

## Bis-tetradentate Complexes of Cd(II) and Hg(II) with N<sub>8</sub> Coordination: Structural and NMR Comparisons

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### ELECTRONIC SUPPLEMENTARY INFORMATION

Table of Contents with Abbreviated Descriptions	
Table S1. Selected bond angles for <b>1</b>	S2
Table S2. Selected bond angles for <b>2</b> and <b>3</b>	S2
Table S3. Selected bond angles for <b>4</b> and <b>5</b>	S3
Table S4. Average M-N bond lengths in <b>1</b> – <b>5</b>	S3
Figure S1. Overviews of aromatic ring packing in <b>2</b> & <b>3</b>	S4
Figure S2. Overviews of aromatic ring packing in <b>4</b> & <b>5</b>	S5
Figure S3. Structurally characterized N <sub>8</sub> Cd(II) and Hg(II) complexes	S6
Figure S4. Proton NMR spectra of <b>5</b> in various solvents at 20 °C	S7
Figure S5. Proton NMR of <b>1</b> in CD <sub>3</sub> CN at 20 °C & -40 °C	S8
Figure S6. Proton NMR of <b>2</b> in acetone- <i>d</i> <sub>6</sub> at 20 °C, -40 °C and -80 °C	S9
Figure S7. Proton NMR of <b>3</b> and <b>5</b> in acetone- <i>d</i> <sub>6</sub> at -80 °C	S10
Figure S8. Variable temperature <sup>1</sup> H NMR spectra of <b>4</b> in CD <sub>3</sub> CN	
Figure S9. Temperature dependence of H <sub>e</sub> resonance for <b>5</b>	S11
Table S5. Vertical separations of methine C & H adjacent to bound N <sub>Py/Im</sub> in <b>1</b> – <b>5</b>	S12
Figure S10. Highlights of the ligand interface of <b>2</b>	S12
References	S13

**Table S1.** Selected Bond Angles (°) for **1**

Angle	1
N1-M-N1#1	180.00(5)
N1-M-N2	60.86(5)
N1-M-N4	61.57(5)
N1-M-N6	60.96(5)
N1-M-N2#1	119.13(5)
N1-M-N4#1	118.43(5)
N1-M-N6#1	119.04(5)
N2-M-N2#1	180.00(5)
N2-M-N4	99.73(5)
N2-M-N6	99.38(5)
N2-M-N4#1	80.27(5)
N2-M-N6#1	80.62(5)
N4-M-N4#1	180.00(5)
N4-M-N6	96.79(5)
N4-M-N6#1	83.21(5)
N6-M-N6#1	180.00(5)

**Table S2.** Selected Bond Angles (°) for **2** and **3**.

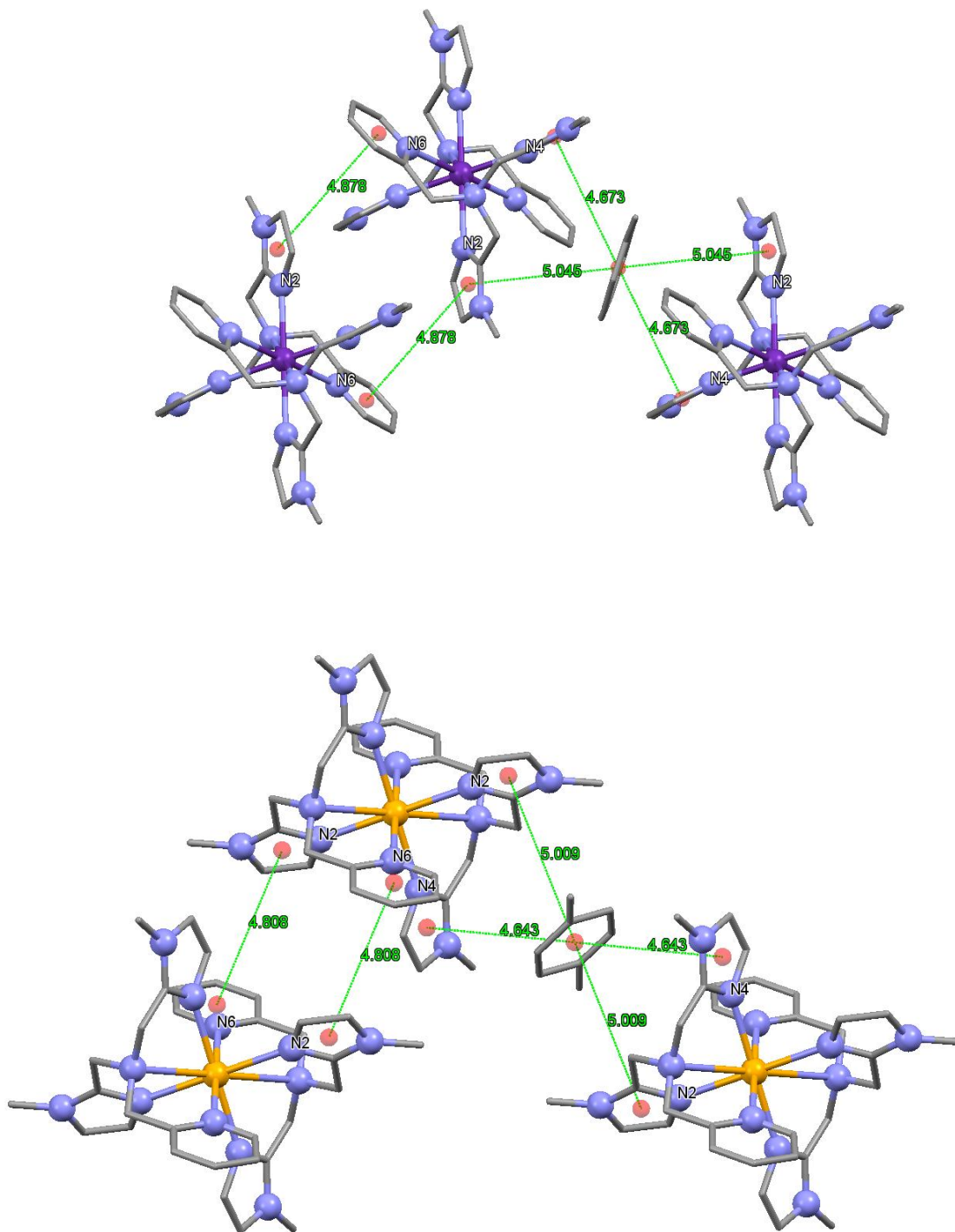
Angle	2	3
N1-M-N1#	180.00(13)	180.00(16)
N1-M-N2	62.57(13)	62.98(13)
N1-M-N4	62.92(12)	62.99(11)
N1-M-N6	61.12(14)	59.42(11)
N1-M-N2#1	117.43(13)	117.02(13)
N1-M-N4#1	117.08(12)	117.01(11)
N1-M-N6#1	118.88(14)	120.57(16)
N2-M-N2#1	180.00(13)	180.00(16)
N2-M-N4	99.54(14)	98.87(15)
N2-M-N6	99.86(17)	99.70(16)
N2-M-N4#1	80.46(14)	81.13(15)
N2-M-N6#1	80.14(17)	80.29(15)
N4-M-N4#1	180.00(13)	180.00(16)
N4-M-N6	100.59(14)	99.83(14)
N4-M-N6#1	79.41(14)	80.17(14)
N6-M-N6#1	180.00(13)	180.00(16)

**Table S3.** Selected Bond Angles (°) for **4** and **5**

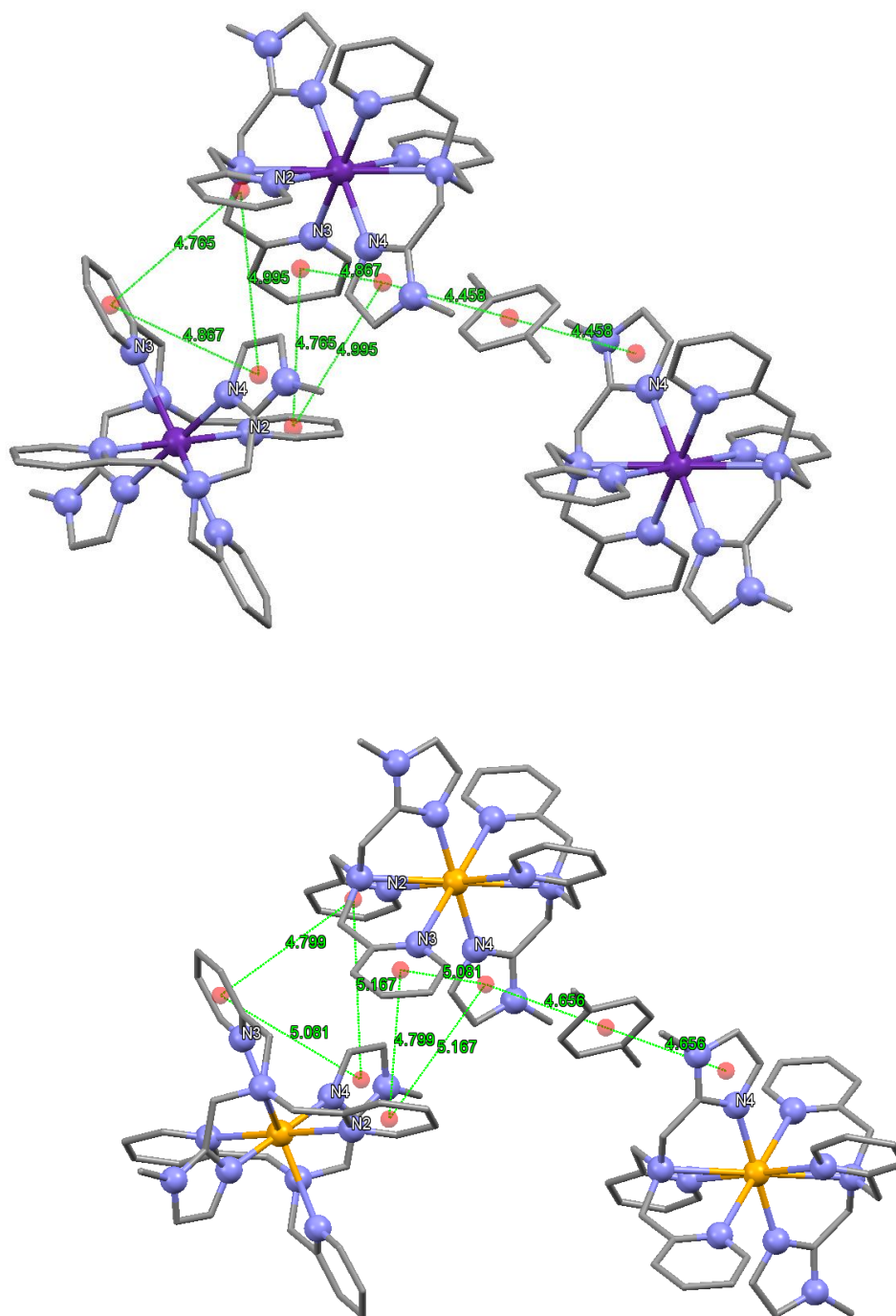
Angle	<b>4</b>	<b>5</b>
N1-M-N1#	180.00(8)	180.00(19)
N1-M-N2	64.14(6)	62.7(2)
N1-M-N3	61.24(6)	58.31(19)
N1-M-N4	64.85(6)	66.5(2)
N1-M-N2#1	115.86(6)	117.27(19)
N1-M-N3#1	118.76(6)	121.70(19)
N1-M-N4#1	115.15(6)	113.5(2)
N2-M-N2#1	180.00(8)	180.00(19)
N2-M-N3	102.53(7)	101.9(2)
N2-M-N4	98.74(6)	98.7(2)
N2-M-N3#1	77.47(7)	78.07(19)
N2-M-N4#1	81.26(6)	81.3(2)
N3-M-N3#1	180.00(8)	180.00(19)
N3-M-N4	103.03(6)	100.1(2)
N3-M-N4#1	76.97(6)	79.9(2)
N4-M-N4#1	180.00(8)	180.0

**Table S4.** Average M-N bond distances (Å) for Cd(ClO<sub>4</sub>)<sub>2</sub> and Hg(ClO<sub>4</sub>)<sub>2</sub> complexes of **L1-L4**

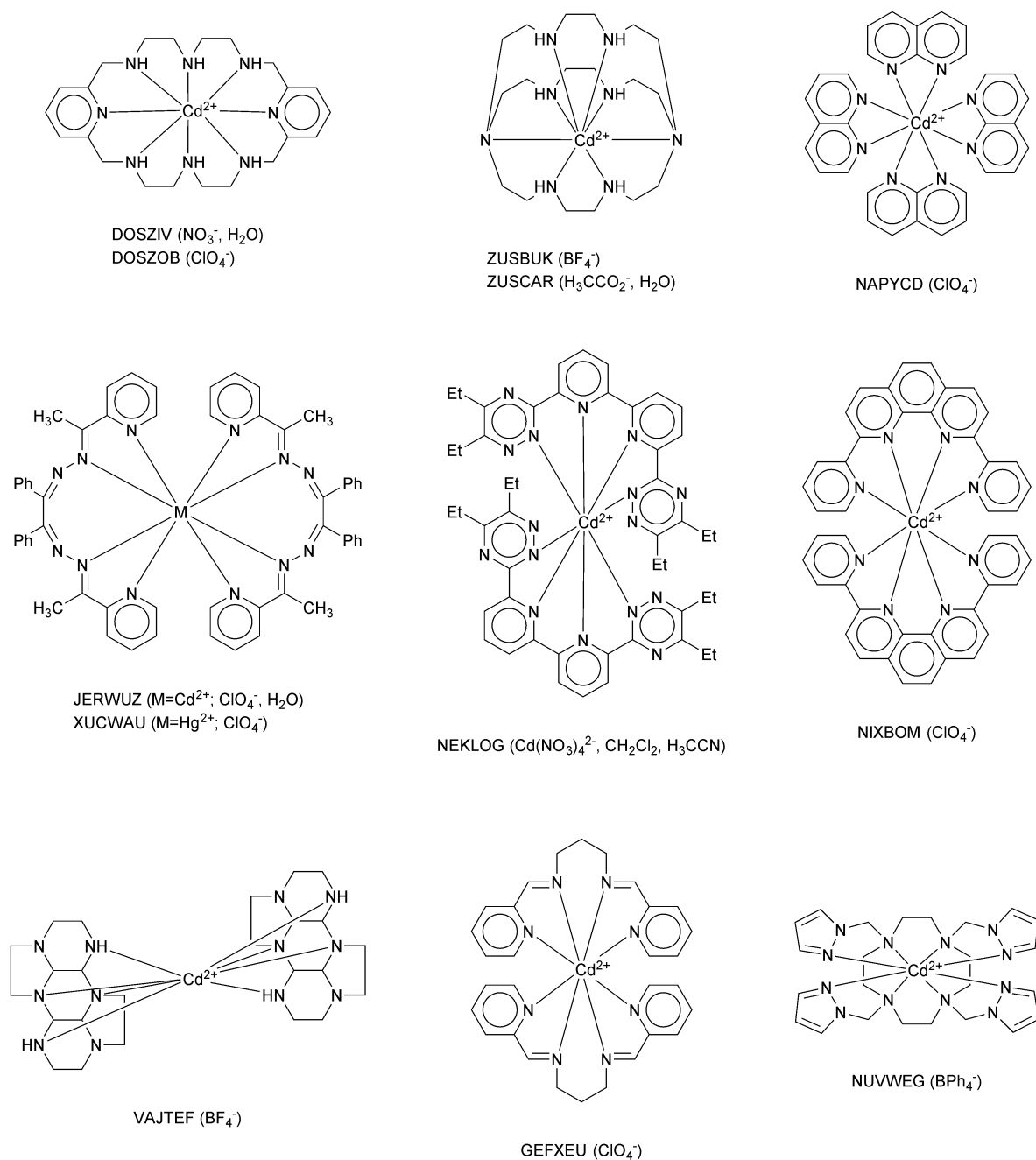
Ligand	<b>L1</b>		<b>L2</b>		<b>L3</b>		<b>L4</b>	
Metal	Cd (1)	Hg <sup>a</sup>	Cd (2)	Hg(3)	Cd (4)	Hg (5)	Cd <sup>b</sup>	Hg <sup>c</sup>
M-N <sub>Amine</sub>	2.9715(14)	2.957(6)	2.848(4)	2.881(3)	2.7633(19)	2.830(6)	2.53(6)	2.560(3)
M-N <sub>Pyridyl</sub>	-	-	2.564(5)	2.735(4)	2.57(12)	2.79(13)	2.54(6)	2.583(18)
M-N <sub>Imidazolyl</sub>	2.40(4)	2.48(19)	2.40(2)	2.40(4)	2.328(2)	2.161(6)	-	-
M-N <sub>Overall</sub>	2.5(3)	2.6(3)	2.6(2)	2.6(2)	2.56(19)	2.6(3)	2.54(6)	2.578(19)



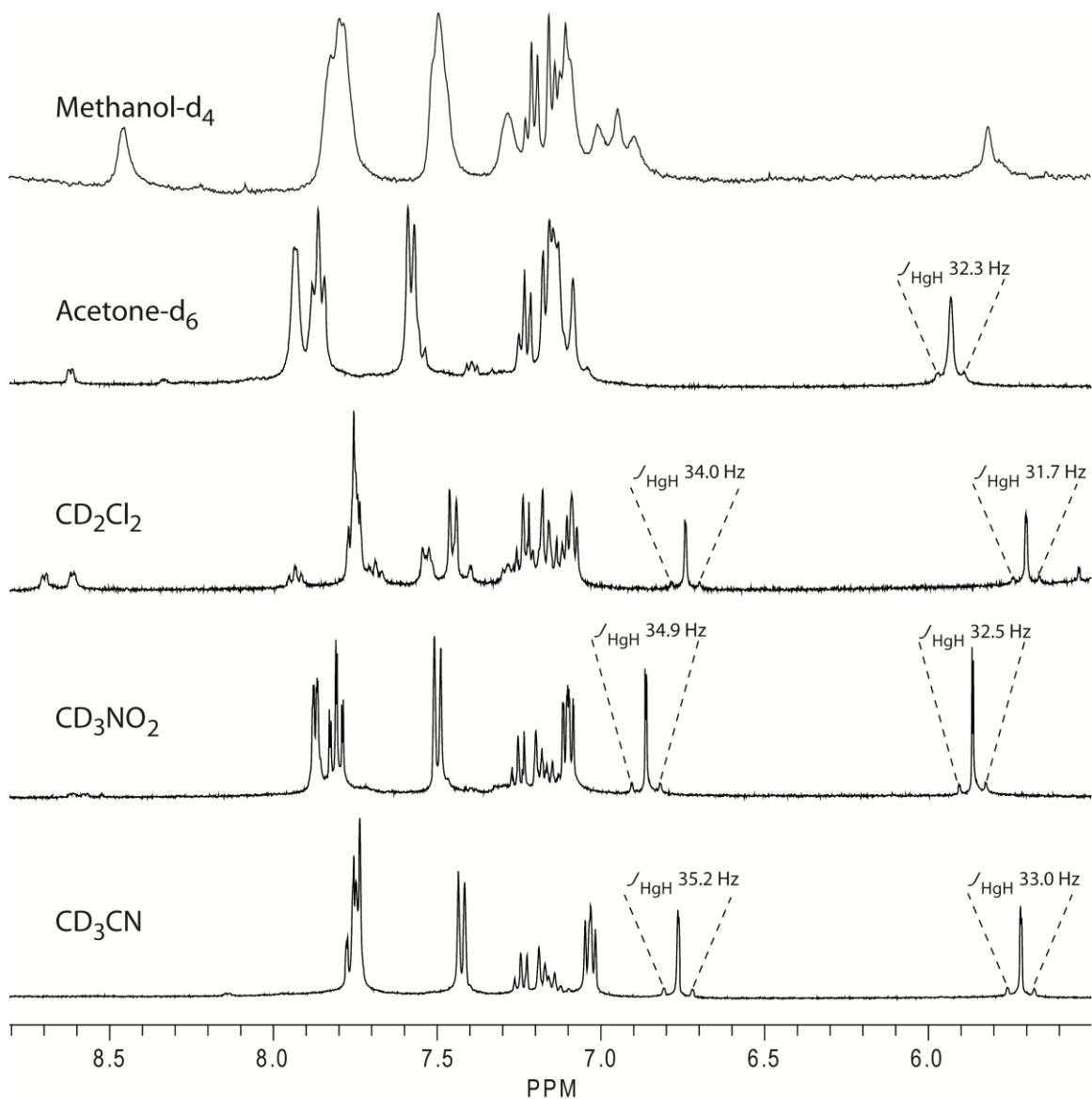
**Figure S1.** Overviews of parallel displaced aromatic ring packing between the disordered toluene and the two pairs of imidazolyl ring of neighboring complexes and intermolecular T-shaped packing between the pyridyl ring and the N2 imidazolyl rings in **2** (top) and **3** (bottom) with distances (Å).



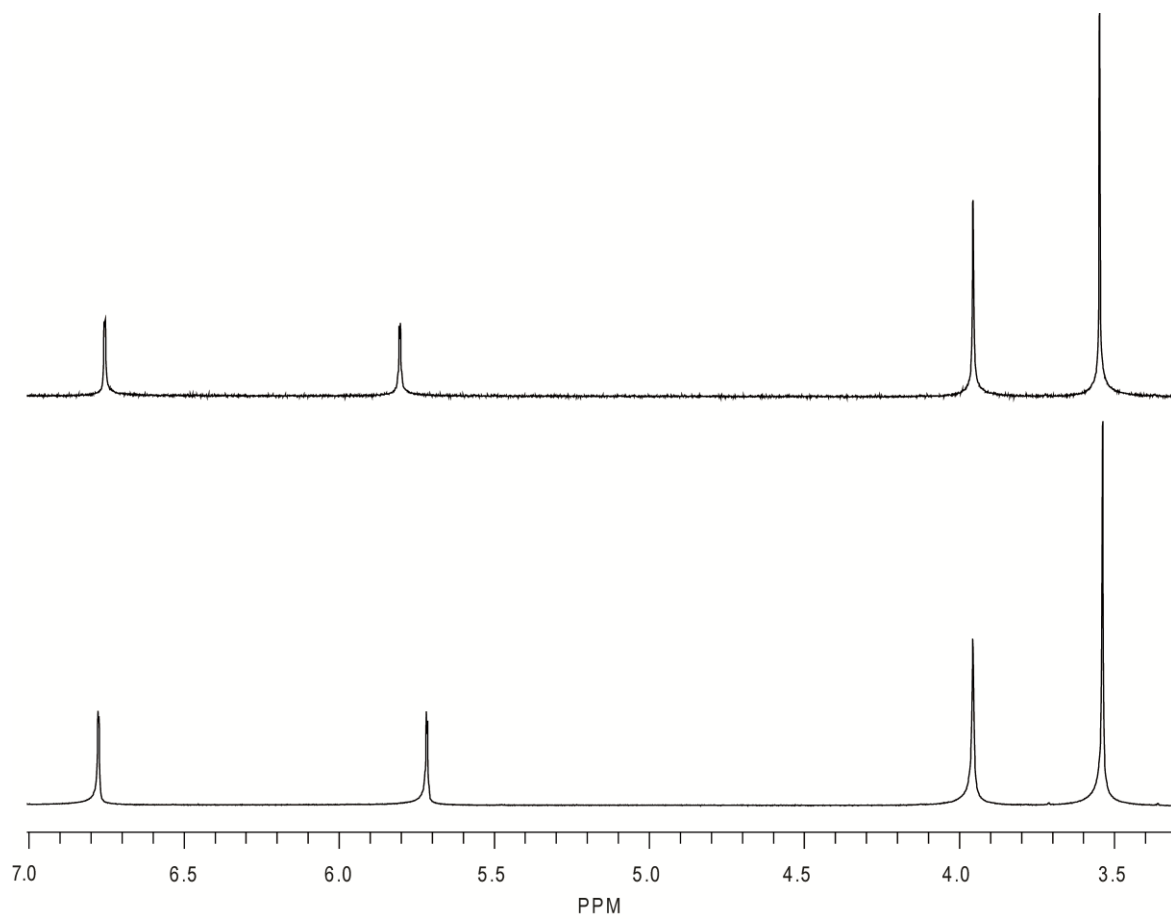
**Figure S2.** Overview of parallel displaced aromatic ring packing between the disordered toluene and a pair of imidazolyl ring of neighboring complexes in **4** (top) and **5** (bottom) with distances (Å). Inter- and intramolecular T-shaped packing between the imidazolyl rings and two pyridyl rings are also shown.



**Figure S3.** Schematic diagrams of all structurally characterized Cd(II) and Hg(II) complexes with eight nitrogen within the sum of the M-N van der Waals radii. References: DOSZIV & DOSZOB,<sup>1</sup> ZUSBUK & ZUSCAR,<sup>2</sup> NAPYCD,<sup>3</sup> JERWUZ,<sup>4</sup> XUCWAU,<sup>5</sup> NEKLOG,<sup>6</sup> NIXBOM,<sup>7</sup> VAJTEF,<sup>8</sup> GEFXEU,<sup>9</sup> NUVWEG.<sup>10</sup>

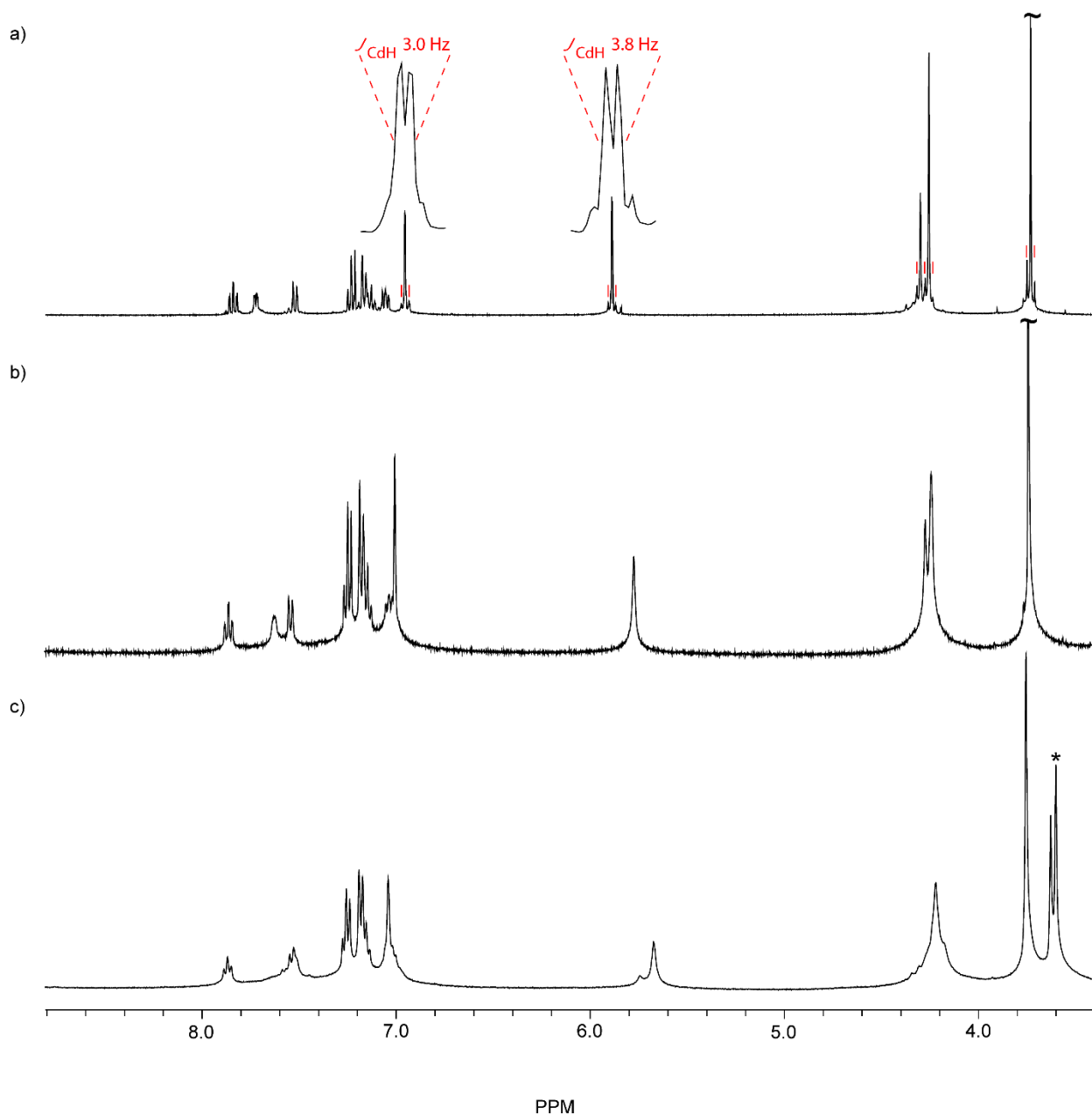


**Figure S4.**  $^1\text{H}$  NMR spectra of **5** in various solvents at 20 °C after extended storage. Samples were prepared from nominally 1 mg of **5** and 600  $\mu\text{L}$  of deuterated solvent. A single set of ligand resonances was observed in  $\text{CD}_3\text{CN}$  and  $\text{CD}_3\text{NO}_2$  and the NMR was unchanged over time. The acetone- $d_6$  and  $\text{CD}_2\text{Cl}_2$  samples were saturated. The resonances downfield of 8.3 ppm in the top three spectra reflect significant decomposition of **5** to  $[\text{HgL3}]^{2+}$  and/or free **L3**.

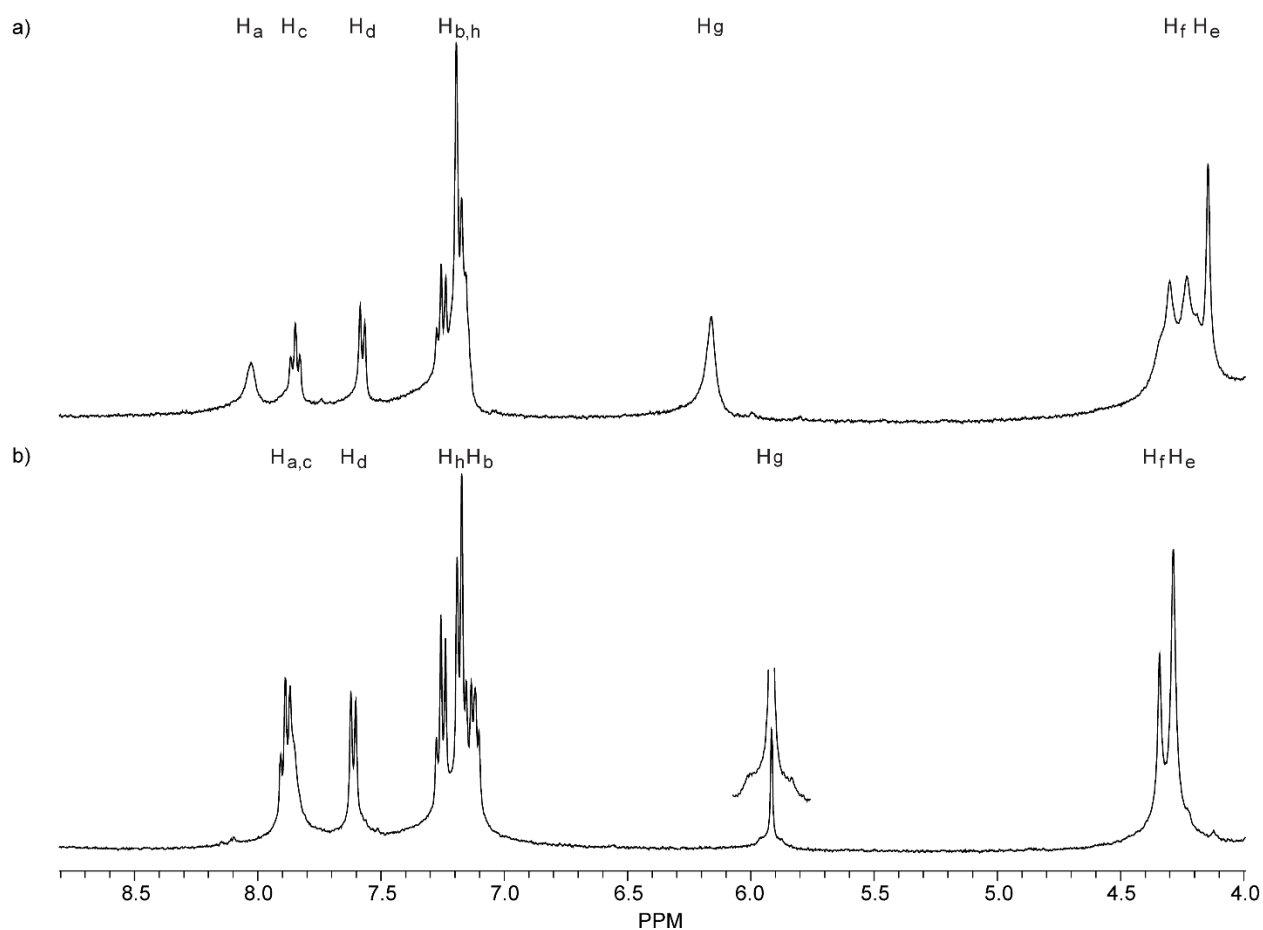


**Figure S5.** Proton NMR of **1** in CD<sub>3</sub>CN at 20 °C (top) and -40 °C (bottom).

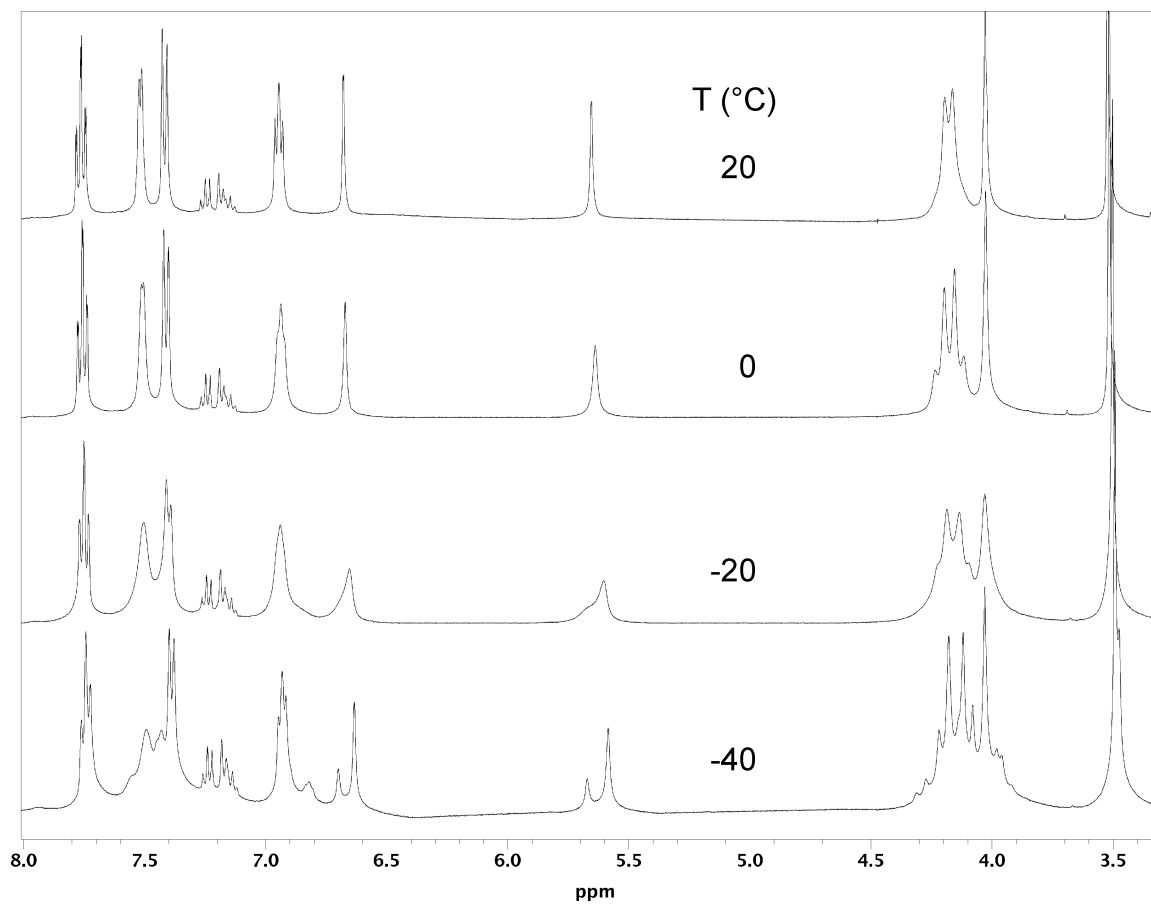




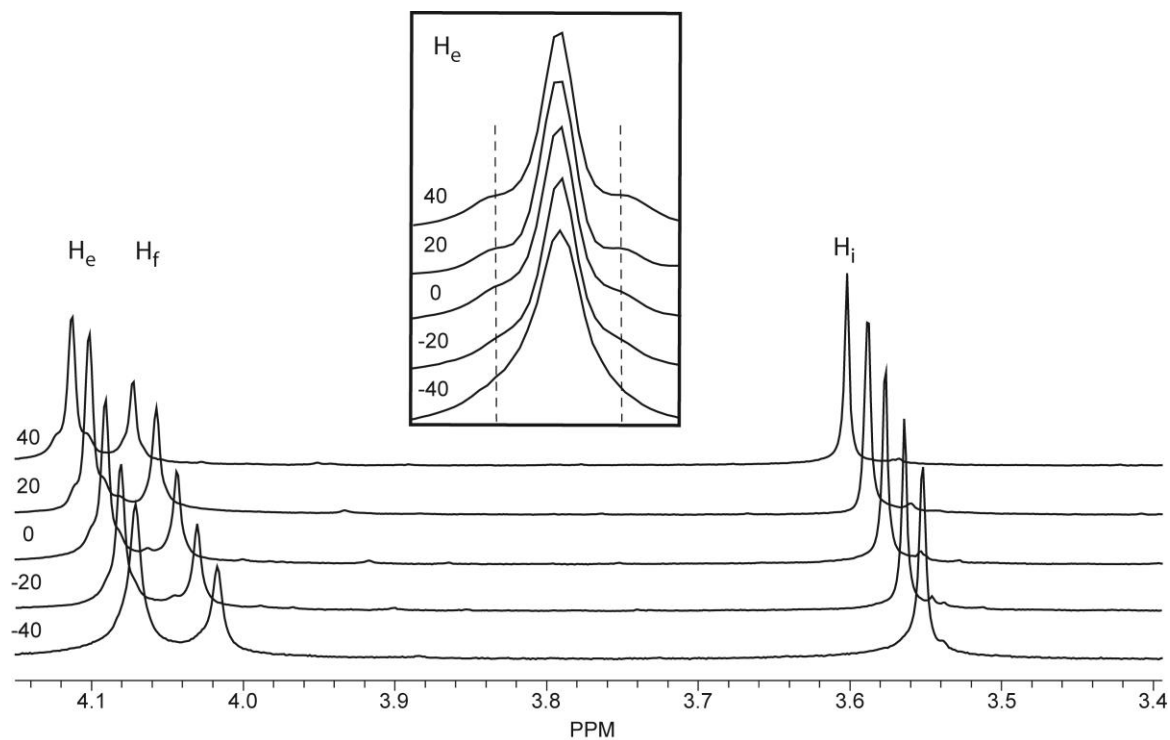
**Figure S6.**  $^1\text{H}$  NMR spectra of nominally 1 mg **2** 600  $\mu\text{L}$  acetone- $d_6$  at a) 20  $^\circ\text{C}$  (15.7 Hz spinning side bands marked with short red bar), b) -40  $^\circ\text{C}$  and c) -80  $^\circ\text{C}$  (water resonance marked with \*) shortly after dissolution. Two distinct resonances are observed for  $\text{H}_g$  (~5.7 ppm) and  $\text{H}_i$  (~3.7 ppm) at -80  $^\circ\text{C}$ , consistent with slow exchange on the  $\delta_{\text{H}}$  time scale. The absence of resonances around 8.5 ppm suggests insignificant complex decomposition. Small  $J(^{111/113}\text{Cd}^1\text{H})$  to the imidazole ring protons at 20  $^\circ\text{C}$  were not resolved when the spectrum was taken in  $\text{CD}_3\text{CN}$ .



**Figure S7.**  $^1\text{H}$  NMR features providing evidence for slowing intramolecular isomerization in acetone- $d_6$  at  $-80^\circ\text{C}$  shortly after dissolution (nominally 2 mg/mL). a) For complex **3**, resonances for ligand interface protons  $\text{H}_a$  and  $\text{H}_g$  are significantly broadened and partial geminal resolution of  $\text{H}_f$  is observed. b) For complex **5**, possible approach to slow intramolecular exchange conditions are suggested by broadening of  $J(^{199}\text{Hg}^1\text{H})$  satellites for  $\text{H}_g$  (see Figure S4). Singlets for  $\text{H}_i$  not shown. Resonances for  $\text{H}_b$  and  $\text{H}_h$  are superimposed on those for the toluene fo solvation between 7.1-7.3 ppm. The absence of resonances around 8.5 ppm suggests insignificant complex decomposition.



**Figure S8.** Variable temperature  $^1\text{H}$  NMR spectrum of **4** (nominally 2 mM in  $\text{CD}_3\text{CN}$ ).

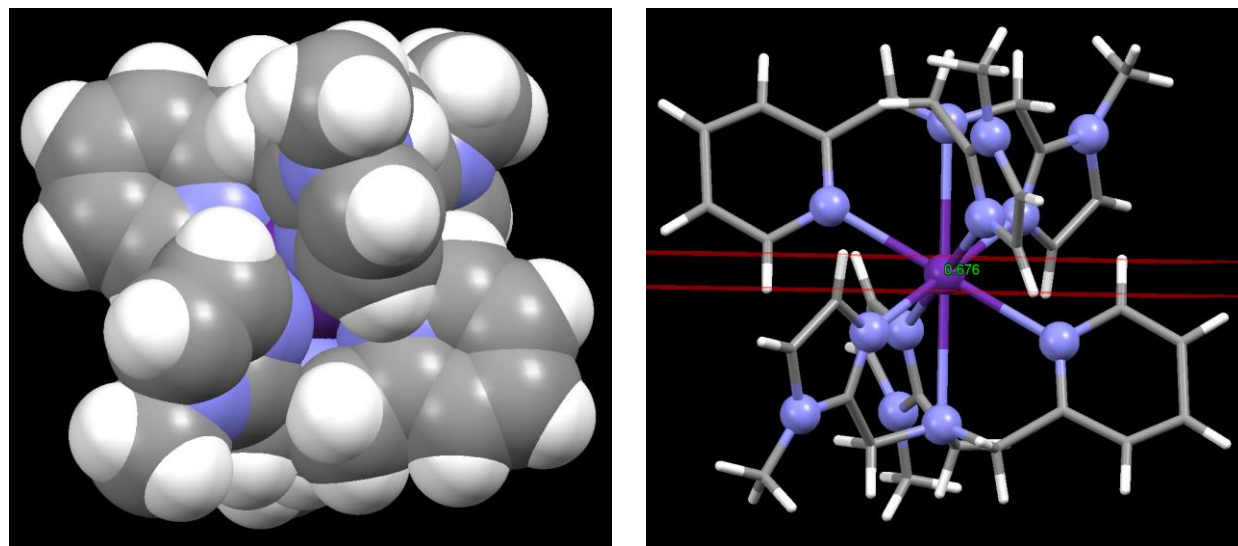


**Figure S9.** Highlights of methyl and methylene region of the  $^1\text{H}$  NMR spectrum of **5** (nominally 2 mM in  $\text{CD}_3\text{CN}$ ) as a function of temperature from -40 to 40  $^\circ\text{C}$ . In the inset, the  $\text{H}_e$  resonances are centered on the main peak to display the broadening to obscurity of the  $J(^{199}\text{Hg}-^1\text{H})$  satellites associated with the  $\text{H}_e$  resonance as the temperature is lowered while the line width of the main resonance is largely unaffected. Other than moderate broadening, changes in the rest spectrum were negligible (full spectrum at 20  $^\circ\text{C}$  is shown in Figure 4c of the manuscript).

**Table S5.** Vertical interligand distance between methine carbons & hydrogens adjacent to bound nitrogens in **1 - 5**

Ligand	Methine Carbon (Å)		Methine Hydrogen (Å) <sup>a</sup>	
	Cd(II)	Hg(II)	Cd(II)	Hg(II)
<b>L1</b>	1.221 <sup>b</sup>		-0.511 <sup>b</sup>	
<b>L2</b>	1.127 <sup>c</sup>	1.277 <sup>c</sup>	-0.676 <sup>c</sup>	-0.532 <sup>c</sup>
<b>L3</b>	0.967 <sup>b</sup>	1.229 <sup>c</sup>	-0.897 <sup>b</sup>	-0.597 <sup>c</sup>

<sup>a</sup> Negative values indicate vertical overlap; <sup>b</sup> 100 K structure; <sup>c</sup> 296 K structure



**Figure S10.** Figures highlighting the proximity of atoms at the ligand interface of **2**. The space filling diagram (left) depicts restrictions to rotation about the pseudo-three fold axis due to overlap in the van der Waals radii of methine carbons adjacent to metal-bound nitrogens. The ball and stick diagram (right) demonstrates significant overlap between planes calculated based on the positions of H<sub>a</sub> and H<sub>g</sub> in the separate ligands.

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