Synthesis and Structure of the Copper Complex \([\text{CuL}(4,4′\text{-bipy})(\text{H}_2\text{O})_2](\text{H}_2\text{O})(\text{ClO}_4)\]

Zhaodong Wang* 1

1 College of Chemistry and Environmental Engineering, Chongqing University of Arts And Sciences, Yongchuan 402160, China.
Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Yongchuan 402160, China.

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, \([\text{CuL}(4,4′\text{-bipy})(\text{H}_2\text{O})_2](\text{H}_2\text{O})(\text{ClO}_4)\) (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 mental 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.

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\text{Scheme. 1 Structure of HL and 4,4′-bipy used in this work}
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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...
with a Perkin-Elmer 2400 Series II analyzer. Powder X-ray diffraction (PXRD) was performed on a Shimadzu XRD-6000 instrument by using Cu Kα radiation at room temperature.

2.2 Synthesis of [CuL(4,4′-bipy)(H₂O)₂]ClO₄ (I)

A solution of Cu(ClO₄)₂·6H₂O (0.0926 g, 0.25 mmol) in methanol was added to a solution of HL (0.0535 g, 0.25 mmol) and triethylamine (25.0 mg, 0.25 mmol) in methanol, leading to the formation of dark blue solution, then, the methanoic solution of 4,4′-bipy (0.0392 g, 0.25 mmol) 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. C₃₁H₂₃CuClN₆O₈: 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 I was carried out with a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) by using a ω-scan mode. The structure of I was solved by direct methods and refined by full-matrix least-squares methods on F² using the program SHEXL 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.

CCDC: 1487818, I.

3. Results and discussion

3.1 Crystal structure of complex I

Single crystal X-ray analysis reveals that complex I crystallizes in the triclinic P-1 space group. The structure of I 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 H₂O 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 H₂O. 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 0.1915(5) -0.2082(5) nm. The two monomer units are connected by the hydrogen bond of O-H···N between the hydrogen atoms from H₂O and the neighboring N from 4,4′-bipy to form a dimeric unit as shown in Fig. 2. The hydrogen bond distance O-H···N is 0.2897 nm.

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

Fig. 2 Intermolecular hydrogen bonding diagram of complex I
3.2 Powder X-ray diffraction (PXRD)

In order to check the phase purity of complex 1, the X-ray powder diffraction (PXRD) patterns were carried out at room temperature as shown in Fig.3. The peak positions of the simulated and experimental PXRD patterns 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 |
| T/K               | 293(2) |
| Crystal system    | Triclinic |
| Space group       | P-1 |
| a/nm              | 7.701 2(9) |
| b/nm              | 10.803 3(10) |
| c/nm              | 15.269 9(14) |
| α/°               | 81.802 (8) |
| β/°               | 84.229 (8) |
| γ/°               | 80.456 (8) |
| V/nm³             | 123 6.2(2) |
| Z                 | 2 |
| D₀/ (g. cm⁻³)     | 1.576 |
| μ/mm⁻¹            | 1.050 |
| F(000)            | 602 |
| θ range/ (°)      | 2.69 ~ 25.02 |
| Reflections collected/unique | 7 855/4 360 (R_{int}=0.0539) |
| Data / restraints / parameters | 4 360/930/344 |
| Final R indices (I>2σ(I)) | R₁=0.0737, wR₂=0.1655 |
| R indices (all data) | R₁=0.1251, wR₂= 0.2047 |
| Goodness of fit on F² | 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) |
Acknowledgments

This research work is supported by the Chongqing University of Arts and Sciences major scientific research project Cultivation Fund (P2017CH110); Chongqing Yongchuan District Science and Technology Bureau Natural Science Foundation program funded project (2020nb0224)

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