Supplementary Information

pH-induced formation of metalloligand: increasing structure dimensionality by tuning number of ligand functional sites

Wen-Xiu Ni, Mian Li, Xiao-Ping Zhou, Zhen Li, Xiao-Chun Huang and Dan Li*
Department of Chemistry, Shantou University, Shantou, Guangdong, 515063, P. R. China
Fax: (+86)-754-2902767 Email: dli@stu.edu.cn

Synthetic Procedures

4-pyridinecarbaldehyde isonicotinoyl hydrazone (4-Hpcih)

4-pyridinecarboxaldehyde (2.14 g, 20 mmol) was added to isonicotinic acid hydrazide (2.74g, 20mmol) in ethanol (50mL) with stirring. The mixture was refluxed for 6 hours with vigorous stirring. The resulting solution was concentrated, and then cooled to collect a white precipitate by filtration. A white powder was obtained after being washed with ethanol and dried in air (yield 90%). Mp: 246-247 °C, Anal. Found: C, 63.78; H, 4.48; N, 24.74. Calc. for $C_{12}H_{10}N_4O$: C, 63.71; H, 4.46; N, 24.76. IR (KBr pellet, cm^{-1}): 3448s, 3189m, 3006s, 2842w, 1688s, 1602w, 1569s, 1493w, 1416s, 1362m, 1333m, 1286s, 1221w, 1150s, 1060m, 1000w, 925m, 828s, 743m.

4-Hpcih (0.046g, 0.2mmol) in 8 mL MeCN were sealed in a 15-mL Teflon-lined stainless steel reactor, and then heated in an oven to 120°C for 72h. After the sample was slowly cooled to room temperature at a rate of $3°C·h^{-1}$, colorless block crystals were collected, which were suitable for X-ray Crystallography.

$[Cu_2(CN)_2(4\text{-Hpcih})]_n$, 1

A mixture of CuCN (0.018g, 0.2mmol), ligand 4-Hpcih (0.023g, 0.1mmol) in the ratio 2:1 in 8mL MeCN, which the pH was adjusted to 0.08 by addition of small amounts of standard 0.1 M H_2SO_4. The mixture was stirred for 15min and then transferred and sealed in a 15-mL Teflon-lined stainless steel reactor, heated in an oven to 120°C for 72h. After the sample was slowly cooled to room temperature at a rate of $3°C·h^{-1}$, orange column crystals were collected and dried in air (yield 37%). Anal. Calcd for $C_{28}H_{20}Cu_4N_{12}O_2$: C, 41.48; H, 2.49; N, 20.73. Found: C, 41.45; H, 2.50; N, 20.70. IR (KBr, cm^{-1}) for **1**: 3443s, 3029m, 2924w, 2130m, 2109s, 1670w, 1650s, 1566s, 1550m, 1488w, 1417m, 1370m, 1310s, 1158w, 1093s, 1009m, 929m, 843m, 755w.

$\{[Cu_2(CN)_{1.5}(4\text{-pcih})]\cdot 1.25H_2O\}_n$, 2

A mixture of CuCN (0.018g, 0.2mmol), ligand 4-Hpcih (0.023g, 0.1mmol) in the ratio 2:1 in 8mL MeCN (pH= 6.34) was stirred for 15min and then transferred and sealed in a 15-mL Teflon-lined stainless steel reactor, which was heated in an oven to 120°C for 72h, and then cooled to room temperature at a rate of $3°C·h^{-1}$. X-ray-quality black block crystals of compound **2** were obtained in ca. 20% yield. Anal. Calcd for $C_{27.5}H_{17.5}Cu_4N_{11.5}O_2$: C, 41.54; H, 2.22; N, 20.26. Found: C, 41.59; H, 2.20; N, 20.21. IR (KBr, cm^{-1}) for **2**: 3434s, 2923m, 2117s, 1681w, 1614s, 1566m, 1539w, 1492s, 1455w, 1384m, 1368m, 1315w, 1234w, 1027s, 848w, 810m.

The pH values in the syntheses of compounds **1** and **2** need not be very precise, but the procedures reported in this presentation are suitable for the formation of good-quality crystals.

X-ray Crystallography

Single-crystal X-ray diffraction data collection for **4-Hpcih**, **1** and **2** was performed on a Bruker Smart Apex CCD diffractometer (MoKα radiation, λ = 0.71073 Å) by using frames of 0.38 oscillation ($4.56 < 2\theta < 50°$). The structures were solved by direct methods, and all non hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares methods on F^2 by using the SHELXTL program. All hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters. The hydrogen atoms of the water molecules were located from the difference Fourier map and refined isotropically. The bridge C/N atoms of CN^- in **1** and **2** asymmetric unit are undistinguished, and were assigned randomly as C or N atom, but the terminal C/N atoms were refined with a 50% probability of being C or N labeled C/N. The asymmetric unit of **2** contains solvent water molecules in the lattice and they were disordered by translation over three sites, having site occupancy factors of 0.5, 0.5 and 0.25, respectively.

X-ray structure of 4-pyridinecarbaldehyde isonicotinoyl hydrazone

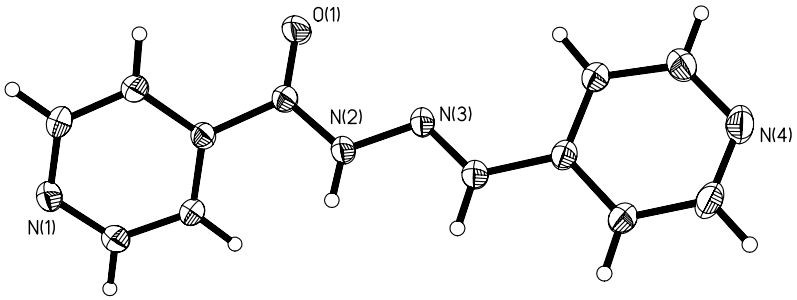

Fig. S1 XP drawing of 4-Hpcih with the thermal ellipsoids drawn of the 30% probability level, shown with the labeling scheme.

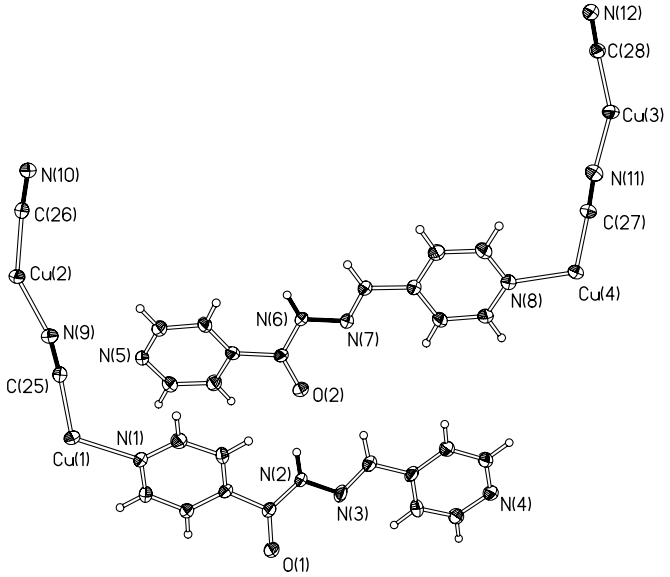

Fig. S2 XP drawing of complex **1** with the thermal ellipsoids drawn of the 30% probability level, shown with the labeling scheme.

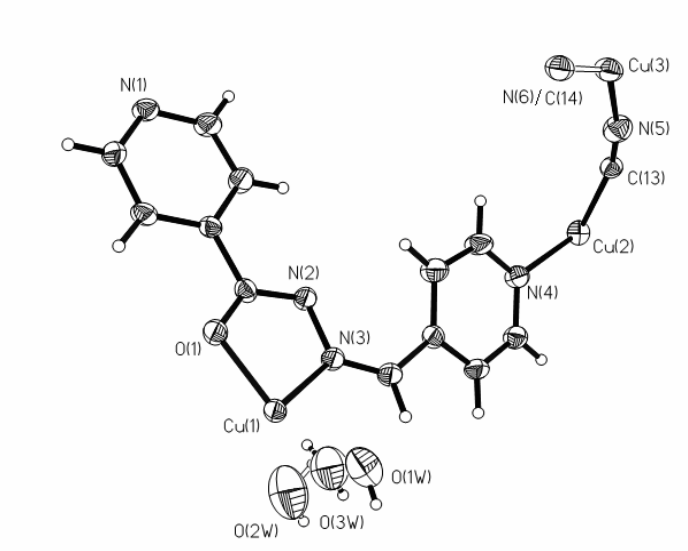

Fig. S3 XP drawing of the asymmetric unit of complex **2** with the thermal ellipsoids drawn of the 30% probability level, shown with the labeling scheme.

The asymmetric unit of **2** consists of three crystallographically independent copper atoms, one and a half cyanides, one deprotonated ligand (4-pcih) and water molecules as indicated in Figure S3.

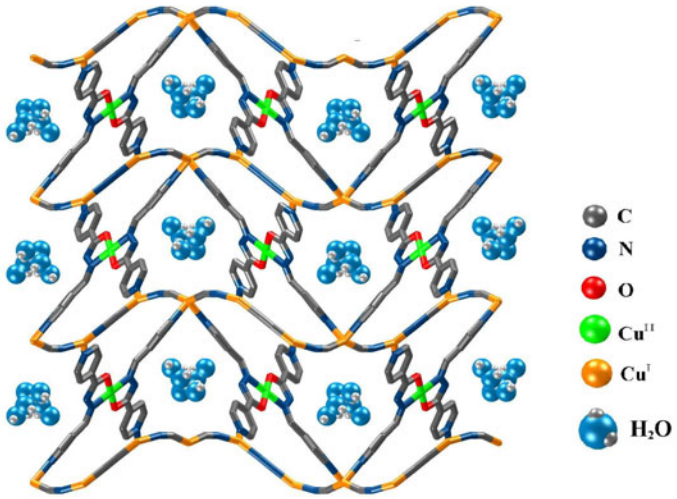

Fig. S4 The structure of complex **2** filled with the water molecules, all hydrogen atoms of ligands are omitted for clarity.