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# Synthesis and Crystal Structure of a Novel Hydrogen Bonded Supramolecular Complex Derived from Pyrimidine-2-sulfonate: $[CuL_2]\cdot H_2O$

HUA-ZE DONG*, WEN-TAO BI† and HAI-BIN ZHU‡
*Department of Chemistry and Chemical Engineering,*
*Hefei Teachers College, Hefei 230061, P.R. China*
*E-mail: dapdong@163.com*

A novel 3D supramolecular complex with a formula as $[CuL_2]\cdot H_2O$, was formed by the reaction of 4-pyridine-2-yl-pyrimidine-2-sulfonate (NaL) with copper salt, in which metal ion was in a six-coordinated environments with a distorted octahedral geometry. Then independent mononuclear units are linked each other and pack in 3D-superamolecular network *via* hydrogen bonds and some π-π stacking interactions. The crystal is monoclinic, space group C2/c with unit cell parameters: $a = 28.384(6)$ Å, $b = 7.849(16)$ Å, $c = 19.090(4)$ Å, $\alpha = 90°$, $\beta = 105.259(4)°$, $\gamma = 90°$, $V = 4103.1(15)$ Å$^3$, $Z = 8$, $Mr = 554.01$, $Dc = 1.794$ g/cm$^3$, $\mu = 1.327$ mm$^{-1}$, $F(000) = 2248$, $R = 0.0405$, $wR = 0.0739$ for 1970 reflections with $I > 2\sigma(I)$.

**Key Words: 4-Pyridine-2-yl-pyrimidine-2-sulfonate, Supramolecule, Hydrogen bonds.**

## INTRODUCTION

There has been increasing interest of assembling supramolecules *via* hydrogen bonds in the field of coordination chemistry[1-6]. In our previous paper, we reported some 3D supramolecular complexes derived from a multidentate ligand, sodium 4-pyridine-2-yl-pyrimidine-2-sulfonate[7,8]. Herein reported is a new 3D hydrogen-bonding supramolecular copper complex $[CuL_2]\cdot H_2O$.

## EXPERIMENTAL

All reagents for synthesis were commercially available and employed as received or purified by standard methods prior to use. 4-Pyridine-2-yl-pyrimidine-2-sulfonate (NaL) was prepared by general procedure reported in the literature[7]. Analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Infrared spectra (4000-400 cm$^{-1}$) were recorded with a Bruker Vector 22 FT-IR spectrophotometer on KBr disks.

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†School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, P.R. China.
‡School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, P.R. China. E-mail: zhuhaibin@seu.edu.cn

**Synthesis:** $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol) was mixed with NaL (0.2 mmol) in 20 mL of $H_2O$. The reaction mixture was stirred for 1 h and then filtered. The green mother solution was allowed for 1 week to evaporate slowly and obtained green crystals block-shaped single crystals **1** suitable for X-ray analysis. Yield 71 %. Anal. Calcd. for $C_{18}H_{14}N_6O_7S_2Cu$: C, 39.02; H, 2.53; N, 15.18. Found: C, 39.21; H, 2.47; N, 15.21. Main IR (KBr, $cm^{-1}$): 3397m, 1583s, 1546m, 1497w, 1456m, 1370w, 1257s, 1211s, 1038s, 1016m.

**Crystal structure determination:** A single crystal of compound with dimensions of 0.4 mm × 0.2 mm × 0.2 mm was selected for crystallographic data collection at 291(2) K and structure determination on a Bruker SMART CCD-4K diffractometer employing graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). A total of 9895 reflections were collected in the range of $2.2° \leq \theta \leq 25.0°$, of which 3611 reflections were unique with $R_{int} = 0.059$. The data were collected using SMART and reduced by the program SAINT. All the structures were solved by direct methods and refined by full-matrix least squares method on $F^2_{obs}$ by using SHELXTL-PC software package. Non-hydrogen atoms were placed in geometrically calculated positions. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 307 variable parameters for 3611 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of:

$$R1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0| = 0.0405 \qquad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2-F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.0739 \qquad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.0214P)^2]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.47 and -0.35 e/Å$^3$, respectively.

## RESULTS AND DISCUSSION

The selected bond lengths and bond angles are given in Table-1. Fig. 1 shows the molecular structure of the title compound. Fig. 2 shows the packing diagram of the title compound. From the Fig. 1, it is easy to see that the copper(II) ion is six-coordinated with four N atoms and two O atoms, which is very similar to other complexes in previous paper[7].

In crystal packing, both sulfonato groups, the lattice water molecule and aromatic rings of the ligand participate in intermolecular hydrogen bonding, leading to the construction of novel hydrogen-bonded supramolecule. All hydrogen bond patterns are given in Table-2. Two independent mononuclear units are linked each other *via* hydrogen bonds, leading to a one dimensional hydrogen-bonded chain, As shown in Fig. 2, the hydrogen bonds C(17)···O(5) and C(18)···O(6) are formed by the uncoordinated sulfonato oxygen atom O(5) and O(6) with aromatic hydrogen, respectively. Additionally, it is interesting to note that the water molecule plays dual roles, that is, hydrogen donor in hydrogen bond O(7)···N(5) and O(7)···O(3)

TABLE-1
SELECTED BOND DISTANCES (Å) AND ANGLES (°)

| | | | | | |
|---|---|---|---|---|---|
| Cu–O(1) | 2.231(2) | S(1)–O(3) | 1.431(3) | O(1)–Cu–N(3) | 159.00(11) |
| Cu–N(1) | 1.941(3) | S(1)–O(2) | 1.420(3) | O(1)–Cu–N(1) | 80.08(12) |
| Cu–N(4) | 1.963(3) | S(2)–O(4) | 1.456(3) | O(1)–Cu–N(6) | 94.37(11) |
| Cu–O(4) | 2.230(3) | S(2)–O(6) | 1.424(3) | N(1)–Cu–N(3) | 79.19(13) |
| Cu–N(3) | 2.092(3) | S(2)–O(5) | 1.434(3) | N(1)–Cu–N(4) | 173.48(13) |
| Cu–N(6) | 2.147(3) | O(4)–Cu–N(4) | 79.82(11) | N(4)–Cu –N(6) | 78.29(13) |
| S(2)–C(10) | 1.781(4) | N(1)–Cu–N(6) | 108.24(13) | O(1)–Cu–O(4) | 87.12(9) |
| S(1)–O(1) | 1.461(3) | N(1)–Cu–N(3) | 79.19(13) | O(1)–Cu–N(4) | 99.83(12) |

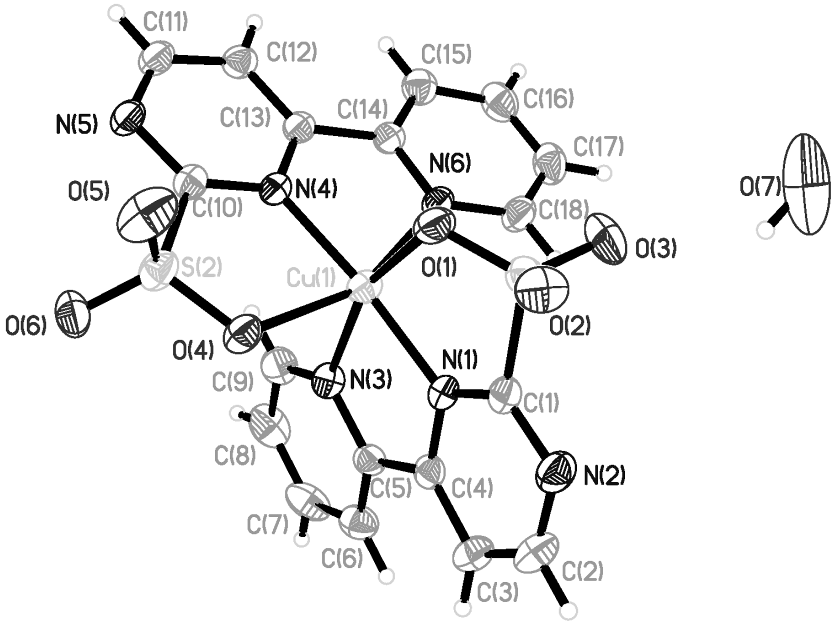

Fig. 1. Molecular structure of the title complex

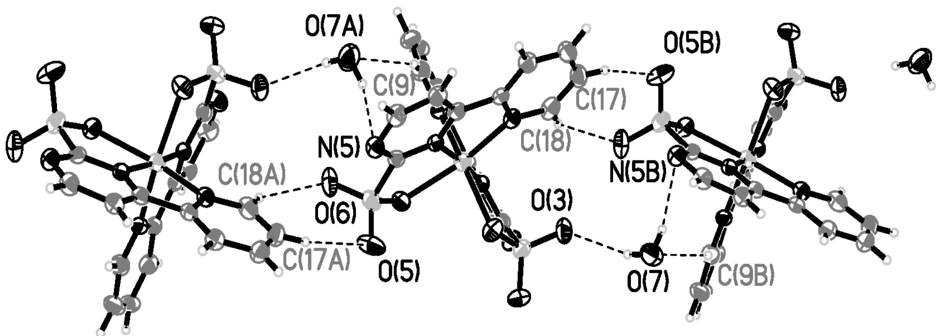

Fig. 2. 1D network *via* five type of hydrogen bonds

TABLE 2
HYDROGEN BOND DISTANCES (Å) AND ANGLES (°)

| Type (D-H···A) | d(D-H) | d(H···A) | ∠ (DHA) | d(D···A) | A |
|---|---|---|---|---|---|
| O7-H7A···N6 | 0.8500 | 2.5300 | 125.00 | 3.094(5) | N6 [x,1-y,1/2+z] |
| O7-H7B···O1 | 0.8500 | 2.1900 | 133.00 | 2.842(5) | |
| C7-H7···O4 | 0.9300 | 2.4400 | 140.00 | 3.213(6) | O4 1/2-x,3/2-y,-z] |
| C8-H8···O4 | 0.9300 | 2.4100 | 156.00 | 3.282(5) | O4 [x,1+y,z] |
| C9-H9···O7 | 0.9300 | 2.5700 | 141.00 | 3.345(5) | O7 [x,1-y,-1/2+z] |
| C12-H12···O3 | 0.9300 | 2.4500 | 147.00 | 3.268(5) | O3 [-x,1-y,-z] |
| C17-H17···O5 | 0.9300 | 2.5300 | 158.00 | 3.410(5) | O5 [x,1-y,1/2+z] |
| C18-H18···O6 | 0.9300 | 2.5300 | 142.00 | 3.314(5) | O6 [x,1-y,1/2+z] |

and hydrogen acceptor in hydrogen bond C(9)···O(7). Further, the resulted chain is spread out through hydrogen bonds C(7)···O(4), C(8)···O(4) and C(12)···O(1) (Fig. 3) to produce 3D hydrogen-bonded network. In addition, there exist aromatic interactions (center-to-center distance: 3.3407 Å) between two adjacent aromatic units.

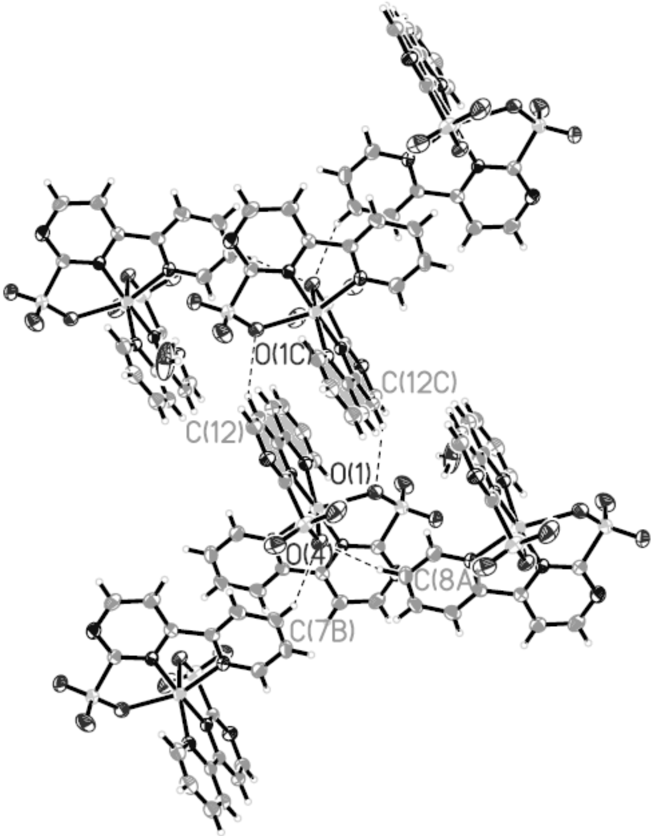

Fig. 3. Hydrogen bonds among 1D network in the complex

## Conclusion

Crystal structure of a novel 3D superamolecular copper(II) complex has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis.

## Supplementary material

Crystallographic data for the structure reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 705136.

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