

Synthesis and Structure of the Copper Complex [CuL(4,4'-bipy)(H₂O)₂](H₂O)(ClO₄)

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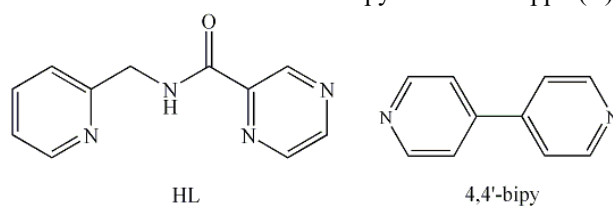
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Abstract: The reaction of N-(pyridine-2-ylmethyl)pyrazine-2-carboxamide (HL), 4,4'-bipyridine(4,4'-bipy) and copper(II) perchlorate leads to the formation of a new copper complex, [CuL(4,4'-bipy)(H₂O)₂](H₂O)(ClO₄) (1), The X-ray crystal analysis reveals that it is a mononuclear complex. CCDC: 1487818,1.

1 Introduction

In the past decades, the construction and crystal engineering of coordination compounds have attracted much more attention in inorganic supramolecular chemistry due to their structural diversity and potential application in catalysis, molecular adsorption, magnetism, non-linear optics and molecular sensing^[1-3]. The designed coordination compounds can be specially obtained by carefully selected metal ions and special organic ligands with considering reaction conditions. The whole self-assemble process is also affected by many factors, such as the solvents^[4], reagent ratios^[5], temperature^[6], PH^[7] and counterions^[8]etc. Pyrazine-containing ligands have played very important role in the copper coordination chemistry. Bis(terdentate)pyrazine based diamide ligands and their transition metal

chemistry have been well studied by Dr. Brooker's and Dr. Stoeckli Evans's group^[9]. As a homolog of the mentioned diamide ligands, one alkylpyridine armed pyrazine-pyridine amide ligand HL was prepared. The coordination chemistry of transition metal based on HL was also investigated by several different groups. Dr. Hubin firstly reported a trinuclear cobalt complex^[10]. Khavasi's group also reported a novel binuclear manganese(II) complex and its catalytic property^[11]. Later, they reported two temperature dependent complexes of 1D and 2D HgCl₂ coordination polymer with HL^[6]. Recently, my previous group reported the synthesis, characterization and structures of five copper complexes with HL and its homolog ligand^[12]. As a complimentary work to my previous research, here, we report the synthesis, crystal structure of a new copper complex obtained from the reaction of HL, 4,4'-bipyridine and copper(II) perchlorate.



Scheme. 1 Structure of HL and 4,4'-bipy used in this work

2 Experimental

2.1 General procedures

All the chemicals commercially available were used as supplied without further purification. The HL was synthesized according to previously reported methods.^[10] Infrared spectra were recorded with a Bruker VERTEX-70 spectrometer as KBr pellets in the frequency range 4000 to 400cm⁻¹. Elemental analyses were performed

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with a Perkin-Elmer 2400 Series II analyzer. Powder X-ray diffraction (PXRD) was performed on a Shimadzu XRD-6000 instrument by using Cu $K\alpha$ radiation at room temperature.

2.2 Synthesis of $[CuL(4,4'-bipy)(H_2O)_2](H_2O)(ClO_4)$ (1)

A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.0926g, 0.25mmol) in methanol was added to a solution of HL (0.0535g, 0.25mmol) and triethylamine (25.0mg, 0.25mmol) in methanol, leading to the formation of dark blue solution, then, the methanolic solution of 4,4'-bipy (0.0392g, 0.25mmol) was added drop by drop to the above mixture, keep stirring for 2h, no obvious color change observed, after the filtration, the blue filtrate was obtained. Slow evaporation of the filtrate lead to the formation of blue crystals in a yield of 64% based on Cu in a period of one week. $C_{21}H_{23}CuClN_6O_8$. Calcd. C 43.01, H 3.95, N 14.33%; found: C 43.22, H 3.98, N 14.40%. IR (KBr): 3379(s), 2397(w), 1641(s), 1361(s), 1119(s), 1080(s), 825(w), 684(w), 617(w), 470(w) (cm^{-1})

2.3 X-ray crystal structure determination

Single crystal X-ray diffraction analyses of complex **1** was carried out with a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by using a ω -scan mode. The structure of **1** was solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHELXL 97^[13]. Using Olex2^[14]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically

calculations, and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table 1. Selected bond and angle parameters are listed in Table 2.

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3. Results and discussion

3.1 Crystal structure of complex 1

Single crystal X-ray analysis reveals that complex **1** crystallizes in the triclinic $P-1$ space group. The structure of **1** consists of one copper ion, one L^- , one 4,4'-bipy, one perchlorate anion and three water molecules. The copper center is six-coordinate with three N from L^- , one N from the co-ligand 4,4'-bipy and two O from the H_2O molecule, forming a slightly distorted octahedron geometry as shown in Fig. 1. The equatorial plane is formed by four N atoms where three of which come from L^- and the fourth one from 4,4'-bipy. The apical positions are occupied by two O from H_2O . The longer average Cu-O bond distance of about 0.26 nm shows the weak bond interaction. The basal Cu-N bond lengths are in the normal range of 0.191 5(5) - 0.208 2(5) nm. The two monomer units are connected by the hydrogen bond of $O-H \cdots N$ between the hydrogen atoms from H_2O and the neighboring N from 4,4'-bipy to form a dimeric unit as shown in Fig. 2. The hydrogen bond distance $O-H \cdots N$ is 0.289 7nm.

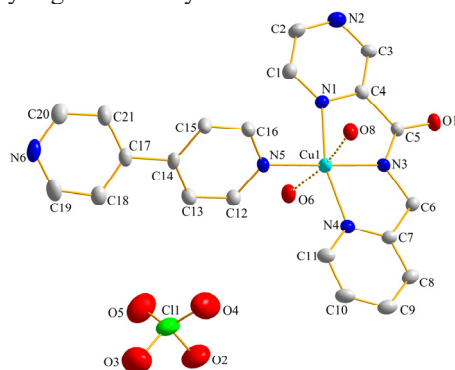
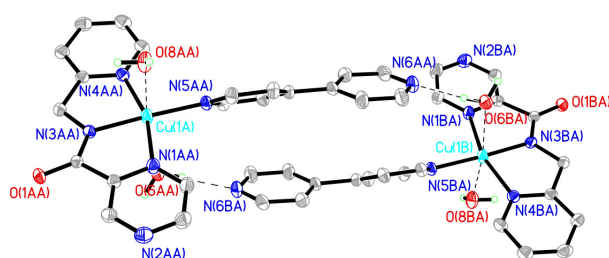


Fig.1 Molecular structure of the complex **1** shown with 30% probability displacement ellipsoids. Hydrogen atoms and the uncoordinated water molecule are deleted for clarity.



3.2 Powder X-ray diffraction(PXRD)

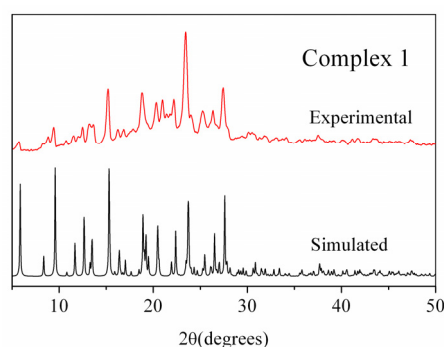


Fig.3 PXRD patters of complexes **1**

In order to check the phase purity of complex **1**, the X-ray powder diffraction (PXRD) patters were carried out at room temperature as shown in Fig.3. The peak positions of the simulated and experimental PXRD patters are in good agreement with each other, demonstrating the phase purity of the products. The different intensities may be assigned as the preferred orientation of the crystalline powder samples.

Conclusions

In summary, we successfully synthesized a new copper(II) complex derived from N-(pyridine-2-ylmethyl)pyrazine-2-carboxamide (HL), 4,4'-bipyridine and copper(II) perchlorate. Comparing with the a similar reported complex, the different coordination modes and geometries of the copper center reveal that different coordinating abilities of anions likely contribute to the varieties of the copper compounds.

Table 1 Crystal data and structure refinement for complex **1**

Complex	1
Empirical formula	C ₂₁ H ₂₃ CuClN ₆ O ₈
Formula weight	586.44
<i>T</i> /K	293(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> /nm	7.701 2(9)
<i>b</i> /nm	10.803 3(10)
<i>c</i> /nm	15.269 9(14)
α / (°)	81.802 (8)
β / (°)	84.229 (8)
γ / (°)	80.456 (8)
<i>V</i> /nm ³	123 6.2(2)
<i>Z</i>	2
<i>D_c</i> / (g. cm ⁻³)	1.576
μ /mm ⁻¹	1.050
<i>F</i> (000)	602
θ range/ (°)	2.69 ~ 25.02
Reflections collected/unique	7 855/4 360(<i>R</i> _{int} =0.0539)
Data / restraints / parameters	4 360/930/344
Final <i>R</i> indices (<i>I</i> > 2 δ (<i>I</i>))	<i>R</i> ₁ =0.0737, <i>wR</i> ₂ =0.1655
<i>R</i> indices (all data)	<i>R</i> ₁ =0.1251, <i>wR</i> ₂ = 0.2047
Goodness of fit on <i>F</i> ²	1.040

Table 2 Selected bond distances (nm) and angles (°) for complex **1**

Complex 1					
Cu1-N1	0.2082(5)	Cu1-N3	0.1915(5)	Cu1-N4	0.2039(5)
Cu1-N5	0.1998(5)				
N3-Cu1-N5	177.5(2)	N3-Cu1-N4	81.09(19)	N5-Cu1-N4	100.4(2)

N3-CuI-OI	80.96(19)	N5-CuI-NI	97.6(2)	N4-CuI-NI	162.0(2)
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Acknowledgments

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References

- [1] (a) Swiegers G F, Malefestse T J. (2000) New Self-Assembled Structural Motifs in Coordination Chemistry. *Chem. Rev.*,100:3483-3538.
- (b) Fromm K M. (2008) Coordination Polymer Networks with S-block Metal Ions. *Coord. Chem. Rev.*, 252: 856-885.
- [2] (a) Kaye S S, Daily A, Yaghi O M, Long J R.(2007) Impact of Preparation and Handling on the Hydrogen Storage Properties of Zn₄O(1,4-benzenedicarboxylate)₃(MOF-5). *J.Am.Chem.Soc.*, 139:14176-14177.
- (b) Horike S, Bureekaew S, Kitagawa S.(2008) Coordination Pillared-layer Type Compounds Having Pore Surface Functionalization by Anionic Sulfonate Groups. *Chem. Commun*, 471-473.
- [3] (a) Inoue K, Imai H, Ghalsasi P S, et al. (2001) A Three-Dimensional Ferrimagnet with a High Magnetic Temperature (T_c) of 53K Based on a Chiral Molecule. *Angew. Chem. Int.Ed.*40:4242-4245. (b) Shimomura S, Matsuda R, Tsujino T, et al. (2006) TCNQ Dianion-Based Coordination Polymer Whose Open Framework Shows Charge-Transfer Type Guest Inclusion. *J.Am.Chem.Soc.*,128:16416-16417.
- [4] Ma L, Lin W.(2008) Chirality-Controlled and Solvent-Templated Catenation Isomerism in Metal-Organic Frameworks. *J.Am.Chem.Soc.*130:13834-13835.
- [5] Seo J S, Whang D, Lee H, Jun S I, Oh J, Jeon Y J, Kim K.(2000).A Homochiral Metal-Organic Porous Material for Enantioselective Separation and Catalysis. *Nature*. 404:982-986.
- [6] Khavasi H R, Sadegh B M, Temperature-Dependent Supramolecular Motif in Coordination Compounds.(2010) *Inorg. Chem.* 49: 5356-5358.
- [7] F. Yu, X.-J.Kong, Y.-Y.Zheng, Y. P. Ren, L.-S.Long, R. B. Huang, L.-S. Zheng. pH-dependent assembly of 0D to 3D Keggin-based coordination polymers: Structure and catalytic properties. (2009) *Dalton Trans.*9503-9509.
- [8]Huang W, Jin, Y C, Wu D Y,Wu G H. Anion-Tunable Configuration Isomerism and Magnetic Coupling in a Tetranuclear Discrete, One-Dimensional(1D) Chiral Chain and 1D-Decker Copper(II) Complexes of a Carbohydrazine Derivative.(2014) *Inorg. Chem.* 53:73-79.
- [9] (a) Hausmann J, Jameson G B, Brooker S. Control of molecular architecture by the degree of deprotonation : self-assembled di- and tetranuclear copper(II) complexes of N,N-bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide. (2003) *Chem. Commun.* 2992-2993. (b)Hausmann J, Brooker S.Control of molecular architecture by use of the appropriate ligand isomer: a mononuclear “corner-type” versus a tetranuclear[2x2] grid-type cobalt(III) complex.(2004) *Chem. Commun.*1530-1531. (c)Klinge J, Boas J F, Pilbrow J R, Moubarki B, Murray K S, Berry K J, Hunter K A, Jameson G B, Boyd P D, Brooker S. A [2x2] nickel(II) grid and a copper(II) square result from differing binding modes of a pyrazine-based diamide ligand. (2007) *Dalton. Trans.* 633-645.
- [10]Cockriel D L, McClain J M, Patel K C, Ullon R, Hubin T J. The design and synthesis of pyrazine amide ligands for the “tiles” approach to molecular weaving with octahedral metal ions (2008) *Inorg. Chem. Commun*,11:1-4.
- [11]Khavasi H R, Sasan K, Pirouzmand M, Ebrahimi S N. Highly Efficient Isobutyraldehyde-Mediated Oxidation of Cyclic Alkenes with Dioxxygen Catalyzed by a Novel Dimeric Maganese (II) Complex Containing an Easy-to-Prepare Flexible Carboxamide Ligand. (2009) *Inorg.Chem.* 48, 5593-5595.
- [12] Houser R P, Wang Z D, Powell D R,Hubin T J.Copper(I) and copper(II) complexes with pyrazine-containing pyridylalkylamide ligands N-(pyridin-2-ylmethyl)pyrazine-2-carboxamide and N-(2-pyridin-2-yl)ethyl)pyrazine-2-carboxamide *Journal of Coordination Chemistry*, **2013**,66:4080-4092.
- [13] Sheldrick G M, *SHELXTL NT*, version 5.1, Program for Solution and Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, **1997**.
- [14] Dolomanov O V, Bourhis L J, Gildea R J,Howard J A K, Puschmann H. A complete structure solution, refinement and analysis program. (2009) *J. Appl. Crystallogr.* 42:339-341.