

New third-generation bis-, tris- and tetrakis(pyrazolyl)borate ligands with 3-pyridyl and 4-pyridyl substituents: synthesis and coordination chemistry

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Electronic Supporting Information

(Table S1 and Figures S1 – S6)

Table S1. Hydrogen bond details for 3-(3-pyridyl)pyrazole (two polymorphs) and 3-(4-pyridyl)pyrazole.^a

	N-H (Å)	(N)H...N (Å)	N...N (Å)	N-H...N (°)
3-(3-pyridyl)pyrazole polymorph I				
N10-H1...N2 ⁱ	1.19(3)	1.66(3)	2.840(3)	167(2)
3-(3-pyridyl)pyrazole polymorph II				
N2-H2...N108	0.94(2)	1.96(2)	2.892(3)	169(2)
N102-H102...N8 ⁱⁱ	1.00(2)	1.85(2)	2.852(3)	170(2)
3-(4-pyridyl)pyrazole				
N2-H2...N9 ⁱⁱⁱ	0.91(2)	2.04(2)	2.899(2)	158(2)

^a Symmetry operations: (i): x, y-1, z; (ii): x+1, y-1, z; (iii): x-1, 1/2-y, z+1/2.

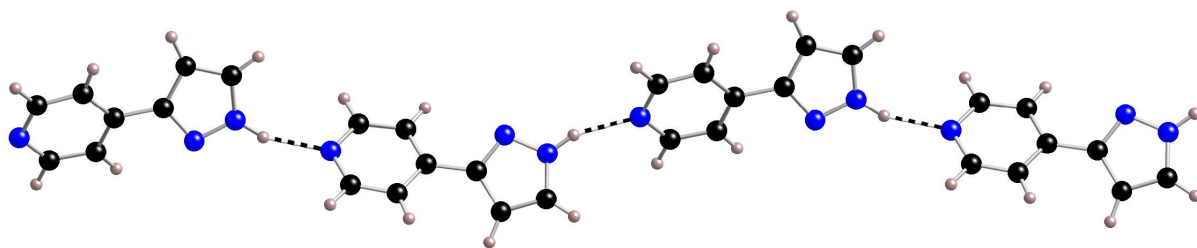


Figure S1. Hydrogen bonded chains in the structure of (a) 3-(4-pyridyl)pyrazole. Hydrogen bonds are shown by the striped bonds.

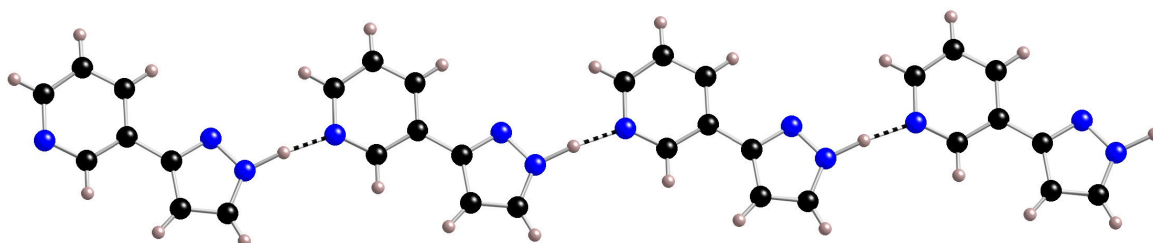


Figure S2. Hydrogen bonded chains in the structure of (a) 3-(3-pyridyl)pyrazole, polymorph I. Hydrogen bonds are shown by the striped bonds.

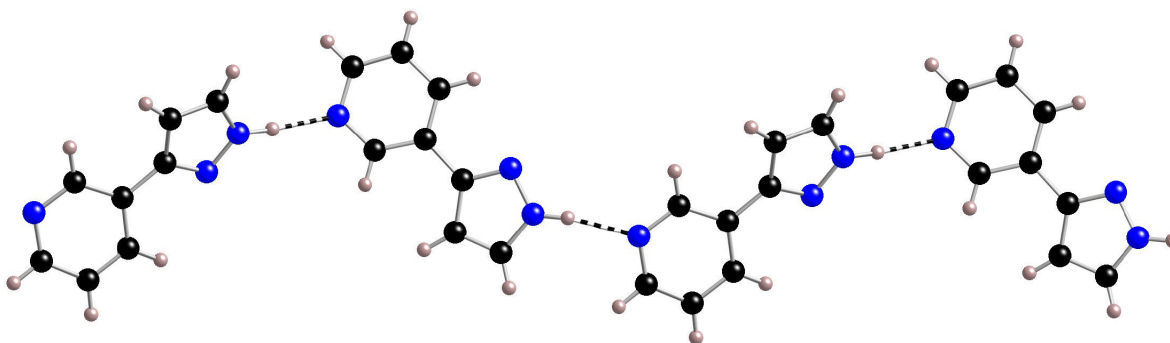
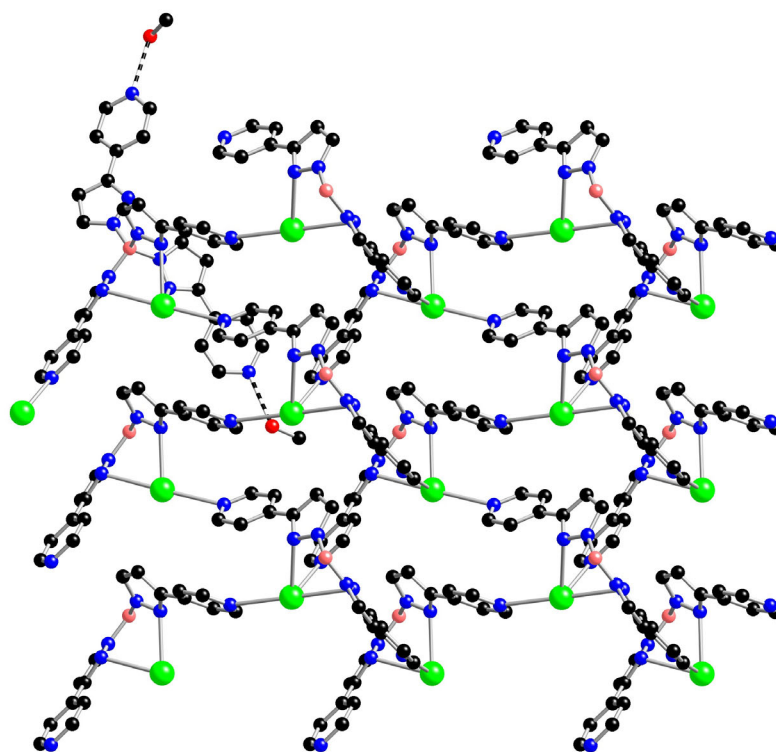
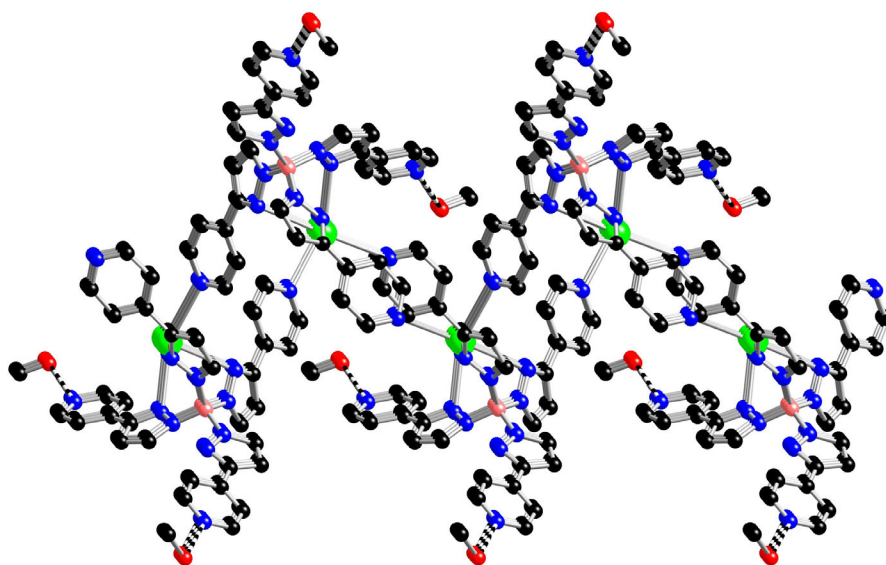


Figure S3. Hydrogen bonded chains in the structure of 3-(3-pyridyl)pyrazole, polymorph II. Hydrogen bonds are shown by the striped bonds.



(a)



(b)

Figure S4. (a) The 2D (4,4) sheet motif in the structure of $[\text{Tl}(\text{Tkp}^{4\text{py}})] \cdot 2\text{MeOH}$. For clarity, a complete $\text{Tkp}^{4\text{py}}$ ligand is shown only at top left (along with the corresponding hydrogen bonded methanol molecules); the rest of the sheet is represented only by the Tl atoms (green), the B atoms (pink), and the 4-pyridylpyrazolyl moieties which bridge the Tl atoms. (b) The same sheet viewed side-on, with all 4-pyridylpyrazolyl groups and methanol molecules shown. Hydrogen bonds are represented by the striped connections.

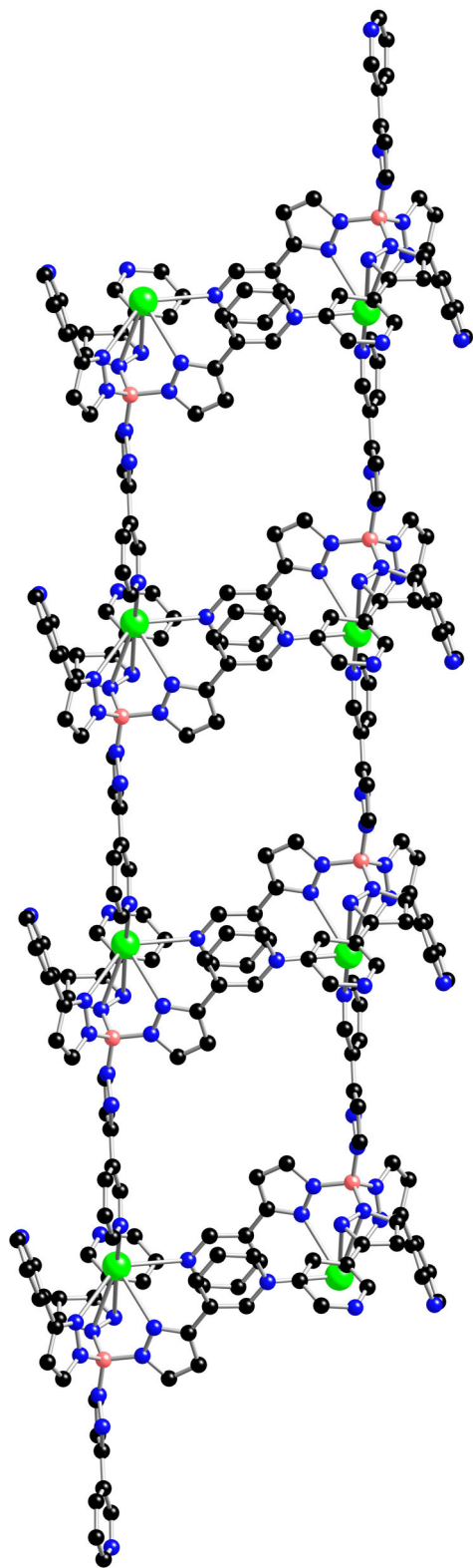


Figure S5. The ladder motif in the structure of $[\text{Tl}(\text{Tkp}^{3\text{py}})].\text{H}_2\text{O}$.

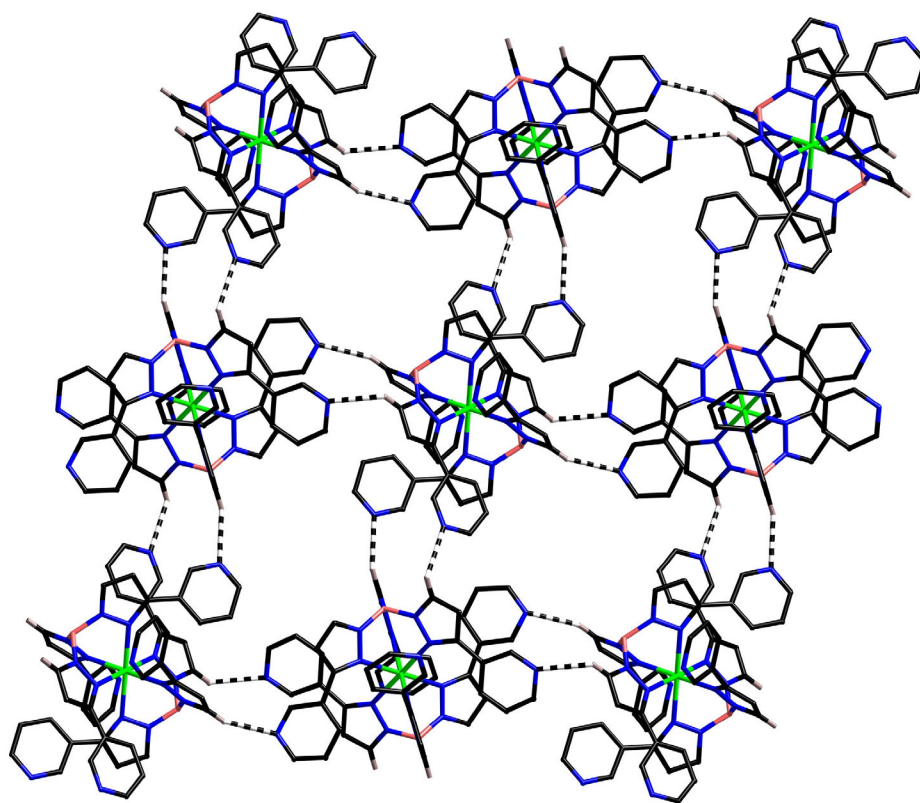


Figure S6. The 2D (4,4) sheet motif in the packing structure of $[\text{Ni}(\text{Tp}^{3\text{py}})_2]$, as defined by weak C-H...N interactions (striped bonds).