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Supramolecular Architecture from the Self-assembly of One-dimensionalCoordination Polymers and Hydrogen Bonds

Chun Hua GE[1,2], Xiang Dong ZHANG[1], Wei GUAN[3], Qi Tao LIU[1] *, Zhan YU[1], Li Yan LIU[1]

[1]Institute of Chemical Science & Engineering, Liaoning University, Shenyang 110036
[2]Faculty of Chemistry, Northeast Normal University, Changchun 130024
[3] Department of Environmental Science, Liaoning University, Shenyang 110036

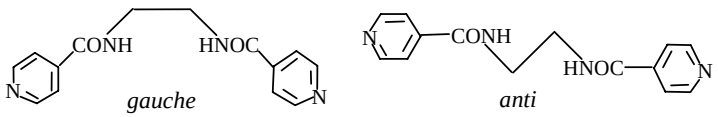
Abstract: The novel one-dimensional coordination polymer $\{[Cu(L)_2(H_2O)]\cdot 2BF_4\cdot 6H_2O\}_\infty$ [**1**, L=1,2-bis(4-pyridinecarboxamido)ethane] was synthesized as single crystals and characterized by means of X-ray diffraction analysis, elemental analysis, IR spectroscopy and TG measurement. Structure **1** consists of looped chains. In addition, linked by hydrogen bonds, the one-dimensional chains were transformed into three-dimensional framework, which shows channels filled with anions and uncoordinated water molecules.

Keywords: Crystallization, coordination polymer, supramolecular chemistry.

The synthesis and characterization of coordination polymers have been a rapid growth area in recent years. The coordination polymers consist of 1D chains, 2D sheets or 3D networks in which metal-organic building blocks connected *via* coordinate and hydrogen bonds. They received considerable attention because of their versatile intriguing architectures, topologies and potential applications in materials[1,2] .

As rigid rod-like spacers, 4,4'-bipyridine and its analogues have been used to give rise a large number of interesting supramolecular architectures[3]. However, flexible bridging ligands have not been frequently employed to construct coordination polymers with transition metal ions[4]. Such ligands are attractive for their flexibility and conformation freedom (*gauche* and *anti*, **Scheme 1**), both conformers are able to perform as bifunctional ligands. Here we report our recent successful result about the construction of novel coordination Cu(Ⅱ) polymer using a flexible ligand. We employ 1, 2-bis(4-pyridinecarboxamido)ethane (**L**) as the ligand, because this compound has a

Scheme 1



* E-mail: qtliu@lnu.edu.cn

long ditopic bridging spacer and the amido groups which are good donor and acceptor of hydrogen bond.

{[Cu(**L**)$_2$(H_2O)]· 2BF_4· 6H_2O}$_\infty$ (**1**) was synthesized by adding an aqueous solution of Cu(Ⅱ) to ethanolic solution of **L**, after 24 hours of stirring at room temperature, the resulting solution was filtered, and the filtrate was then allowed to stand at room temperature. Several weeks later, blue X-ray quality single crystals were obtained (41% yield).

The structure was confirmed by elemental analysis[5] and IR spectroscopy[6]. The signals at 1660, 1640 cm^{-1} in IR spectrum, suggesting that the C=O stretch and N atom from pyridyl ring is coordinated with Cu atom.

A single-crystal X-ray diffraction study revealed that **1** consists of linear chains[7]. The each Cu(Ⅱ) atom is bonded to four pyridine nitrogens and one water molecule with pyramidal geometry. The copper ions are bridged by two crystallographically independent ligands forming looped chain as shown in **Figure 1**, which provides an intermetallic distance of 12.813Å. Each ligand adopts *gauche*-conformation. The N6-C21-C22-N7 and N2-C7-C8-N3 torsion angles are -73.8˚ and -61.9˚ in **1**, these parameters show that there is conformational difference between the two independent ligands. Ligands of each side of the chain has the same conformation. Chirality arising from that O(1), O(2), O(4) point outside the cycle and O(3) points inside the cycle which is included in the asymmetric unit .

The hydrogen bonds (N6···O2 2.911Å, N6-H6A···O2 163.3˚, symmetry code: 1/2+x, 1/2-y, 1/2+z) connect each chain with its two neighbors forming a two-dimensional layer (**Figure 2b**). Further hydrogen bonds (O1W···O3 2.775 Å, O1W-H1A···O3 152.2˚, symmetry code: 3/2-x, 1/2+y, 1/2-z) link adjacent layers into three-dimensional framework, and the arrangement of those layers is in an A-B fashion (**Figure 2c**). As a result, chains are connected through 36- and 56-membered rings. By doing so, two different motifs channels come into being (labeled as C1 and C2 in **Figure 2c**). The channels, which are roughly parallelogram in shape with dimensions of 9.0 × 5.7 $Å^2$ for C1 and 15.4 × 5.7 $Å^2$ for C2. The uncoordinated water molecules and anions are arranged in such a way as to fill the large channels for its corrugated architecture, running on both sides of a single layer.

Figure 1 ORTEP drawing of the looped chain structure of **1** with 50% probability ellipsoids, uncoordinated water molecules and anions are omitted for clarity.

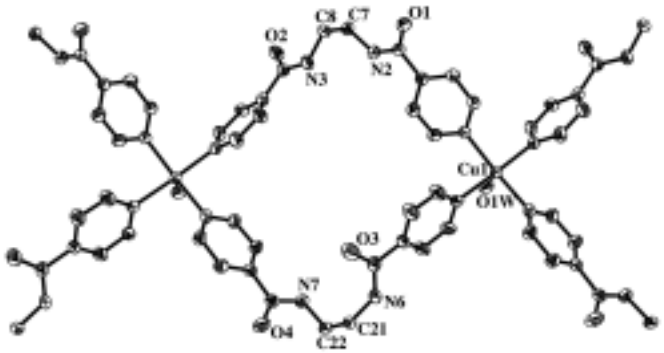
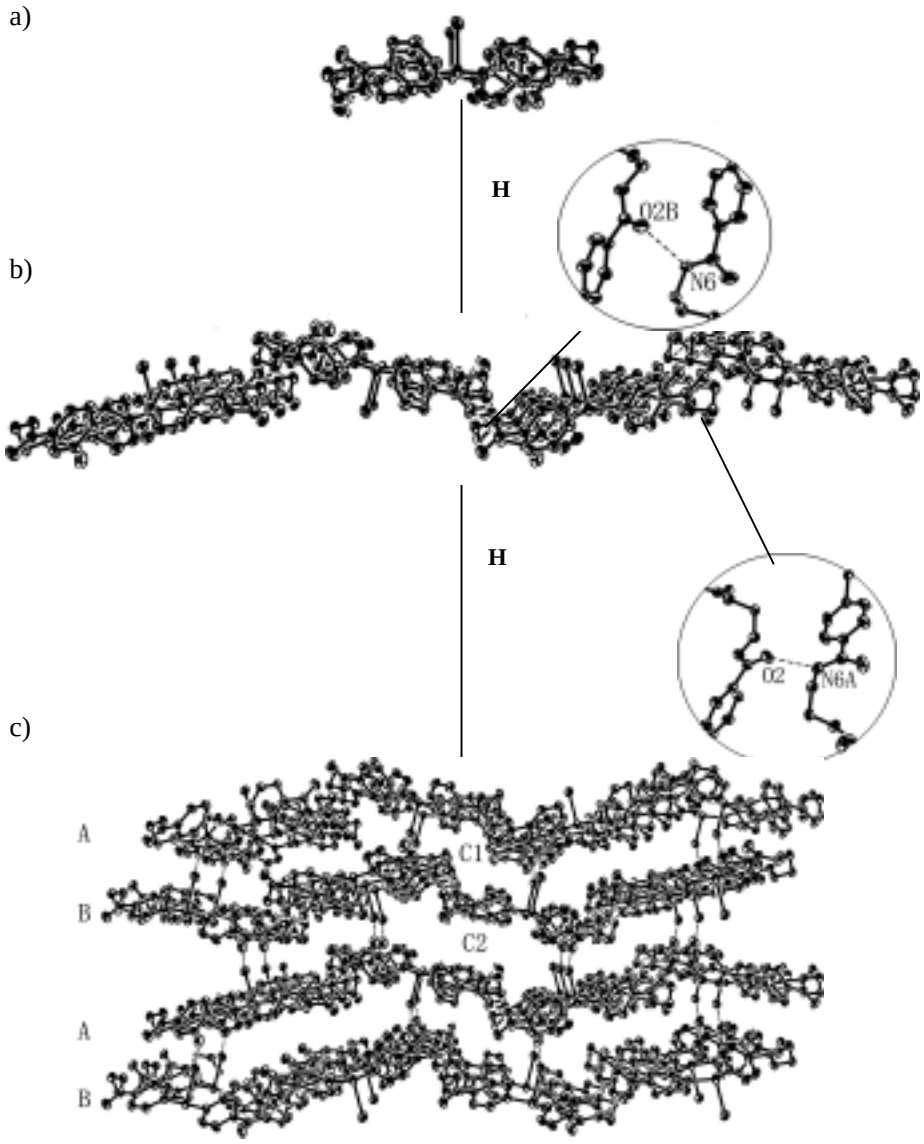


Figure 2 Formation of the three-dimensional framework



a) View of a one-dimensional chain down *a* axis; b) two-dimensional layer; c) three–dimensional framework showing stacked layers in A-B fashion; C1, C2 are different channels. Uncoordinated water molecules and anions are omitted for clarity; H=hydrogen bond.

Thermal gravimetric analysis (TGA) shows that **1** undergoes a gradual loss of 12.18% of total weight between 81.2°C and 109.1°C, corresponding to the loss of six uncoordinated water molecules per formula unit (expected 11.96%). Above 109.1°C, the sample shows no further weight loss up to 244.8°C at which temperature the compound decomposed.

Acknowledgment

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References and Notes

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5. Anal. Calcd for $C_{28}H_{42}B_2Cu_1F_8N_8O_{11}$ **1**: C, 37.21; H, 4.68; N, 12.40. Found: C, 37.46; H, 4.55; N, 12.81.
6. Selected IR (KBr,cm^{-1}): 3440 (s), 3296 (s), 3080 (w), 2940 (w), 1660 (s), 1640 (m), 1475 (m),1385 (s), 1300 (m), 860(w).
7. Crystal data for **1**: monoclinic, space group $P2_1/n$, with a=12.813(5)Å, b=12.734(5)Å, c=22.911(10)Å, β=92.777(7)°, V=3734 (3)$Å^3$, Z=4, D_c=1.608 g/cm^3, R1=0.0622, wR2= 0.1480[I>2 σ (I)]. Other crystallographic parameters have been deposited in the editorial office of CCL.

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