)        | 2.110(2) | Ni(1B)-N(4B) | 2.085(2) |
| Ni(1)-N(5)        | 2.116(2) | Ni(1B)-N(5B) | 2.093(2) |
| Ni(1)-N(6)        | 2.090(2) | Ni(1B)-N(6B) | 2.124(2) |

| Bond Angles (°) |     |     |     |
|----------------|-----|-----|-----|
| N(1)-Ni(1)-N(2) | 77.69(10) | N(1B)-Ni(1B)-N(2B) | 77.54(9) |
| N(1)-Ni(1)-N(3) | 97.85(10) | N(1B)-Ni(1B)-N(4B) | 93.79(9) |
| N(1)-Ni(1)-N(4) | 91.61(10) | N(1B)-Ni(1B)-N(5B) | 170.75(9) |
| N(1)-Ni(1)-N(5) | 170.30(10) | N(1B)-Ni(1B)-N(6B) | 95.65(9) |
| N(1)-Ni(1)-N(6) | 95.55(10) | N(2B)-Ni(1B)-N(6B) | 87.96(9) |
| N(3)-Ni(1)-N(2) | 172.86(9) | N(3B)-Ni(1B)-N(1B) | 92.66(9) |
| N(3)-Ni(1)-N(4) | 78.14(9) | N(3B)-Ni(1B)-N(2B) | 169.55(9) |
| N(3)-Ni(1)-N(5) | 90.51(9) | N(3B)-Ni(1B)-N(4B) | 78.68(10) |
| N(3)-Ni(1)-N(6) | 96.58(9) | N(3B)-Ni(1B)-N(5B) | 94.69(9) |
| N(4)-Ni(1)-N(2) | 96.29(9) | N(3B)-Ni(1B)-N(6B) | 96.72(9) |
| N(4)-Ni(1)-N(6) | 171.64(9) | N(4B)-Ni(1B)-N(2B) | 98.13(9) |
| N(5)-Ni(1)-N(2) | 94.45(10) | N(4B)-Ni(1B)-N(5B) | 93.15(9) |
| N(5)-Ni(1)-N(4) | 94.93(10) | N(4B)-Ni(1B)-N(6B) | 169.69(9) |
| N(5)-Ni(1)-N(6) | 78.53(10) | N(5B)-Ni(1B)-N(2B) | 95.43(9) |
| N(6)-Ni(1)-N(2) | 89.45(9) | N(5B)-Ni(1B)-N(6B) | 77.93(9) |
Table S34 Selected least-squares planes data for [Ni(L7)3](PF6)0.52(ClO4)1.48 (10).

| Least-squares planes description | Max. deviation/Å | Atom | Dihedral Angle (°) |
|---------------------------------|-----------------|------|--------------------|
| Benzimidazole 1                 | 0.024           | C1   | 7.70(9)            |
| N1 C1 C2 C3 C4 C5 C6 N7 C8      |                 |      |                    |
| Pyrimidine 1                    | 0.015           | C12  |                    |
| N2 C12 N8 C11 C10 C9            |                 |      |                    |
| Benzimidazole 2                 | 0.030           | C16- | 9.68(10)           |
| N3 C13 C14 C15 C16 C17 C18 N9 C19|                 |      |                    |
| Pyrimidine 2                    | 0.012           | C23  |                    |
| N4 C23 N10 C22 C21 C20          |                 |      |                    |
| Benzimidazole 3                 | 0.037           | N5   | 18.04(11)          |
| N5 C25 C26 C27 C28 C29 C30 N11 C32|                 |      |                    |
| Pyrimidine 3                    | 0.029           | C33  |                    |
| N6 C36 N12 C35 C34 C33          |                 |      |                    |
| Benzimidazole 1B                | 0.032           | C8B  | 13.01(8)           |
| N1B C8B N7B C6B C5B C4B C3B C2B|                 |      |                    |
| C1B                             |                 |      |                    |
| Pyrimidine 1B                   | 0.015           | C9B  |                    |
| N2B C9B C10B C11B N8B C12B      |                 |      |                    |
| Benzimidazole 2B                | 0.038           | C19B | 9.53(8)            |
| N3B C13B C14B C15B C16B C17B C18B|                 |      |                    |
| N9B C19B                        |                 |      |                    |
| Pyrimidine 2B                   | 0.013           | C20B |                    |
| N4B C23B N10B C22B C21B C20B    |                 |      |                    |
| Benzimidazole 3B                | 0.014           | C30B | 4.74(9)            |
| N5B C25B C26B C27B C28B C29B C30B|                 |      |                    |
| N11B C32B                       |                 |      |                    |
| Pyrimidine 3B                   | 0.025           | C33B |                    |
| N6B C36B N12B C35B C34B C33B    |                 |      |                    |
**Figure S46** ORTEP view of *mer*-\([\text{Ni(L7)}_3]^{2+}\) cations in the crystal structure of \([\text{Ni(L7)}_3](\text{BF}_4)_2\)-(CH$_3$OH)-(CH$_3$CN)$_{0.5}$ (11) (ellipsoids are drawn at 40% probability) with numbering scheme. Hydrogen atoms and counter anions are omitted for clarity.
Table S35  Selected bond distances (Å) and bond angles (°) of [Ni(L7)3][BF₄]₂·(CH₃OH)·(CH₃CN)₀.₅ (11).

| Bond Distances (Å) |  |
|--------------------|---|
| Ni(1)-N(1)         | 2.0595(18) |
| Ni(1)-N(3)         | 2.1161(18) |
| Ni(1)-N(5)         | 2.0894(18) |
| Ni(1)-N(7)         | 2.0936(18) |
| Ni(1)-N(9)         | 2.0799(18) |
| Ni(1)-N(11)        | 2.0950(18) |

| Bond Angles (°) |  |
|----------------|---|
| N(1)-Ni(1)-N(3)| 78.13(7) |
| N(1)-Ni(1)-N(5)| 170.87(7) |
| N(1)-Ni(1)-N(7)| 94.79(7) |
| N(1)-Ni(1)-N(9)| 98.11(7) |
| N(1)-Ni(1)-N(11)| 91.91(7) |
| N(1)-Ni(1)-N(11)| 95.46(7) |
| N(1)-Ni(1)-N(3)| 78.49(7) |
| N(1)-Ni(1)-N(11)| 95.46(7) |

Table S36  Selected least-squares planes data for [Ni(L7)₃][BF₄]₂·(CH₃OH)·(CH₃CN)₀.₅ (11).

| Least-squares planes description | Max. deviation/Å | Atom | Dihedral Angle (°) |
|----------------------------------|------------------|------|--------------------|
| Benzimidazole 1                  | 0.018            | C3   | 10.09(9)           |
| C7 N1 C1 C2 C3 C4 C5 C6 N2       |                  |      |                    |
| Pyrimidine 1                     | 0.017            | C9   |                    |
| N3 C12 C11 C10 N4 C9             |                  |      |                    |
| Benzimidazole 2                  | 0.022            | C19  | 8.72(5)            |
| N5 C13 C14 C15 C16 C17 C18 N6 C19|                  |      |                    |
| Pyrimidine 2                     | 0.014            | C24  |                    |
| N7 C24 C23 C22 N8 C21            |                  |      |                    |
| Benzimidazole 3                  | 0.006            | C26  | 7.52(8)            |
| N9 C25 C26 C27 C28 C29 C30 N10 C31|                  |      |                    |
| Pyrimidine 3                     | 0.005            | C36  |                    |
| N11 C33 N12 C34 C35 C36          |                  |      |                    |
Figure S47 ORTEP view of the two different mer-[Fe(L7)_3]^{2+} cations in the crystal structure of [Fe(L7)_3](PF_6)(BF_4)·CH_3OH (12) (ellipsoids are drawn at 50% probability) with numbering scheme. Hydrogen atoms and counter anions are omitted for clarity.
Table S37 Selected bond distances (Å) and bond angles (°) of [Fe(L7)3](PF6)(BF4)∙CH3OH (12).

| Bond Distances (Å) | Bond Angles (°) |
|--------------------|-----------------|
| Fe(1)-N(1)   1.9645(16) Fe(1B)-N(1B) 1.9715(16) | N(1)-Fe(1)-N(2) 80.26(7) N(1B)-Fe(1B)-N(2B) 80.75(6) |
| Fe(1)-N(2)   1.9970(16) Fe(1B)-N(2B) 1.9799(16) | N(1)-Fe(1)-N(3) 96.78(7) N(1B)-Fe(1B)-N(5B) 173.31(6) |
| Fe(1)-N(3)   1.9791(16) Fe(1B)-N(3B) 1.9635(16) | N(1)-Fe(1)-N(4) 90.86(7) N(1B)-Fe(1B)-N(6B) 94.14(7) |
| Fe(1)-N(4)   1.9828(16) Fe(1B)-N(4B) 1.9655(16) | N(1)-Fe(1)-N(5) 172.11(7) N(2B)-Fe(1B)-N(5B) 95.17(7) |
| Fe(1)-N(5)   1.9892(16) Fe(1B)-N(5B) 1.9950(16) | N(1)-Fe(1)-N(6) 94.46(7) N(2B)-Fe(1B)-N(6B) 88.38(7) |
| Fe(1)-N(6)   1.9970(16) Fe(1B)-N(6B) 2.0026(16) | N(3)-Fe(1)-N(2) 174.91(7) N(3B)-Fe(1B)-N(1B) 92.50(6) |
| N(1)-Fe(1)-N(2) 80.26(7) N(1B)-Fe(1B)-N(2B) 80.75(6) | N(3)-Fe(1)-N(3) 96.78(7) N(1B)-Fe(1B)-N(5B) 173.31(6) |
| N(1)-Fe(1)-N(3) 96.78(7) N(1B)-Fe(1B)-N(5B) 173.31(6) | N(3)-Fe(1)-N(4) 90.86(7) N(1B)-Fe(1B)-N(6B) 94.14(7) |
| N(1)-Fe(1)-N(4) 90.86(7) N(1B)-Fe(1B)-N(6B) 94.14(7) | N(3)-Fe(1)-N(5) 172.11(7) N(2B)-Fe(1B)-N(5B) 95.17(7) |
| N(1)-Fe(1)-N(5) 172.11(7) N(2B)-Fe(1B)-N(5B) 95.17(7) | N(3)-Fe(1)-N(6) 94.46(7) N(2B)-Fe(1B)-N(6B) 88.38(7) |
| N(1)-Fe(1)-N(6) 94.46(7) N(2B)-Fe(1B)-N(6B) 88.38(7) | N(4)-Fe(1)-N(2) 89.82(6) N(3B)-Fe(1B)-N(4B) 80.69(7) |
| N(3)-Fe(1)-N(2) 80.48(6) N(3B)-Fe(1B)-N(4B) 80.69(7) | N(4)-Fe(1)-N(3) 95.12(6) N(3B)-Fe(1B)-N(5B) 91.80(7) |
| N(4)-Fe(1)-N(3) 95.12(6) N(3B)-Fe(1B)-N(5B) 91.80(7) | N(4)-Fe(1)-N(4) 95.36(6) N(3B)-Fe(1B)-N(6B) 94.81(7) |
| N(5)-Fe(1)-N(2) 93.46(7) N(4B)-Fe(1B)-N(1B) 92.26(6) | N(4)-Fe(1)-N(5) 94.40(7) N(4B)-Fe(1B)-N(1B) 92.26(6) |
| N(5)-Fe(1)-N(3) 93.46(7) N(4B)-Fe(1B)-N(2B) 96.81(6) | N(5)-Fe(1)-N(4) 173.48(6) N(4B)-Fe(1B)-N(2B) 96.81(6) |
| N(5)-Fe(1)-N(4) 173.48(6) N(4B)-Fe(1B)-N(2B) 96.81(6) | N(5)-Fe(1)-N(5) 90.60(7) N(4B)-Fe(1B)-N(6B) 172.34(7) |
| N(5)-Fe(1)-N(5) 90.60(7) N(4B)-Fe(1B)-N(6B) 172.34(7) | N(5)-Fe(1)-N(6) 89.27(6) N(5B)-Fe(1B)-N(6B) 80.39(7) |
Table S38 Selected least-squares planes data for [Fe(L7)3](PF6)(BF4)∙CH3OH (12).

| Least-squares planes description | Max. deviation/Å | Atom | Dihedral Angle (°) |
|----------------------------------|------------------|------|--------------------|
| Benzimidazole 1                  | 0.03             | C8   | 9.79(8)            |
| C8 N1 C1 C2 C3 C4 C5 C6 N7       |                  |      |                    |
| Pyrimidine 1                     | 0.02             | N2   |                    |
| C9 C10 C11 N8 C12 N2             |                  |      |                    |
| Benzimidazole 2                  | 0.03             | C18  | 4.79(9)            |
| C13 C14 C15 C16 C17 C18 N9 C19   |                  |      |                    |
| Pyrimidine 2                     | 0.01             | C23  |                    |
| N4 C20 C21 C22 N10 C23           |                  |      |                    |
| Benzimidazole 3                  | 0.05             | C27  | 15.53(10)          |
| N5 C25 C26 C27 C28 C29 C30 N11 C32|                  |      |                    |
| Pyrimidine 3                     | 0.03             | N6   |                    |
| N6 C36 N12 C35 C34 C33           |                  |      |                    |
| Benzimidazole 1B                 | 0.03             | C8B  | 12.45(7)           |
| N1B C1B C2B C3B C4B C5B C6B N7B  |                  |      |                    |
| C8B                             |                  |      |                    |
| Pyrimidine 1B                    | 0.01             | C9-N8B|                   |
| C9B C10B C11B N8B C12B N2B       |                  |      |                    |
| Benzimidazole 2B                 | 0.04             | C19B | 9.47(7)            |
| N3B C13B C14B C15B C16B C17B     |                  |      |                    |
| C18B N9B C19B                    |                  |      |                    |
| Pyrimidine 2B                    | 0.01             | N4B  |                    |
| N4B C23B N10B C22B C21B C20B     |                  |      |                    |
| Benzimidazole 3B                 | 0.01             | C32B-C28B|                |
| N5B C32B N11B C30B C29B C28B     |                  |      |                    |
| C27B C26B C25B                    |                  |      |                    |
| Pyrimidine 3B                    | 0.02             | C33B |                    |
| N6B C36B N12B C35B C34B C33B     |                  |      |                    |
Figure S48 ORTEP view of the two different mer-[Fe(L7)3]^2+ cations in the crystal structure of [Fe(L7)3](PF$_6$)$_{1.72}$(ClO$_4$)$_{0.28}$·CH$_3$OH (13) (ellipsoids are drawn at 50% probability) with numbering scheme. Hydrogen atoms and counter anions are omitted for clarity.
Table S39  Selected bond distances (Å) and bond angles (°) of [Fe(L7)3][PF6]1.72(ClO4)0.28·CH3OH (13).

| Bond Distances (Å) | Fe(1)-N(1) 1.989(4) | Fe(1B)-N(1B) 1.950(4) |
|-------------------|----------------------|------------------------|
|                   | Fe(1)-N(2) 2.009(5)  | Fe(1B)-N(2B) 2.015(5)  |
|                   | Fe(1)-N(3) 1.977(4)  | Fe(1B)-N(3B) 1.991(5)  |
|                   | Fe(1)-N(4) 1.991(4)  | Fe(1B)-N(4B) 2.008(5)  |
|                   | Fe(1)-N(5) 1.966(5)  | Fe(1B)-N(5B) 1.983(5)  |
|                   | Fe(1)-N(6) 1.970(4)  | Fe(1B)-N(6B) 1.995(5)  |

| Bond Angles (°) | N(1)-Fe(1)-N(2) 80.31(18) | N(1B)-Fe(1B)-N(2B) 94.02(19) |
|----------------|--------------------------|-----------------------------|
|                | N(1)-Fe(1)-N(4) 95.27(18) | N(1B)-Fe(1B)-N(3B) 171.94(19) |
|                | N(3)-Fe(1)-N(1) 172.60(18) | N(1B)-Fe(1B)-N(4B) 80.12(19) |
|                | N(3)-Fe(1)-N(2) 93.71(18)  | N(1B)-Fe(1B)-N(5B) 97.51(18) |
|                | N(3)-Fe(1)-N(4) 80.23(17)  | N(1B)-Fe(1B)-N(6B) 91.10(19) |
|                | N(4)-Fe(1)-N(2) 89.37(18)  | N(3B)-Fe(1B)-N(2B) 80.92(19) |
|                | N(5)-Fe(1)-N(1) 90.85(18)  | N(3B)-Fe(1B)-N(4B) 93.58(19) |
|                | N(5)-Fe(1)-N(2) 94.54(19)  | N(3B)-Fe(1B)-N(6B) 94.52(19) |
|                | N(5)-Fe(1)-N(3) 93.98(17)  | N(4B)-Fe(1B)-N(2B) 90.53(19) |
|                | N(5)-Fe(1)-N(4) 173.22(17) | N(5B)-Fe(1B)-N(2B) 94.19(18) |
|                | N(5)-Fe(1)-N(6) 80.48(19)  | N(5B)-Fe(1B)-N(3B) 89.16(18) |
|                | N(6)-Fe(1)-N(1) 93.79(18)  | N(5B)-Fe(1B)-N(4B) 174.86(18) |
|                | N(6)-Fe(1)-N(2) 172.28(18) | N(5B)-Fe(1B)-N(6B) 80.09(19) |
|                | N(6)-Fe(1)-N(3) 92.54(17)  | N(6B)-Fe(1B)-N(2B) 172.79(18) |
|                | N(6)-Fe(1)-N(4) 96.17(18)  | N(6B)-Fe(1B)-N(4B) 95.35(19) |
Table S40 Selected least-squares planes data for [Fe(L7)₃](PF₆)₁.₇₂(ClO₄)₀.₂₈∙CH₃OH (13).

| Least-squares planes description | Max. deviation/Å | Atom | Dihedral Angle (°) |
|----------------------------------|------------------|------|-------------------|
| Benzimidazole 1 N1 C1 C2 C3 C4 C5 C6 N7 C39 | 0.02 | C4 |                |
| Pyrimidine 1 N2 C11 N8 C10 C9 C8 | 0.032 | C8 | 7.5(2) |
| Benzimidazole 2 N3 C19 N9 C17 C16 C15 C14 C13 C12 | 0.02 | C12-C19 | 9.8(2) |
| Pyrimidine 2 C20 C21 C22 N10 C23 N4 | 0.014 | C22 |        |
| Benzimidazole 3 N5 C24 C25 C26 C27 C28 C29 N11 C31 | 0.038 | C26 | 9.3(1) |
| Pyrimidine 3 C32 C33 C34 N12 C35 N6 | 0.005 | C32 |        |
| Benzimidazole 1B C39B N1B C1B C2B C3B C4B C5B C6B N7B | 0.025 | C1B | 8.03(16) |
| Pyrimidine 1B N4B C20B C21B C22B N10B C23B | 0.02 | N4B |        |
| Benzimidazole 2B C19B N9B C17B C16B C15B C14B C13B C12B N3B | 0.061 | C14B | 15.5(2) |
| Pyrimidine 2B N2B C11B N8B C10B C9B C8B | 0.027 | C8B |        |
| Benzimidazole 3B C24B C25B C26B C27B C28B C29B N11B C31B | 0.025 | N5B | 4.0(2) |
| Pyrimidine 3B N6B C32B C33B C34B N12B C35B | 0.008 | C34B |        |
### Table S41 Structural data of complexes 1-7 incorporating ligand L6 in the solid-state.\(^a\)

| Complex                                      | Crystal System | Configuratio  | \(T/ K\) | \(d (M-N_{bz})\) | \(d (M-N_{py})\) | \(\alpha/\degree\) | \(\beta/\degree\) | \(\gamma/\degree\) | Octahedron |
|----------------------------------------------|----------------|---------------|----------|-------------------|-------------------|-------------------|-------------------|------------------|-------------|
| \([\text{Zn(L6)}_3][\text{ClO}_4]_2\) (CH₃CN)₂.₅ (1) | Triclinic      | facial        | 180      | 2.16(8)           | 2.24(18)         | 8.2(2.7)          | 83.1(1.9)         | 75.0(2.3)       | 3.13        |
| \([\text{Zn(L6)}_3][\text{BF}_4]_2\) (CH₃CN)₂ (2) | Triclinic      | facial        | 180      | 2.04(6)           | 2.33(9)          | 6.4(3.5)          | 83.7(1.6)         | 74.6(1.6)       | 3.126       |
| \([\text{Ni(L6)}_3][\text{ClO}_4]_2\) (3) | Triclinic      | meridional    | 100      | 2.10(3)           | 2.24(1)          | 11.9(4.6)         | 83.6(3.1)         | 75.7(5)         | 1.91        |
| \([\text{Ni(L6)}_3][\text{ClO}_4]_2\) CH₃CN (4) | Monoclinic     | facial        | 180      | 2.04(7)\(^e\)    | 2.15(8)\(^e\)   | 8.2(5.5)\(^e\)   | 88.0(1.4)\(^e\)  | 78.3(9)\(^e\)   | 1.377\(^e\) |
| \([\text{Ni(L6)}_3][\text{BF}_4]_2\) CH₃CN (5) | Monoclinic     | facial        | 180      | 2.069(7)          | 2.11(2)          | 11.6(4.5)         | 86.6(1.2)         | 78.4(2)         | 1.142       |
| \([\text{Fe(L6)}_3][\text{ClO}_4]_2\) (6)   | Triclinic      | meridional    | 180      | 2.068(5)          | 2.12(2)          | 11.6(4.5)         | 86.9(1.5)         | 78.3(3)         | 1.15        |
| \([\text{Fe(L6)}_3][\text{BF}_4]_2\) (C₅H₁₂O)₀.₅ (C₂H₅N)₀.₅ (7) | Triclinic      | facial        | 180      | 2.03(3)\(^e\)    | 2.06(5)\(^e\)   | 7.2(3.9)\(^e\)   | 88.6(8)\(^e\)   | 83.3(5.7)\(^d\) | 1.067\(^e\) |

\(\alpha\) = interannular intraligand angles, \(\beta\) = interchelate angles and \(\gamma\) = chelate bite angles. \(^b\) \(bz\) = benzimidazole. \(^c\) \(py\) = pyrimidine. \(^d\) SHAPE’s scores as compared to an ideal octahedron or trigonal prismatic geometry.\(^1\)\(^1\)\(^5\)\(^e\) Average value for more than two complexes in the asymmetric unit.
Table S42 Structural data of complexes 8-13 incorporating ligand L7 in the solid-state.\textsuperscript{a}

|                  | [Zn(L7)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{2} | [Zn(L7)\textsubscript{3}](PF\textsubscript{6})\textsubscript{2} | [Ni(L7)\textsubscript{3}](PF\textsubscript{6})\textsubscript{0.52} | [Ni(L7)\textsubscript{3}](BF\textsubscript{4})\textsubscript{2}CH\textsubscript{3}OH (CH\textsubscript{3}CN)\textsubscript{0.5} | [Fe(L7)\textsubscript{3}](PF\textsubscript{6}) | [Fe(L7)\textsubscript{3}](PF\textsubscript{6})\textsubscript{1.72} CH\textsubscript{3}OH (13) |
|------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|------------------------------------------|-------------------------------------------------|
| \(T / K\)       | 180                                            | 150                                            | 120                                            | 150                                            | 150                                      | 150                                            |
| Crystal System   | Trigonal                                       | Monoclinic                                     | Monoclinic                                     | Triclinic                                       | Monoclinic                                | Monoclinic                                     |
| Configuration    | facial                                         | facial                                         | meridional                                     | meridional                                      | meridional                                | meridional                                     |
| \(d (M-N_{bz})\)\textsuperscript{b} | 2.083(6)                                       | 2.101(14)                                      | 2.068(20)\textsuperscript{e}                  | 2.076(15)                                      | 1.980(12)\textsuperscript{e}              | 1.975(15)\textsuperscript{e}                  |
| \(d (M-N_{py})\)\textsuperscript{c} | 2.307(13)                                       | 2.227(77)                                      | 2.111(13)\textsuperscript{e}                  | 2.101(12)                                      | 1.984(13)\textsuperscript{e}              | 1.991(24)\textsuperscript{e}                  |
| \(\alpha / ^\circ\) | 20.2(4)                                        | 10.4(7.8)                                      | 10.5(4.6)\textsuperscript{e}                  | 8.8(1.0)                                       | 9.8(4.0)\textsuperscript{e}              | 9.0(3.8)\textsuperscript{e}                  |
| \(\beta / ^\circ\) | 83.8(3)                                        | 85.6(2.6)                                      | 89.9(1.7)\textsuperscript{e}                  | 88.7(4)                                        | 88.7(8)\textsuperscript{e}              | 89.1(7)\textsuperscript{e}                  |
| \(\gamma / ^\circ\) | 74.5(3)                                        | 75.8(7)                                        | 78.1(5)\textsuperscript{e}                    | 78.5(4)                                        | 80.5(2)\textsuperscript{e}              | 80.4(3)\textsuperscript{e}                  |
| Octahedron \(d\) | 2.131                                          | 1.727                                          | 1.143\textsuperscript{e}                      | 1.040                                           | 0.706\textsuperscript{e}              | 0.727\textsuperscript{e}                  |

\textsuperscript{a} \(\alpha\) = interannular intraligand angles, \(\beta\) = interchelate angles and \(\gamma\) = chelate bite angles. \textsuperscript{b} bz= benzimidazole. \textsuperscript{c} py= pyrimidine. \textsuperscript{d} SHAPE’s scores as compared to an ideal octahedron or trigonal prismatic geometry.\textsuperscript{115} \textsuperscript{e} Average value for more than two complexes in the asymmetric unit.
Table S43 Comparison of the structural data for hexa-coordinate Fe$^{II}$ centers in the complexes [Fe(L$_6$)$_3$](ClO$_4$)$_2$ (6) and [Fe(L$_6$)$_3$](BF$_4$)$_2$·(C$_5$H$_{12}$O)$_{0.5}$·(C$_2$H$_5$N)$_{0.5}$ (7) in the solid-state at 100 K and 180 K.$^a$

|                | mer-[Fe(L$_6$)$_3$](ClO$_4$)$_2$ | fac-[Fe(L$_6$)$_3$](BF$_4$)$_2$ |
|----------------|-------------------------------|-------------------------------|
| $T$ / K        | 100K                          | 180K                          | 100K                          | 180K                          |
| Crystal System | Monoclinic                    | Triclinic                     | Triclinic                     | Triclinic                     |
| $d$ (M-N$_{bz}$)$^b$ | 1.988(7)                      | 2.03(3)$^e$                   | 1.99(2)                       | 2.09(2)                       |
| $d$ (M-N$_{py}$)$^c$ | 1.994(16)                     | 2.06(5)$^e$                   | 1.99(1)                       | 2.148(5)                      |
| $\alpha / ^\circ$ | 7.4(4.7)                      | 7.2(3.9)$^e$                  | 8.2(4.2)                      | 10.3(3.7)                     |
| $\beta / ^\circ$ | 88.9(2)                       | 88.58(82)$^e$                 | 88.8(7)                       | 86.1(3.1)                     |
| $\gamma / ^\circ$ | 80.7(2)                       | 83.3(5.7)$^e$                 | 80.4(2)                       | 77.0(4)                       |
| Octahedron$^d$ | 0.75                          | 1.067$^e$                     | 0.728                         | 1.443                         |

$^a$ $\alpha$ = interannular intraligand angles, $\beta$ = interchelate angles and $\gamma$ = chelate bite angles. $^b$ bz= benzimidazole. $^c$ py= pyrimidine. $^d$ SHAPE’s scores as compared to an ideal octahedron or trigonal prismatic geometry.$^{115}$ $^e$ Average value for more than two complexes in the asymmetric unit.
Table S44 Crystal data, structure refinement and Fe-N distances for variable-temperature X-ray diffraction of [Fe(L6)](ClO4)2 (6) (heating rate 4K/min).

| Temperature (K) | 100.0(2) | 130.0(1) | 160.2(4) | 170.2(3) | 180.0(1) | 190.1(2) | 200.2(3) |
|----------------|----------|----------|----------|----------|----------|----------|----------|
| Crystal system | Monoclinic| Monoclinic| Monoclinic| Triclinic| Triclinic| Triclinic| Triclinic|
| Space group    | P21/c    | P21/c    | P21/c    | P-1      | P-1      | P-1      | P-1      |
| Cell dimensions|           |           |           |           |           |           |           |
| a (Å)          | 14.7997(4)| 14.8156(2)| 14.8371(4)| 14.8301(10)| 14.846(7)| 14.8537(5)| 14.8683(5)|
| b (Å)          | 14.3249(4)| 14.3681(3)| 14.4044(4)| 14.4509(8)| 14.4714(7)| 14.5135(7)| 14.5298(6)|
| c (Å)          | 16.9540(4)| 16.9875(3)| 17.0101(4)| 17.0059(9)| 17.0415(6)| 17.0261(8)| 17.0382(8)|
| α (°)          | 90        | 90        | 90        | 90.327(5) | 90.483(3)| 89.144(4) | 90.938(4) |
| β (°)          | 94.392(2) | 94.4281(16)| 94.413(2)| 94.189(5) | 94.246(3)| 94.348(3)| 94.310(3)|
| γ (°)          | 90        | 90        | 90        | 89.740(5) | 89.407(4)| 90.793(3)| 89.116(3)|
| Volume (Å³)    | 3583.77(16)| 3605.35(12)| 3624.60(16)| 3634.7(4)| 3650.5(3)| 3659.2(3)| 3669.5(3)|
| Z              | 4         | 4         | 4         | 4         | 4         | 4         | 4         |
| dcalc (g/cm³)  | 1.641     | 1.631     | 1.623     | 1.618     | 1.611     | 1.607     | 1.603     |
| μ (mm⁻¹)       | 5.385     | 5.352     | 5.324     | 5.309     | 5.286     | 5.274     | 5.259     |
| Crystal size (mm³) | 0.272 x 0.245 x | 0.277 x 0.231 x | 0.272 x 0.245 x | 0.272 x 0.245 x | 0.357 x 0.22 x | 0.277 x 0.231 x | 0.277 x 0.231 x |
| θ range for data collection (°) | 2.995 - 68.868 | 2.992 - 68.784 | 2.987 - 68.748 | 2.605 - 68.962 | 2.600 - 69.000 | 2.603 - 69.354 | 2.601 - 69.276 |
| Index ranges   | -14≤h≤17, | -17≤h≤13, | -14≤h≤17, | -14≤h≤17, | -17≤h≤17, | -17≤h≤17, | -17≤h≤14, |
|                | -16≤k≤17, | -17≤k≤17, | -16≤k≤17, | -16≤k≤17, | -17≤k≤16, | -16≤k≤17, | -16≤k≤17, |
|                | -18≤l≤20, | -20≤l≤19, | -17≤l≤20, | -17≤l≤20, | -17≤l≤20, | -20≤l≤20, | -20≤l≤20, |
| Nref collected | 15691     | 15670     | 15821     | 16251     | 30197     | 29441     | 29431     |
| Independent reflections / $R_{int}$ | 6510 / 0.0261 | 6587 / 0.0232 | 6588 / 0.0261 | 10644 / 0.0310 | 13344 / 0.0335 | 13340 / 0.0426 | 13379 / 0.0418 |
| Completeness (to $\theta = 67.5^\circ$) | 99.4% | 99.9% | 99.4% | 80.4% | 99.8% | 99.6% | 99.6% |
| Data / restraints / parameters | 6510 / 0 / 535 | 6587 / 0 / 535 | 6588 / 0 / 535 | 10644 / 0 / 1072 | 13344 / 0 / 1073 | 13340 / 0 / 1062 | 13379 / 0 / 1097 |
| GOF on $F^2$ | 1.051 | 1.040 | 1.046 | 1.060 | 1.041 | 1.055 | 1.044 |
| $R_1$, $wR_2$ (I>2σ(I)) | 0.0506, 0.1361 | 0.0553, 0.1504 | 0.0623, 0.1708 | 0.0692, 0.1768 | 0.0754, 0.2104 | 0.0902, 0.2540 | 0.0891, 0.2501 |
| $R_1$, $wR_2$ (all data) | 0.0541, 0.1390 | 0.0592, 0.1544 | 0.0680, 0.1769 | 0.0796, 0.1863 | 0.0890, 0.2307 | 0.1049, 0.2694 | 0.1055, 0.2674 |
| Largest diff. peak / hole (e⁻.Å⁻³) | 1.110 / -0.575 | 1.433 / -0.587 | 1.504 / -0.633 | 0.729 / -0.764 | 1.286 / -0.799 | 1.739 / -0.717 | 1.848 / -0.547 |
| dFe – N (Å) | Fe1 N1 | 1.985(3) | 1.985(3) | 1.991(3) | 1.991(4) | 1.995(4) | 2.063(5) | 1.993(5) |
| Fe1 N3 | 2.020(3) | 2.024(3) | 2.041(3) | 2.060(5) | 2.036(5) | 2.194(6) | 2.025(5) |
| Fe1 N5 | 1.982(2) | 1.986(3) | 1.999(3) | 2.009(4) | 2.009(4) | 2.088(4) | 2.002(5) |
| Fe1 N7 | 1.984(2) | 1.994(3) | 2.006(3) | 1.997(4) | 2.013(4) | 2.124(5) | 2.004(4) |
| Fe1 N9 | 1.999(3) | 2.000(3) | 2.009(3) | 2.011(5) | 2.012(4) | 2.096(5) | 2.004(5) |
| Fe1 N11 | 1.982(2) | 1.988(3) | 1.997(3) | 1.998(4) | 2.006(4) | 2.114(5) | 1.994(5) |
| Fe1B N1B | 2.029(4) | 2.065(4) | 2.002(5) | 2.101(4) |
| Fe1B N3B | 2.098(5) | 2.145(5) | 2.026(5) | 2.215(5) |
| Fe1B N5B | 2.007(4) | 2.043(4) | 1.992(5) | 2.083(5) |
| Fe1B N7B | 2.039(4) | 2.083(4) | 2.007(5) | 2.142(5) |
| Fe1B N9B | 2.035(5) | 2.068(5) | 2.004(5) | 2.110(5) |
| Fe1B N11B | 2.023(5) | 2.075(5) | 1.994(5) | 2.133(5) |
| Temperature (K)   | 210.2(4)  | 230.2(3)  | 240.2(3)  | 250.2(3)  | 265.2(3)  | 281(8)   |
|------------------|-----------|-----------|-----------|-----------|-----------|----------|
| Crystal system   | Triclinic | Triclinic | Triclinic | Monoclinic| Monoclinic | Monoclinic|
| Space group      | P-1       | P-1       | P-1       | P2₁/c     | P2₁/c     | P2₁/c    |
| Cell dimensions  |           |           |           |           |           |          |
| a (Å)            | 14.8681(9)| 14.8989(6)| 14.8958(7)| 14.9289(3)| 14.9377(4)| 14.9848(3)|
| b (Å)            | 14.5584(8)| 14.5767(7)| 14.6045(7)| 14.6273(4)| 14.6510(4)| 14.7075(3)|
| c (Å)            | 17.0585(9)| 17.0816(8)| 17.1060(6)| 17.1269(3)| 17.1339(4)| 17.1641(3)|
| α (°)            | 90.879(4) | 90.775(4) | 90.341(3) | 90        | 90°       | 90       |
| β (°)            | 94.097(5) | 94.220(3) | 94.040(3) | 94.0683(18)| 94.087(2) | 93.9532(15)|
| γ (°)            | 88.911(5) | 89.272(3) | 89.554(4) | 90        | 90        | 90       |
| V (Å³)           | 3681.9(4) | 3699.1(3) | 3711.9(3)| 3730.57(13)| 3740.26(18)| 3773.78(11)|
| Z                | 4         | 4         | 4         | 4         | 4         | 4        |
| dᵣᵣ (g/cm³)     | 1.597     | 1.590     | 1.584     | 1.577     | 1.572     | 1.558    |
| μ (mm⁻¹)         | 5.241     | 5.217     | 5.199     | 5.173     | 5.159     | 5.114    |
| Crystal size     | 0.272 x 0.245 x | 0.277 x 0.231 x | 0.272 x 0.245 x | 0.277 x 0.231 x | 0.272 x 0.245 x | 0.364 x 0.222 x |
| 0 range for data collection (°) | 2.597 - 68.903 | 2.594 - 69.417 | 2.590 - 69.101 | 2.968 - 68.777 | 2.966 - 68.969 | 2.956 - 68.760 |
| Index ranges     | -14<=h<=17, -18<=h<=14, -15<=h<=18, -17<=h<=14, -14<=h<=18, -17<=h<=17, | -16<=k<=17, -16<=k<=17, -16<=k<=17, -17<=k<=17, -16<=k<=17, -12<=k<=17, | -17<=l<=20, -20<=l<=20, -17<=l<=20, -20<=l<=19, -17<=l<=20, -13<=l<=20, |
| Nref collected   | 16417     | 29803     | 16690     | 16305     | 14806     | 17075    |
| Independent reflections / Rint | 10747 / 0.034 | 13475 / 0.0424 | 10877 / 0.0309 | 6813 / 0.0256 | 6783 / 0.0323 | 6891 / 0.0187 |
| Completeness (θ = 67.5°) | 80.2 % | 99.6 % | 80.5 % | 99.6 % | 98.9 % | 99.7 % |
| Data / restraints / parameters | 10747 / 0 / 1097 | 13475 / 0 / 1097 | 10877 / 0 / 1097 | 6813 / 0 / 535 | 6783 / 0 / 535 | 6891 / 0 / 535 |
|                        | 1.060   | 1.028   | 1.054   | 1.054   | 1.172   | 1.054   |
|------------------------|---------|---------|---------|---------|---------|---------|
| R₁, wR₂ (I>2σ(I))     | 0.0870, 0.2370 | 0.0852, 0.2333 | 0.0688, 0.1868 | 0.0539, 0.1510 | 0.0730, 0.2093 | 0.0528, 0.1516 |
| R₁, wR₂ (all data)    | 0.1041, 0.2576 | 0.1038, 0.2522 | 0.0854, 0.2028 | 0.0623, 0.1594 | 0.1008, 0.2793 | 0.0603, 0.1603 |
| Largest diff. peak / hole (e⁻.Å⁻³) | 1.574 / -0.687 | 1.490 / -0.530 | 0.766 / -0.527 | 0.940 / -0.406 | 0.665 / -1.328 | 0.743 / -0.484 |
| dFe – N (Å)            |         |         |         |         |         |         |
| Fe₁ N1                 | 1.999(5) | 2.021(5) | 2.051(4) | 2.085(3) | 2.067(5) | 2.110(3) |
| Fe₁ N3                 | 2.040(6) | 2.085(5) | 2.159(5) | 2.215(3) | 2.237(5) | 2.263(3) |
| Fe₁ N5                 | 2.013(5) | 2.038(4) | 2.069(4) | 2.100(2) | 2.097(4) | 2.130(2) |
| Fe₁ N7                 | 1.994(5) | 2.045(4) | 2.088(4) | 2.155(3) | 2.167(5) | 2.195(2) |
| Fe₁ N9                 | 2.012(6) | 2.033(5) | 2.069(5) | 2.107(3) | 2.120(5) | 2.131(3) |
| Fe₁ N11                | 1.991(5) | 2.036(5) | 2.074(5) | 2.136(3) | 2.155(5) | 2.175(3) |
| Fe₁B N1B               | 2.115(5) | 2.111(4) | 2.106(4) |         |         |         |
| Fe₁B N3B               | 2.243(6) | 2.231(5) | 2.223(5) |         |         |         |
| Fe₁B N5B               | 2.095(5) | 2.084(5) | 2.075(4) |         |         |         |
| Fe₁B N7B               | 2.156(5) | 2.160(5) | 2.152(4) |         |         |         |
| Fe₁B N9B               | 2.123(6) | 2.119(5) | 2.115(5) |         |         |         |
| Fe₁B N11B              | 2.142(6) | 2.150(5) | 2.134(5) |         |         |         |
**Figure S49** Differential scanning calorimetric (DSC) trace recorded for [Fe(L6)3](ClO4)2 (5) under an inert atmosphere.
Figure S50 Plots of high-spin mole fractions ($x_{hs}$) versus temperature ($T$) between 5-300 K for a) [Fe(L6)3](ClO4)2 (6, facial isomers) and 4-400 K for b) [Fe(L6)3](BF4)2·(C5H12O)0.5 (7, meridional isomers) and c) [Fe(L7)3](PF6)(BF4)·CH3OH (12, meridional isomers). The red points represents the experimentally measured values while the dashed black traces are built by using the fitted values of $\Delta H_{sco}$, $\Delta S_{sco}$, and $\gamma$ (Table 4, see text).
Figure S51 Plots of high-spin mole fractions ($x_{hs}$) versus temperature ($T$) in the 4-400 K range computed from the plots of molar paramagnetic susceptibility ($\chi M$) versus temperature ($T$) with eq. (17) for a complete heating/cooling cycle for [Fe(L6)$_3$](BF$_4$)$_2$(C$_5$H$_{12}$O)$_{0.5}$ (7). The bump during the cooling cycle between 200-150 K is probably the result of the loss of interstitial tert-butyl-methylether during the heating process.