Supporting Information

Static and dynamic coordination behaviours of copper(I) ions in hexa(2-pyridyl)benzene ligand systems

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1. General Information

**Chemical reagents.** 2-phenylpyridine, triphenylphosphine, potassium carbonate, 2-bromopyridine, 2-bromo-5-methylpyridine, copper(I) chloride and triethylamine were purchased from commercial sources and used as received without further purification. 5-methyl-2-phenylpyridine and \([\eta^6-C_6H_6]RuCl_2\) was synthesized following the procedure described in reference. N-methyl-2-pyrrolidone (NMP) was dried by molecular sieves (3 Å) prior to use. Tetrahydrofuran (THF) was distilled over sodium benzophenone and stored in molecular sieves (3 Å) prior to use. Acetonitrile and d<sub>3</sub>-acetonitrile were distilled over P<sub>2</sub>O<sub>5</sub> and stored in 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 <sup>1</sup>H and <sup>13</sup>C acquisitions, respectively. Elemental analysis (EA) for C, H, and N were 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 Å) and Cu Kα radiation (λ = 1.54178 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 Olex<sup>3</sup>, the structure was solved by ShelXT<sup>4</sup> using Intrinsic Phasing and refined by ShelXTL<sup>5</sup> using Least Squares minimization. Crystal data and experimental details are listed in Table 1.

**Sample Preparation for <sup>1</sup>H VT NMR and 2D EXSY Experiment of 2a.** A saturated solution of complex 2a was prepared by stirring 2.0 mg of the complex in 1 mL of CD<sub>3</sub>CN and filtered. The solution was loaded in a screw-cap NMR tube.

**Sample Preparation for <sup>1</sup>H VT NMR and 2D EXSY Experiment of 1 and 2b.** The nmr sample of 1 was prepared by loading 1.0 mg of complex 1 with 500 μL of CD<sub>3</sub>CN in a screw-cap NMR tube. The NMR sample of 2b was prepared by loading 1.0 mg of complex 1 with 500 μL of CD<sub>3</sub>CN in a screw-cap NMR tube.
2. PXRD data

Figure S1. PXRD patterns of \([L_{12}Cu_4Cl_4]_n\) (3) (a), \([L_MCu_4Cl_4(CH_3CN)]_n\) (4) (b) and \([L_MCu_4Cl_4\cdot THF]_n\) (5) (c).
3. NMR data

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

Figure S3. $^{13}$C NMR spectrum of hexa(2-pyridyl)benzene ($L_H$) in CD$_3$CN.
Figure S4. $^1$H NMR spectrum of hexa(2-(5-methylpyridyl))benzene ($L_M$) in CD$_3$CN.

Figure S5. $^{13}$C NMR spectrum of hexa(2-(5-methylpyridyl))benzene ($L_M$) in CD$_3$CN.
**Figure S6.** $^1$H NMR spectrum of $L_M$CuCl(CH$_3$CN) (1) in CD$_3$CN at 298K.

**Figure S7.** $^1$H NMR spectrum of $L_M$CuCl(CH$_3$CN) (1) in CD$_3$CN at 223K.
**Figure S8.** $^{13}$C NMR spectrum of $L_M$CuCl(CH$_3$CN) (1) in CD$_3$CN at 298K.

**Figure S9.** $^1$H NMR spectrum of $L_H$Cu$_2$Cl$_2$(CH$_3$CN)$_2$ (2a) in CD$_3$CN at 298K.
Figure S10. $^1$H NMR spectrum of $L_{\text{H}}\text{Cu}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$ (2a) in CD$_3$CN at 223K.

Figure S11. $^1$H NMR spectrum of $L_{\text{M}}\text{Cu}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$ (2b) in CD$_3$CN at 298K.
Figure S12. $^1$H NMR spectrum of $L_M Cu_2 Cl_2 (CH_3 CN)_2$ (2b) in CD$_3$CN at 223K.

Figure S13. $^{13}$C NMR spectrum of $L_M Cu_2 Cl_2 (CH_3 CN)_2$ (2b) in CD$_3$CN at 298K.
Figure S14. $^1$H 2D EXSY of complex 2a in CD$_3$CN at 233K. ($\tau = 0.3$ sec)

Figure S15. $^1$H 2D EXSY of complex 2b in CD$_3$CN at 223K. ($\tau = 0.2$ sec)
4. Analysis of $^1$H NMR studies of 1 and 2b

Solution Behaviours of 2b At 298K, in the $^1$H NMR spectra of 2b, only three signals at 8.08, 7.15, and 6.89 ppm at the arene region and one signal at 2.11 ppm for methyl groups were observed. The coalescence of the signal was achieved at 253K. At 223K, an almost complete peak splitting was observed. In Figure S16, all signals at the arene region are consistent with the structure obtained from single crystal x-ray diffraction ($H_{1b}$ for the protons in pyridine binding with copper and $H_{n}$ for the protons in non-coordinating pyridine, $n = 1 - 3$). The peak splitting in $H_{1b}$ and $H_{3b}$ can be explained by different moieties given by the non-coordinating pyridine. In Figure S15, we can observe the cross peaks between $H_{1b}$, $H_{1n}$, $H_{2b}$-$H_{2n}$, and $H_{3b}$-$H_{3n}$. Also, cross peaks between the major peaks and the peaks of the intermediate are observed as well. From the 1D and 2D $^1$H NMR spectra of 2b, it is obvious that complex 2b remains in the solution as a major compound and there is an intermediate in the course of dynamic process.

![Diagram](image)

Figure S16. $^1$H VT-NMR spectra of complex 2b in CD$_3$CN.
At 298K, in the $^1$H NMR spectra of 1, only three signals at 8.03, 7.13 and 6.88 ppm at arene region and one signal at 2.10 ppm for methyl groups were observed. These signals are shifted to the upfield compare to the signals of 2b and downfield compare to the signals of the ligand. In Figure S17, the coalescence of the signal was achieved around 233K. At 223K, the peak splitting was not completed showing different pattern compare to 2b. Further analysis was unsuccessful due to poor resolution. Nevertheless, it is obvious that complex 1 remains in the solution in a distinctive relation to 2b.

Figure S17. $^1$H VT-NMR spectra of complex 1 in CD$_3$CN.

Figure S18. (a) $^1$H NMR spectra of the solution of the complex 2a and the solutions with 1, 3, 6 equivalent of CuCl in the CD$_3$CN solution at 233K. (b) $^1$H NMR spectra of the CD$_3$CN solution of the complex 1 and 2b at 233K.
5. Rate constant calculations and Eyring plot of a dynamic behaviour of 2a

Since the 1st signal at 8.3 ppm didn’t fully merged in a practicable temperature range, it was unfeasible to measure a rate constant of each sample by a line shape analysis. Instead, the rate constants at a specific temperature was measured from $^1$H 2D EXSY. The rate constants, $k_{\text{obs}}$, can be deduced from the spectrum according to the following equation:

$$ M = \exp(R/t_m)M_0 $$

[1]

Where $M$ is a matrix whose components are the integrated intensity of the signals in 2D EXSY spectra, $M_0$ is a diagonal matrix representing the EXSY spectra acquired with a mixing time ($t_m$) of zero, can be alternatively obtained from the signal intensities of 1D spectrum of the fully relaxed system. A matrix $R$ is our aim of the calculation to derive exchange and relaxation rate constants.

For the case without cross relaxation, $R$ has the form

$$ R = \begin{bmatrix}
-\frac{1}{T_{11}} - k_{12} & \cdots & k_{1n} \\
 0 & -\frac{1}{T_{21}} & \cdots & k_{2n} \\
 \vdots & \vdots & \ddots & \vdots \\
 k_{n1} & 0 & \cdots & -\frac{1}{T_{nn}} - k_{nn}
\end{bmatrix} $$

[2]

The kinetic constant for this motion is deduced from the $H_1$-$H_5$ signal in 2D EXSY because the signals of this hydrogen atom show large separation and are simpler than other signals to integrate.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$k_{+}$ (s$^{-1}$)</th>
<th>$k_{-}$ (s$^{-1}$)</th>
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Table S1. The calculated rate constant of the exchange process of 2a in CD$_3$CN (500 µM).

![Eyring plot analysis and thermodynamic parameters of the exchange process of 2a in CD$_3$CN (500 µM).](image)

Figure S19. Eyring plot analysis and thermodynamic parameters of the exchange process of 2a in CD$_3$CN (500 µM). The upper and lower lines represent the error bands of the linear regression with a 95% confidence level.
6. Photoluminescence spectra of 3, 4 and 5

Figure S20. Solid state emission spectra of 3 (a), 4 (b) and 5 (c). (\(\lambda_{\text{exc}} = 380\) nm) Optical and luminescence photographs of 3, 4 and 5 (d).
6. Structural Analysis by X-ray Crystallography

CCDC 1828474, 1552119, 1828475, 1828476, 1828477, and 1828478 contains the supplementary crystallographic data for 1, 2a, 2b, 3, 4 and 5 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 S21. ORTEP diagram of $L_M$CuCl(CH$_3$CN) (1), Ellipsoids are shown at 25% probability level.

Figure S22. ORTEP diagram of $L_H$Cu$_2$Cl$_2$(CH$_3$CN)$_2$ (2a), Ellipsoids are shown at 50% probability level.
Figure S23. ORTEP diagram of $\text{L}_\text{M} \text{Cu}_2\text{Cl}_2(\text{CH}_3\text{CN})_2$ (2b), Ellipsoids are shown at 50% probability level.

Figure S24. ORTEP diagram of $[\text{L}_\text{H} \text{Cu}_4\text{Cl}_4]_n$ (3), Ellipsoids are shown at 50% probability
Figure S25. ORTEP diagram of $[\text{L}_n\text{Cu}_4\text{Cl}_4(\text{CH}_3\text{CN})]_n(\text{CH}_3\text{CN})_n(4)$, Ellipsoids are shown at 25% probability level.
Figure S26. ORTEP diagram of \([\text{L}_4\text{Cu}_4\text{Cl}_4]_n(\text{THF})_n\) (5), Ellipsoids are shown at 50% probability level.

Crystal data information of 5 (output.cif)

```
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Table 1: Detailed informations about angles and distances of 1, 2a and 2b.

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<th>$D_{a1}$</th>
<th>$D_{a2}$</th>
<th>$\angle_{Cu-N-C}$</th>
<th>$\angle_1$</th>
<th>$\angle_2$</th>
<th>$\angle_3$</th>
<th>$\angle_4$</th>
<th>$\angle_5$</th>
<th>$\angle_6$</th>
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</thead>
<tbody>
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</tbody>
</table>

* $D_h$: Height of the copper atom from the plane of the central benzene
* $D_{a1}$: Distance between the plane of the central arene and the nitrogen in acetonitrile
* $D_{a2}$: Distance between the plane of the central arene and the $sp^3$ carbon in acetonitrile
* $\angle_{Cu-N-C}$: angle between $Cu-sp^3-N-sp^3$ C
* $\angle_1$: angle between the plane of $n$th pyridine and the plane of central benzene
* $\angle_{av}$: average angle of $\angle_1-\angle_6$

**Figure S27.** Detailed informations about angles and distances of 1, 2a and 2b.

**Figure S28.** Detailed informations about the distances between $sp$ carbon in acetonitrile and carbons in central arene in 1 (a), 2a (b) and 2b (c).
Figure S29. Detailed information about the distances between atoms in Cu₄Cl₄ clusters of 3 (a), 4 (b) and 5 (c).

Figure S30. Perspective view for the packing structure of [LiCu₄Cl₄]ₙ (3), Ellipsoids are shown at 50% probability level.
**Figure S31.** Perspective view for the packing structure of $[{\text{L}}_4\text{Mh}_{4}\text{Cl}_4(\text{CH}_3\text{CN})_n(\text{CH}_3\text{CN})_n$ (4), Ellipsoids are shown at 50% probability level. The lattice solvent molecules are omitted in (a) and (c).

**Figure S32.** Perspective view for the packing structure of $[{\text{L}}_4\text{Mh}_{4}\text{Cl}_4]_n(\text{THF})_n$ (5), Ellipsoids are shown at 50% probability level. The lattice solvent molecules are omitted in (a) and (c).
Reference