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A copper–organic complex from hydrothermal reaction involving in situ aromatic nucleophilic substitution of ligand

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Abstract

Reaction of in situ generated 4-(6-(pyridin-4-yl)pyridin-3-yl)phenol (pph) from 5-(4-bromophenyl)-2-(pyridin-4-yl)pyridine (bppy) by an aromatic nucleophilic substitution and copper nitrate in hydrothermal conditions led to the formation of a supramolecular framework, formulated as $[Cu(pph)_2]_2MoO_4 \cdot 1/2H_2O$ (**1**). Compound **1** represents a two-dimensional network based on intermolecular O–H⋯O hydrogen bonds, in which Cu(II) is reduced to Cu(I). The formation mechanism of the aromatic nucleophilic substitution was discussed.

Keywords: Aromatic nucleophilic substitution; Copper; Supramolecular framework

Over the past several years, hydro(solvo)thermal in situ ligand synthesis has rapidly developed as a new bridge between coordination chemistry and organic chemistry, which not only presents the opportunity to generate organic ligands that are difficult to be synthesized but also represents a potential new direction for the construction of metal–organic frameworks (MOFs) through crystal engineering [1]. Under hydrothermal conditions, a variety of synthetic pathways were tested and completed successfully including hydrolysis, oxidation, reduction and substitution reactions of ligands [2], such as hydrolysis of –CN and –COOR groups [3], reduction of $–COO^-$ [4], hydroxylation [5], carbon–carbon bond formation by reductive or oxidative coupling [6], cleavage and formation of disulfide bonds [7], etc. In these examples, considerable attention has been placed on the investigation of copper complexes with organic N-heterocyclic ligands, which was mainly due to their attractive magnetic properties [8], mixed-valence oxidation-state pairs, photoluminescence [9], novel structural features and biological relevance [10]. However, most of the exact transformation mechanism of ligand is not yet well-proven owing to the hydrothermal conditions. Chen and co-workers' experiments confirmed that coordination of bpy and phen to copper ions is critical to their hydroxylation, which is also in agreement with the Gillard mechanism [11]. We report herein the in situ hydrothermal synthesis of 4-(6-(pyridin-4-yl)pyridin-3-yl)phenol (pph) from 5-(4-bromophenyl)-2-(pyridin-4-yl)pyridine (bppy) (see Scheme 1) and its copper coordination compound, formulated as $[Cu(pph)_2]_2MoO_4 \cdot 1/2H_2O$ (**1**). Compound **1** represents a two-dimensional network based on intermolecular O–H⋯O hydrogen bonds, face-to-face, edge-to-face and point-to-face π-stacking interactions, in which Cu(II) is changed to Cu(I) valence state by a reduction-reaction under hydrothermal conditions.

Crystals of **1** were obtained by hydrothermal reaction of $Cu(NO_3)_2$, Na_2MoO_4, oxalic acid, and bppy [12]. Single-crystal X-ray analysis [13] revealed that compound **1** consists of a two-dimensional network via hydrogen bonding interactions, further being stabilized by π-stacking interactions among three-ring organic ligands. In compound **1**, there are two crystallographically independent

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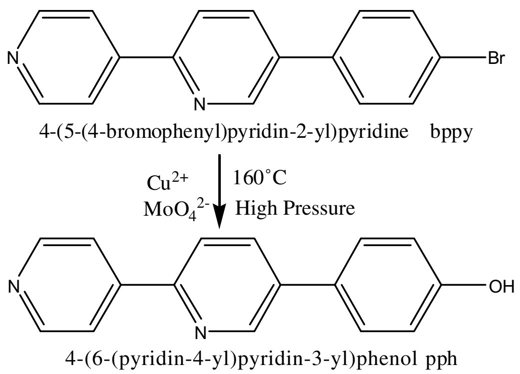

Scheme 1.

but chemically very similar copper atoms (see Fig. 1). Both Cu(1) and Cu(2) show a T-shaped coordination geometry composed of a pair of nitrogen atoms (Cu(1)–N(1) = 1.875(5), Cu(1)–N(7) = 1.875(5); Cu(2)–N(3) = 1.903(4), Cu(2)–N(5) = 1.891(5) Å, respectively) from two pph ligands, and a oxygen atom (Cu(1)–O(1) = 2.499(4); Cu(2)–O(2) = 2.216(4) Å) shared with a MoO_4 tetrahedron. A couple of $Cu(pph)_2$ are bridged by a MoO_4 tetrahedron to form a Chinese character '工' structure. The $Cu(pph)_2$ molecule has a large size of 28.97(1) Å (between hydroxyl oxygen atoms of two pphs). In MoO_4 tetrahedron, Mo–O bond lengths fall into a usual range of 1.713(4)–1.761(4) Å. Both the T-shaped coordination geometry of Cu and the tetrahedral geometry of Mo are interesting in **1**.

Supramolecular chemistry has attracted much attention in organic–inorganic hybrids [14]. The research and application on supramolecular interactions have been extended from the initial work on purely organic systems into MOFs even purely inorganic systems. Even hydrogen bonding was regard as a coordination bond in many MOFs [15]. As shown in Table 1, all hydroxyl oxygen atoms of pph have short distances to the adjacent oxygen atoms of MoO_4 from other $Cu(pph)_2MoO_4$ unit: 2.547(16)–2.761(6) Å, indicating strong hydrogen bond interactions among these $Cu(pph)_2MoO_4$ molecules. All oxygen atoms of $Cu(pph)_2$-MoO_4 unit involve the construction of 2D hydrogen bonding net of crystal **1**. Additional interactions occur through offset face-to-face π–π and point-to-face C–H···π contacts between two adjacent pphs. The distances of centroids of the relevant aryl rings are 3.619–3.391 Å. Fig. 2 shows the two-dimensional supramolecular structure.

The emission spectra of compound **1** and the free bppy ligand in solid state at room temperature are shown (see

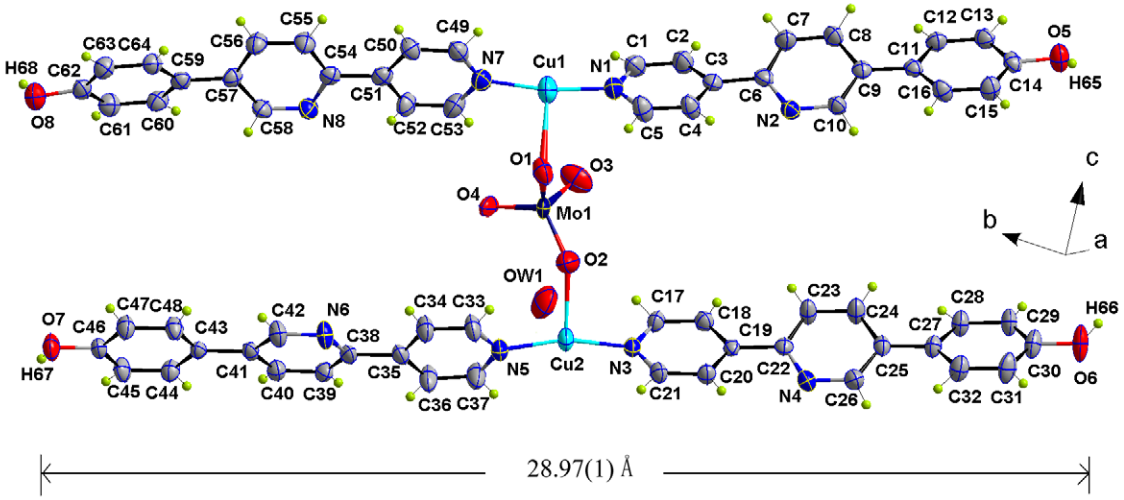

Fig. 1. ORTEP drawing of **1** with a 50% probability of thermal ellipsoid.

Table 1
Short distances involving O–H···O, C–H···N and C–H···O in **1**

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D - H···A (°)
O(5)–H(65)···O(2)#1	0.79(6)	1.83(6)	2.615(6)	173(6)
O(6)–H(66)···O(1)#2	0.78(5)	2.06(6)	2.773(6)	153(6)
O(7)–H(67)···O(4)#3	0.71(5)	1.84(5)	2.546(7)	173(5)
O(8)–H(68)···O(3)#4	0.77(4)	1.90(4)	2.667(7)	178(5)
C(37)–H(37A)···OW(1)#5	0.93	2.33	3.256(11)	173
C(45)–H(45A)···O(4)#3	0.93	2.56	3.199(6)	126
C(52)–H(52A)···N(8)	0.93	2.44	2.762(7)	100

Symmetry transformation used to generate equivalent atoms: #1: $1 - x, -1 - y, 1 - z$; #2: $-1 + x, 1 + y, z$; #3: $2 - x, -3 - y, 2 - z$; #4: $1 + x, -1 + y, z$; and #5: $1 - x, -2 - y, 2 - z$.