Coordination Polymers

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Cu^{2+}-Mediated Dehydrogenative Coupling and Hydroxylation of an N-Heterocyclic Ligand: From Generation of a New Tetratopic Ligand to the Designed Assembly of Three-Dimensional Copper(I) Coordination Polymers**

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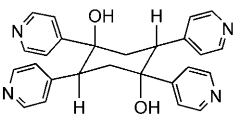
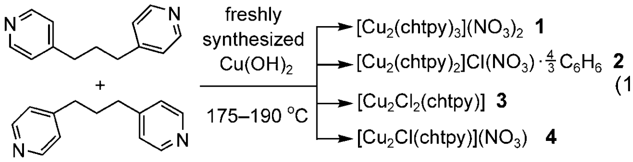
Great interest has been focused on the rapidly expanding field of crystal engineering of two- (2D) and three-dimensional (3D) coordination polymers due to their structural and topological diversity as well as their potential application as functional materials.[1] The main strategy popularly used in this area is a building-block approach,[2] and much effort has been made towards the connection of suitable, predetermined building blocks into networks in order to obtain the desired materials. In this regard, the development of new multitopic building blocks is one of the central tasks. Recently, we have been investigating a few in situ metal/organic reactions such as ligand oxidative coupling, hydrolysis, and substitution by hydrothermal methods,[3] which provide an intriguing pathway for generating new, functional building blocks and coordination polymers. In particular, we have isolated and structurally characterized covalent hydrates of N-heterocyclic ligands in delocalized mixed-valence Cu^I–Cu^{II} complexes, which are not only an important bridge between coordination chemistry and organic heterocyclic chemistry, but can also be successfully applied to the assembly of functional molecular solids.[3a,b] Following our recent report on the in situ metal/ligand redox reaction, in this communication we report a new Cu^{2+}-mediated dehydrogenative coupling and hydroxylation of an N-heterocyclic ligand (chtpy) in four Cu^I coordination polymers, namely $[Cu_2(chtpy)_3](NO_3)_2$ (**1**), $[Cu_2(chtpy)_2]Cl(NO_3)\cdot\frac{4}{3}C_6H_6$ (**2**), $[Cu_2Cl_2(chtpy)]$ (**3**), and $[Cu_2Cl(chtpy)](NO_3)$ (**4**; chtpy = *a*,*a*-1,4-dihydroxy-*e*,*e*,*e*,*e*-1,2,4,5-tetra(4-pyridyl)cyclohexane). This is the first time that simultaneous dehydrogenative coupling and hydroxylation of an N-heterocyclic ligand has been observed to generate a new, potentially tetratopic, coplanar ligand in situ.



chtpy

Pale-yellow or reddish crystals of **1**–**4** (ca. 18–35% yield) were obtained from the in situ hydrothermal treatment of $Cu(OH)_2$ (freshly synthesized from $Cu(NO_3)_2\cdot 3H_2O$ and NaOH) with 1,3-bis(4-pyridyl)propane (bpp), 1,4-cyclohexanedicarboxylic acid, and water in dilute HCl at 175–190°C [Equation (1)]. The component diversification of the resulting Cu^I–chtpy nets can be controlled simply by tuning the molar ratio of the starting materials. Elemental analysis and PXRD (Figure S1 in the Supporting Information) confirmed the phase purity of the bulk materials. Compounds **1**–**4** are air-stable and insoluble in water and most organic solvents.



(1)

One of the most intriguing features regarding the synthesis is the direct observation of dehydrogenative coupling and hydroxylation of 1,3-bis(4-pyridyl)propane mediated by Cu^{2+}. It has been reported previously that dehydrogenative coupling of phenanthroline and 2,2′-bipyridine under hydrothermal conditions leads to two functional tetradentate ligands—biphenanthroline and quaterpyridine, respectively—that are difficult to obtain by common organic reactions.[4] Moreover, hydroxylation of N-heterocyclic ligands such as phenanthroline and 2,2′-bipyridine is now well understood and can be easily carried out under hydrothermal conditions.[3a,b] However, to the best of our knowl-

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edge, the simultaneous dehydrogenative coupling and hydroxylation of an N-heterocyclic ligand is unprecedented.[5] The cyclohexane analogue having both hydroxyl and pyridyl substituent groups that is generated in situ may act as an important organic intermediate. Other interesting cases concerning tetradentate ligands generated in situ have been found in the reaction of silver(I) with 1,2-di(4-pyridyl)ethene,[6a] a template-directed solid-state [2+2] photodimerization of 4-chlororesorcinol with *trans*-1-(2-pyridyl)-2-(4-pyridyl)-ethylene,[6b] and the hydrothermal reaction of $Cd_{10}S_4(SPh)_{12}$ with 4,4′-trimethylenedipyridine and Na_2SO_4.[6c]

An X-ray crystallographic study[7] revealed unequivocally that a six-membered ring is formed by C–C coupling between four of the carbon atoms of each pair of bpp ligands in **1**–**4**. The six C−C bond distances of the ring fall in the range 1.503(8)–1.562(8) Å for **1**, 1.542(7)–1.552(5) Å for **2**, 1.491(9)–1.517(10) Å for **3**, and 1.536(3)–1.553(6) Å for **4**, characteristic of C−C single bonds.[8] Moreover, two hydroxy groups are also formed at the carbon atoms linking the pyridyl groups, with C−O bond lengths of 1.441(9)–1.458(8) Å for **1**, 1.437(11) Å for **2**, 1.466(10)–1.451(10) Å for **3**, and 1.423(4) Å for **4**, which are typical of a C−O single bond. Each cyclohexyl ring of the chtpy ligands in **1**–**4** adopts a chair conformation, with the four pyridyl groups located at the equatorial positions and the two hydroxy groups at the axial positions.

The structure of $[Cu_2(chtpy)_3](NO_3)_2$ (**1**) contains one crystallographically unique tetrahedral Cu^I atom, which lies on a general position, three unique L ligands, all of which lie across inversion centers, and one unique, uncoordinated nitrate counteranion. Two of the unique L ligands act as bidentate bridges between the copper atoms (Cu−N = 2.037(4) and 2.077(5) Å) by coordinating through their pyridyl groups *trans* to each other across the central six-membered ring; the other pyridyl groups are not coordinated. The third type of ligand acts as a tetradentate bridge (Cu−N = 2.050(5) and 2.054(4) Å) and coordinates through all four pyridyl groups (Figure 1 a).

The ligands bridge the copper atoms to form three identical, interpenetrating 3D networks. The network topology can be simplified by considering just the tetrahedral copper atoms and the tetradentate ligands (represented by a square-planar node); the bidentate ligands can be represented simply as links between the copper nodes. The resulting net is shown in Figure 1 b, and has the moganite topology,[9] which is a rare four-connected net with tetrahedral and square-planar nodes in the ratio 2:1. A topological analysis of this net was performed with OLEX.[10] The long topological (O'Keeffe) vertex symbol is $4.8_6.6.6.6.6$ for the Cu node, and $4.4.6_2.6_2.8_2.8_2$ for the chtpy node, which gives the short vertex symbol $(4^2.6^2.8^2)(4.6^4.8)_2$. The three interpenetrating networks are shown in Figure 1 c. We are aware of only three examples of coordination polymers with this topology: the structures of $Cd(CN)_2(H_2O)_{2/3}\cdot t$BuOH and $[Cu_3(pytac)_6]\cdot 14\,H_2O$ (pytac = 2-(4-pyridyl)thiazole-4-carboxylate) contain a single moganite network,[11a,b] while the structure of $[Cu_2(TCNB)_3](PF_6)_2$ (TCNB = 1,2,4,5-tetracyanobenzene) contains two interpenetrating moganite nets.[11c] This structure is particularly relevant as, like the structure of **1**, it contains tetrahedral Cu^I atoms bridged by potential tetradentate ligands, only one-third of which are actually tetradentate and act as square-planar nodes, while the other two-thirds are simply bidentate.

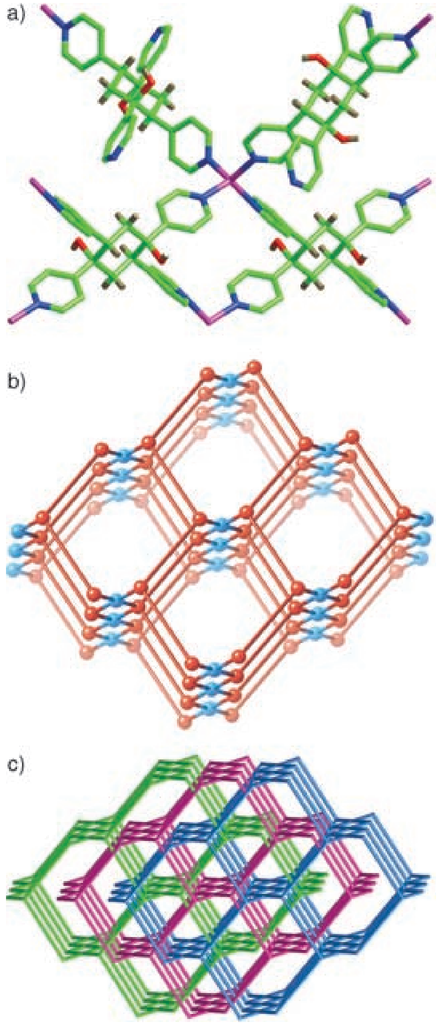

Figure 1. a) Local geometry in the structure of **1**. Each Cu^I center bonds to two crystallographically distinct bidentate ligands (top) and two symmetry-related tetradentate ligands (bottom). For clarity, pyridyl hydrogen atoms and nitrate counterions are not shown; pink Cu, blue N, red O, green C, gray H. b) The moganite topology of the 3D, four-connected nets in the structure of **1**. The red spheres represent copper atoms, while the blue spheres represent the tetradentate ligands. The bidentate ligands are represented by Cu⋯Cu links. c) The three interpenetrating moganite nets in the structure of **1**.

The nitrate anions, although uncoordinated, actually link the three interpenetrating networks together by hydrogen-bonding interactions between one of their oxygen atoms (O5) and the three different types of ligand hydroxide groups—one from each net for each nitrate anion ((O)H⋯O5 = 1.635(4), 1.871(5), and 1.865(6) Å, respectively). One of the hydroxide groups in fact participates in a bifurcated hydrogen bond and interacts with a second oxygen on the same nitrate anion ((O3)H3A⋯O6 = 2.140(5) Å).

The structure of **2** reveals an interesting porous 3D framework with the asymmetric unit consisting of one crystallographically unique tetrahedral Cu^I atom, which lies on a special position, one-quarter of a chtpy ligand with the hydroxy groups showing twofold disorder, one-sixth of a benzene guest molecule, and disordered uncoordinated nitrate and Cl^- counteranions, each with one-eighth occupancy. Each chtpy ligand acts as a tetradentate bridge (Cu–N = 2.025(3) Å) and coordinates through all four pyridyl groups (Figure 2 a).

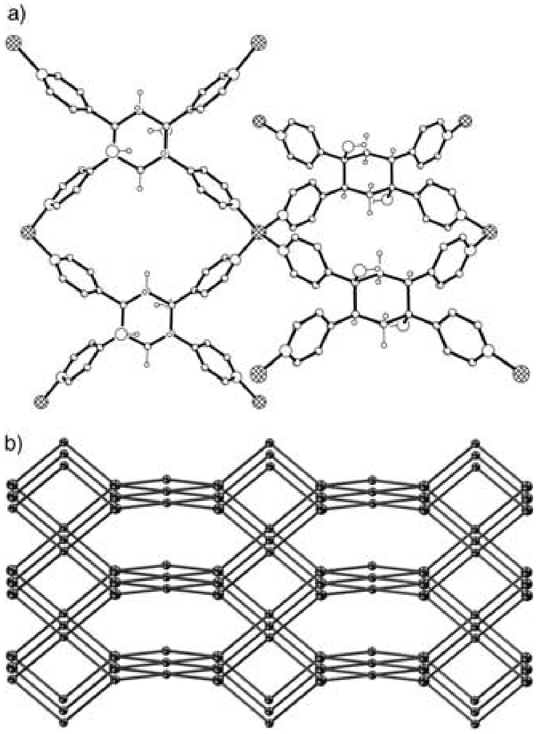

Figure 2. a) Local geometry in the structure of **2**. For clarity, pyridyl hydrogen atoms and counterions are not shown. b) The PtS topology of the 3D, four-connected, noninterpenetrating net in the structure of **2**.

The planar tetratopic chtpy ligands bridge the copper atoms into a noninterpenetrating 3D network. By considering just the copper atoms and the tetradentate ligands as tetrahedral and square-planar nodes, respectively, **2** can be defined as a rare four-connected net with tetrahedral and square-planar nodes in the ratio 1:1. The long topological (O'Keeffe) vertex symbol is $4.4.8_7.8_7.8_7.8_7$ for the Cu node and $4.4.8_2.8_2.8_8.8_8$ for the chtpy node, thus giving a short vertex symbol $4^2.8^4$, which is that of the PtS topology,[9] as shown in Figure 2 b. It is worth noting that there are 3D channels running along the *a*-, *b*-, and *c*-axes in the cationic net structure of **2**, as shown in Figure 2 b. An analysis using PLATON[12] suggested that the channels occupy 58.2 % of the crystal volume. The guest benzene molecules and disordered NO_3^- and Cl^- counteranions are located within these channels. The calculated crystal density (in the presence of guest and the disordered counterions) of 0.914 $g\,cm^{-3}$ is comparable to those found for some porous metal–polycarboxylate coordination materials.[1c]

Compound **3** consists of 2D coordination polymer sheets with the asymmetric unit containing one crystallographically unique Cu^I atom, which lies on a general position, one unique chtpy ligand, which lies across an inversion center, and one unique Cl^- counteranion. Each Cu atom is coordinated in a trigonal geometry by two pyridyl N atoms and one Cl atom (Cu–N = 1.978(5) and 1.993(5) Å; Cu–Cl = 2.167(2) Å; N–Cu–N/Cl = 113.9(2)–125.30(16)°). Each chtpy ligand acts as a tetradentate bridge to connect the CuCl motifs into a 2D (4,4) net (Figure 3). Adjacent (4,4) nets are each twofold interpenetrating in a diagonal/diagonal inclined fashion.[13]

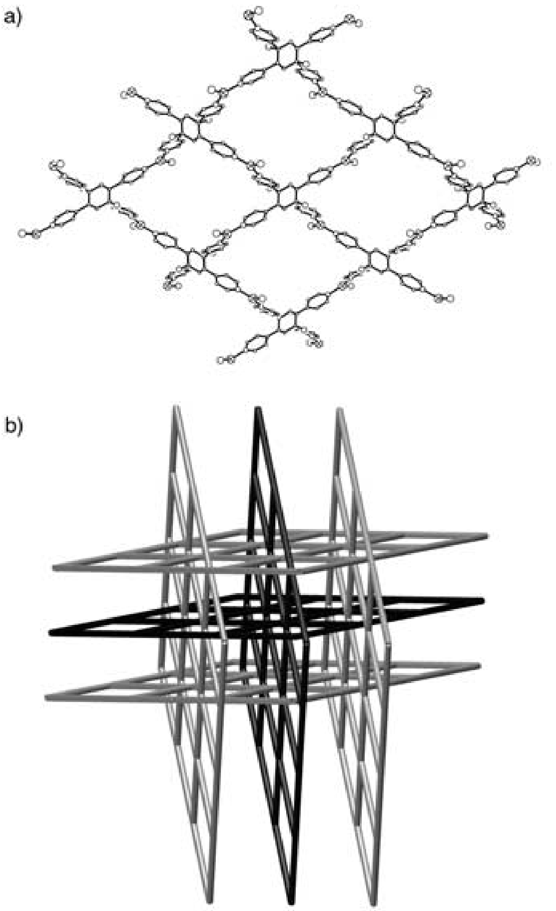

Figure 3. a) The 2D (4,4) coordination layer in the structure of **3**. b) The twofold interpenetrating 2D (4,4) nets in the structure of **3**.

Compound **4** is a 3D coordination network with the asymmetric unit consisting of one crystallographically unique tetrahedral Cu^I atom, which lies on a special position, one unique chtpy ligand, which lies across a fourfold axis, and one unique Cl^- atom and an uncoordinated nitrate, both of which lie on special positions. Similar to those in **3**, each Cu atom is coordinated in a Y-shaped geometry by two pyridyl N atoms and one Cl atom (Cu–N = 1.917(2) Å; Cu–Cl = 2.4802(7) Å; N–Cu–N/Cl = 101.99(8) and 156.01(17)°). Each chtpy ligand acts as a tetradentate bridge to connect the CuCl motifs into a 2D coordination layer of a (4,4) net (Figure 4 a). The most interesting structural feature is that adjacent (4,4) nets are covalently connected by sharing the linear μ_2-Cl bridges, thereby generating two identical, interpenetrating 3D networks. The network topology can be simplified by considering

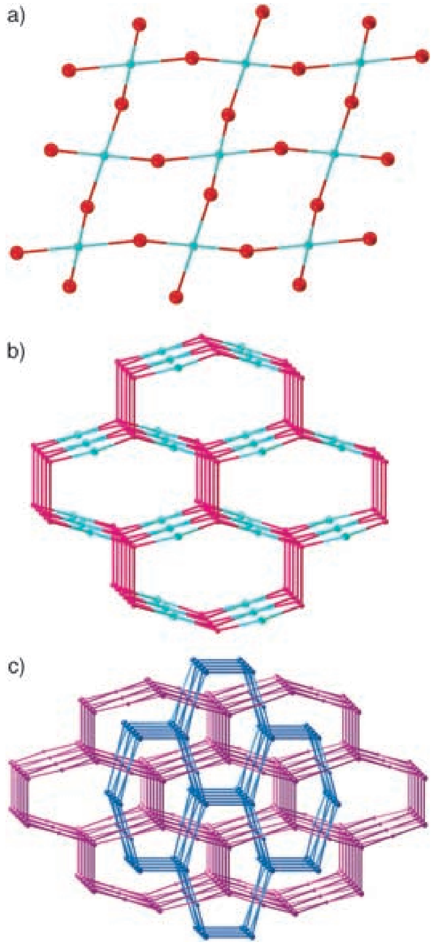

Figure 4. a) The 2D (4,4) coordination subnet motif in the structure of **4**; red Cu, cyan ligand. b) The 3D (3,4)-connected topological net constructed from the 2D (4,4) subnets. c) The two interpenetrating nets in the structure of **4**.

just the three-connected copper atoms and the tetradentate ligands as trigonal nodes and square-planar nodes; the bidentate μ_2-Cl bridges can be represented simply as links between the copper nodes. The resulting net is shown in Figure 4b, and is a rare (3,4)-connected net[14] with trigonal and square-planar nodes in the ratio 2:1. The long topological (O'Keeffe) vertex symbol is $6.6.8_2$ for the Cu node, and $6.6.8.8.10_2.10_2$ for the chtpy node, which gives the short vertex symbol $(6^2.8^2.10^2)(6^2.8)_2$. The twofold interpenetrating networks are shown in Figure 4c.

In order to obtain the newly generated multitopic building block, which will be of further use for the assembly of functional molecular solids, we separated the chtpy ligand from the metal center by treating **1** with $Na_2(H_2edta)$. An X-ray crystallographic study[7] clearly showed that the free chtpy molecule also adopts a chair conformation, with the four pyridyl groups located at the equatorial positions and the two hydroxy groups at the axial positions. Each unique chtpy molecule lies across a twofold axis (Figure 5). The six C–C bond distances of the cyclohexyl ring fall in the range 1.536(4)–1.543(4) Å, in agreement with those found in **1–4** and characteristic of C–C single bonds.[8] The C–O bond length of 1.440(6) Å is indicative of a single-bond character.

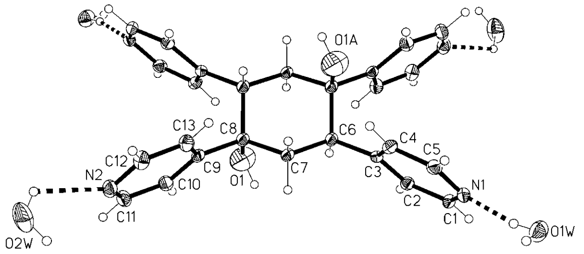

Figure 5. Crystal structure of chtpy·4 H_2O.

In summary, we have prepared and characterized four new examples of copper(I) coordination networks with a new planar tetratopic ligand generated in situ and isolated this tetratopic ligand.[15] Extension of this functional, four-connected ligand to other metal salts and a further systematic investigation of their network connectivity and function is in progress.

Experimental Section

1: A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (0.061 g, 0.25 mmol), NaOH (0.02 g, 0.5 mmol), 1,4-cyclohexanedicarboxylic acid (0.086 g, 0.5 mmol), bpp (0.198 g, 1.0 mmol), and H_2O (9 mL) was placed in a Parr Teflon-lined, stainless-steel vessel and heated at 175 °C for 3 d to yield fine, pale-yellow crystals (yield ca. 25 % based on Cu^{2+}). $C_{39}H_{36}CuN_7O_6$: calcd. C 61.45, H 4.76, N 12.86; found C 61.09, H 4.62 N 12.71.

2: A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (0.121 g, 0.5 mmol), NaOH (0.04 g, 1.0 mmol), 1,4-cyclohexanedicarboxylic acid (0.172 g, 1.0 mmol), bpp (0.198 g, 1.0 mmol), benzene (0.5 mmol), and H_2O (9 mL) was placed in a Parr Teflon-lined, stainless-steel vessel, acidified with HCl (0.25 mmol), then heated at 180 or 190 °C for 3 d to yield fine, pale-yellow crystals (yield 20–30 %). $C_{60}H_{52}ClCu_2N_9O_7$: calcd. C 61.40, H 4.47, N 10.74; found C 61.14, H 4.36, N 10.65.

3: A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (0.484 g, 2.0 mmol), NaOH (0.08 g, 2.0 mmol), 1,4-cyclohexanedicarboxylic acid (0.172 g, 1.0 mmol), bpp (0.198 g, 1.0 mmol), and H_2O (9 mL) was placed in a Parr Teflon-lined stainless-steel vessel, acidified with HCl (0.25 mmol), then heated at 175 °C for 3 d to yield fine, primrose-yellow crystals (yield 18–22 % based on bpp). $C_{26}H_{22}Cl_2Cu_2N_4O_2$: calcd. C 50.33, H 3.57, N 9.03; found C 50.10, H 3.42, N 8.95.

4: Compound **4** was prepared by a similar experimental procedure to that for **3** except for the molar ratio of HCl (0.5 mmol). Yield: 30–35 % based on bpp. $C_{26}H_{22}ClCu_2N_5O_5$: calcd. C 48.26, H 3.43, N 10.82; found C 47.95, H 3.35, N 10.91.

chtpy: A solution of $Na_2(H_2edta)$ (0.149 g, 0.4 mmol) in water (10 mL) was added dropwise to a stirred suspension of **1** (0.145 g) in a mixture of dichloromethane (30 mL) and water (10 mL) at room temperature, followed by stirring for 48 h under nitrogen. The organic phase was then separated from the reaction mixture and the aqueous layers were extracted with dichloromethane (3 × 60 mL). The combined organic phase was concentrated in vacuo. The residue was dissolved in dichloromethane, purified by column chromatography, and dried with anhydrous Na_2SO_4 to give chtpy as a pale-yellow powder. Yield: 0.095 g (78 %). (ESI-MS): $m/z = 425$, 213; ^{1}H NMR (300 MHz, $(CD_3)_2SO$): $\delta = 1.27$ (m, 4 H, C7-H7a, C7-H7b), 2.18 (t, $J = 3.3$ Hz, 2 H, C6-H6), 7.14 (d, $J = 5.1$ Hz, 4 H, C2-H2, C4-H4), 7.54 (d, $J = 5.4$ Hz, 4 H, C10-H10, C13-H13), 8.56 ppm (d, $J = 3.6$ Hz, 8 H, C1-H1, C5-H5, C11-H11, C12-H12); ^{13}C NMR (75 MHz, $(CD_3)_2SO$): $\delta = 30.9$ (C-7), 34.6 (C-6), 79.9 (C-8), 121.9 (C-9), 124.5 (C-2), 150.1 (C-1), 151.1 ppm (C-3). $C_{26}H_{24}N_4O_2$: calcd. C 73.57, H 5.70, N 13.20; found C

73.26, H 5.62, N 13.09. IR (KBr disk): $\tilde{\nu} = 3228$ (m, OH), 1596, 1545 cm^{-1} (s, py). Colorless crystals of chtpy·4 H_2O were obtained by dissolution of the powder in acetonitrile at ambient temperature in air. $C_{26}H_{24}N_4O_2 \cdot 4\,H_2O$: calcd. C 62.89, H 6.50, N 11.28; found C 62.71, H 6.62, N 11.03.

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[7] Crystal data for **1**: $C_{39}H_{36}CuN_7O_6$, $M_r = 762.29$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.774(1)$, $b = 13.475(1)$, $c = 14.152(1)$ Å, $\alpha = 97.358(2)$, $\beta = 112.110(2)$, $\gamma = 113.436(2)°$, $V = 1803.8(2)$ Å^3, $Z = 2$, $T = 293(2)$ K, $F(000) = 792$, $\rho_{calcd} = 1.402$ g cm^{-3}, $\mu(\mathrm{Mo}\,K_\alpha) = 0.663$ mm^{-1} ($\lambda = 0.71073$ Å); $R_1 = 0.0924$, $wR_2 = 0.2523$, and GOF = 1.040 for 478 parameters, 4724 reflections with $|F_o| \geq 4\sigma(F_o)$. Crystal data for **2**: $C_{30}H_{26}Cl_{0.5}CuN_{4.5}O_{3.5}$, $M = 586.82$, orthorhombic, space group *Cccm* (no. 66), $a = 11.399(2)$, $b = 15.971(2)$, $c = 23.417(3)$ Å, $V = 4263.1(10)$ Å^3, $Z = 4$, $T = 123(2)$ K, $F(000) = 1212$, $\rho_{calcd} = 0.914$ g cm^{-3}, $\mu(\mathrm{Mo}\,K_\alpha) = 0.571$ mm^{-1} ($\lambda = 0.71073$ Å); $R_1 = 0.1431$, $wR_2 = 0.3930$, and GOF = 1.736 for 120 parameters, 1470 reflections with $|F_o| \geq 4\sigma(F_o)$. Crystal data for **3**: $C_{26}H_{22}Cl_2Cu_2N_4O_2$, $M = 620.46$, orthorhombic, space group *Pbcn* (no. 60), $a = 11.489(1)$, $b = 11.253(1)$, $c = 19.881(2)$ Å, $V = 2570.3(5)$ Å^3, $Z = 4$, $T = 293(2)$ K, $F(000) = 1256$, $\rho_{calcd} = 1.603$ g cm^{-3}, $\mu(\mathrm{Mo}\,K_\alpha) = 1.894$ mm^{-1} ($\lambda = 0.71073$ Å); $R_1 = 0.0718$, $wR_2 = 0.2119$, and GOF = 1.088 for 172 parameters, 1315 reflections with $|F_o| \geq 4\sigma(F_o)$. Crystal data for **4**: $C_{26}H_{22}ClCu_2N_5O_5$, $M = 647.02$, tetragonal, space group $P4_2/mbc$ (no. 135), $a = 10.010(1)$, $c = 26.540(2)$ Å, $V = 2659.3(3)$ Å^3, $Z = 4$, $T = 293(2)$ K, $F(000) = 1312$, $\rho_{calcd} = 1.616$ g cm^{-3}, $\mu(\mathrm{Mo}\,K_\alpha) = 1.747$ mm^{-1} ($\lambda = 0.71073$ Å); $R_1 = 0.0468$, $wR_2 = 0.1390$, and GOF = 1.104 for 103 parameters, 1383 reflections with $|F_o| \geq 4\sigma(F_o)$. Crystal data for chtpy·4 H_2O: $C_{26}H_{32}N_4O_6$, $M = 496.56$, monoclinic, space group *C2/c* (no. 15), $a = 15.5954(13)$, $b = 11.3662(9)$, $c = 14.0070(11)$ Å, $\beta = 91.097(2)°$, $V = 2482.4(3)$ Å^3, $Z = 4$, $T = 123(2)$ K, $F(000) = 1056$, $\rho_{calcd} = 1.329$ g cm^{-3}, $\mu(\mathrm{Mo}\,K_\alpha) = 0.095$ mm^{-1} ($\lambda = 0.71073$ Å); $R_1 = 0.0965$, $wR_2 = 0.2794$, and GOF = 1.098 for 179 parameters, 2152 reflections with $|F_o| \geq 4\sigma(F_o)$. CCDC-261921 (**1**), -261922 (**2**), -261923 (**3**), -261925 (**4**), and -271176 (chtpy·4 H_2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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[15] By using $(NH_4)_2S$ as the precipitator, another new tetratopic ligand (1,2,4,5-tetra(4-pyridyl)benzene; phtpy) derived from chtpy was isolated by removal of the Cu^+ ions from complexes **1**–**4** at 60 °C in air. Crystal data for phtpy·2 H_2O: $C_{26}H_{22}N_4O_2$, monoclinic, space group *C2/c*, $M_r = 422.48$, $a = 16.344(6)$, $b = 13.697(5)$, $c = 9.748(3)$ Å, $\beta = 97.171(6)°$, $V = 2165.2(13)$ Å^3, $Z = 4$. $R_1 = 0.0644$, $wR_2 = 0.1813$, and GOF = 1.071 for 151 parameters, 1669 reflections with $|F_o| \geq 4\sigma(F_o)$. This compound will be reported in a subsequent full paper.