Supporting Information

Coordination preference of hexa(2-pyridyl)benzene with copper(II) directed by hydrogen bonding

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# Table of Contents

1. General Information .................................................................................. S3
2. PXRD data ................................................................................................. S4
3. NMR data .................................................................................................. S6
4. UV-Vis spectra ......................................................................................... S7
5. TGA data .................................................................................................. S8
6. X-ray Crystallographic Analysis ............................................................... S9
7. Reference ................................................................................................ S16
1. General Information

**Reagents.** 2-phenylpyridine, triphenylphosphine, potassium carbonate, 2-bromopyridine, copper(I) chloride and triethylamine were purchased from commercial sources and used as received without further purification. \([(\eta^6-C_6H_6)RuCl_2]_2\) was synthesized following the procedure described in literature.\(^1\) \(N\)-methyl-2-pyrrrolidone (NMP) was dried over molecular sieves (3 Å) prior to use. Tetrahydrofuran (THF) was distilled from sodium/benzophenone and stored over molecular sieves (3 Å) prior to use. Acetonitrile and \(d_3\)-acetonitrile were distilled from \(P_2O_5\) and stored over molecular sieves (4 Å) prior to use.

**Experiment equipment.** Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX spectrometer operating at 500 MHz and 125 MHz for \(^1H\) and \(^{13}C\) acquisitions, respectively. Elemental analysis (EA) for C, H, and N was conducted using Truspec Micro (Leco). Single crystal X-ray diffraction (SC-XRD) data were collected on a Bruker D8 VENTURE diffractometer equipped with graphite monochromated Mo Kα radiation (\(λ = 0.71073 \ \text{Å}\)) or synchrotron radiation of 2D-SMC at the Pohang Accelerator Laboratory (PAL, Korea) using an ADSC Quantum-210 detector furnished with a silicon (111) double crystal monochromator (DCM) at 100 K.

**X-Ray Crystallography.** Using Olex2, the structures were solved by ShelXT\(^3\) using Intrinsic Phasing and refined by ShelXTL\(^4\) using Least Squares minimization. For all four compounds, all the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added on their ideal positions.
2. PXRD data

(a) Simulated and as-synthesized PXRD patterns.

(b) PXRD patterns of a mixture, as-synthesized, 1, simulated, and 2, simulated.

(c) PXRD patterns of as-synthesized and 2, simulated.
Figure S1. PXRD patterns of the complex 1 (a), the mixture of 1 and 2 (b), 2 (c), 3 (d) and [4] (e).
3. NMR data

Figure S2. $^1$H NMR spectrum of hexa(2-pyridyl)benzene (2-HPB) in CD$_3$CN.

Figure S3. $^{13}$C NMR spectrum of hexa(2-pyridyl)benzene (2-HPB) in CD$_3$CN.
4. UV-VIS spectra

Figure S4. UV-Vis spectra of a 100 μM the complex 1 aqueous solution (a), a 100 μM 2 aqueous solution (b), 100 μM free ligand aqueous solution (2-HPB) (c) and the comparison of UV-Vis spectra (a) (blue), (b) (green) and (c) (gray) (d)
5. TGA data

Figure S5. TGA of (a) 1, (b) 2, (c) 3 and (d) 4.
6. X-ray Crystallographic Analysis

CCDC 1552123, 1552124, 1846816, and 1552125 contains the supplementary crystallographic data for 1, 2, 3, and 4 respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/cgibin/catreq.cgi (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CD21EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). For all six compounds, all the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added to their ideal positions.

**Figure S6.** ORTEP diagram of (A,B)(C,D)-trans-Cu₂Cl₄(H₂O)₂(2-HPB)∙4.75H₂O (1), ellipsoids are shown at 25% probability level.

**Figure S7.** ORTEP diagram of (A,B)(D,E)-trans-Cu₂Cl₄(H₂O)₂(2-HPB)∙5.5H₂O (2), ellipsoids are shown at 50% probability level.
Figure S8. ORTEP diagram of (A,B)(D,E)-trans-Cu₂Cl₄(MeOH)₂(2-HPB) (3), ellipsoids are shown at 50% probability level.

Figure S9. ORTEP diagram of [(A,B)(C,D)-trans-Cu₂Cl₄(2-HPB)·DMF]ₙ ([4]ₙ), ellipsoids are shown at 50% probability level.
Figure S10. Molecular structure of complexes 1 (a) side view, (b) top view and 2 (c) side view, (d) top view.
Figure S11. Optical microscope image of 1 (blue crystals) and 2 (green crystals). The crystals of 1 were added deliberately for comparison.

Figure S12. Details concerning angles and distances in 1, 2, 3 and 4.
Figure S13. The Cu$_2$Cl$_4$ cluster composed of [Cu$_2$(μ-Cl)$_2$] core and two chlorides in 4.

Figure S14. Perspective view of the packing in the crystal structure of 1. Ellipsoids are shown at 25% probability level. Hydrogen atoms and lattice solvent molecules are omitted for clarity. The hydrogen bonds are described as dotted lines.
Figure S15. Perspective view of the packing in the crystal structure of 2. Ellipsoids are shown at 25% probability level. Hydrogen atoms and lattice solvent molecules are omitted for clarity. The hydrogen bonds are described as dotted lines.

Figure S16. Perspective view of the packing in the crystal structure of 3. Ellipsoids are shown at 25% probability level. Hydrogen atoms and lattice solvent molecules are omitted for clarity. The hydrogen bonds are described as dotted lines.
Table S1. Hydrogen Bonding Contact Distances (Å) and Angles (°) in 1 and 2\textsuperscript{a}

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<th>1 (DH···A)</th>
<th>r(D···A) (Å)</th>
<th>r(H···A) (Å)</th>
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Reference


