

A Novel Azide Copper Complex: [[Azido{bis[2-(piperidin-1-ylmethyl)pyridine]}copper(II)]perchlorate] Hydrate¹

C. F. Wang*, Z. L. Zhang, Y. L. Wang, and G. L. Dai

School of Pharmaceutical and Chemical Engineering, Taizhou University, Linhai, Zhejiang 317000, P.R. China

*e-mail: 041022032@fudan.edu.cn

Received February 3, 2009

Abstract—Synthesis and single crystal X-ray diffraction study were carried for compound $\{[\text{Cu}(\text{C}_{11}\text{H}_{16}\text{N}_4)_2(\text{N}_3)](\text{ClO}_4)\} \cdot \text{H}_2\text{O}$ (**I**). The structure is molecular, and the Cu^{2+} ion is in a five-coordinated compressed trigonal bipyramid environment. Copper ion is bound to five N atoms, in which four N atoms are from two chelating ligands 2-(piperidin-1-ylmethyl)pyridine and the fifth N donor is from a monodentate azido ligand. The complex cations $[\text{Cu}(\text{C}_{11}\text{H}_{16}\text{N}_4)_2(\text{N}_3)]^+$, the perchlorate anions, and solvent water molecules are further joined into three dimensional supramolecular networks by rich hydrogen bonds including strong $\text{O}-\text{H}\cdots\text{N}$ between solvent water and azide ion and $\text{O}-\text{H}\cdots\text{O}$ between solvent water and perchlorate ion, and weak hydrogen bonds $\text{C}-\text{H}\cdots\text{O}$, and weak bifurcated hydrogen bonds $\text{C}-\text{H}/\text{C}-\text{H}\cdots\text{N}$ in which N atom of azide ion serving as bifurcated acceptor and two C–H groups as donors.

DOI: 10.1134/S1070328409100145

INTRODUCTION

Metallosupramolecular polymers are new functional polymers that are composed of monomeric units held together by kinetically stable metal ligand interactions. They possess useful properties such as in optical, electronic, and magnetic area [1], which are expected to have potential applications in many fields such as biomedicine [2], nanomaterials science [3], and catalysis [4].

Derivatives of pyridine play a pivotal role in modern coordination chemistry, and a number of complexes with these ligands have been synthesized and characterized. The flexible azide ion is one of the most versatile ligands, which provide coordination compounds of great structural and qualitative variety [5–8].

We are interested in coordination chemistry, structure, and properties of the azide complex. As our continuing research results, herein we report a novel copper complex with 2-(piperidin-1-ylmethyl)pyridine (**L**) and azido ligand (**I**).

EXPERIMENTAL

All chemicals were of reagent grade, obtained commercially from Adrich, and used without further purification.

Synthesis of ligand L. 2-Picolyl chloride hydrochloride (10 mmol) and triethylamine (3 ml) were added to a solution of piperidine (10 mmol) in acetonitrile (30 ml). This reaction mixture was stirred for 48 h at room temperature and then poured into a solution of sodium hydroxide (1 M, 40 ml). After being extracted with dichloromethane (2×40 ml) and dried (MgSO_4), a brown solid crude product was obtained through evaporation. The crude product was dissolved in ethyl ether (25 ml), decolorized, and subsequently evaporated to give colorless crystalline solid of the ligand.

Synthesis of complex I. 5 ml of an aqueous solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.186 g, 0.5 mmol) and 5 ml of an aqueous solution of NaN_3 (0.065 g, 1 mmol) were added to a solution of the ligand (0.088 g, 0.5 mmol) in water (30 ml) in turn. The mixture was filtered, and the bluish green filtrate was left to stand at room temperature. Blue block crystal of **I** appeared after several days. The yield was 0.220 g (76%).

For $\text{C}_{22}\text{H}_{34}\text{ClN}_7\text{O}_5\text{Cu}$ ($M = 575.55$)

anal. calcd, %: C, 45.98; H, 5.97; N, 17.07.

Found, %: C, 45.91; H, 5.92; N, 17.29.

Elemental analyses (C, H, N) were performed on a Perkin Elmer 240 analyzer. IR spectra were recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan microscope in the range 4000–400 cm^{-1} . Main peaks (cm^{-1}): 2048 and 1093, the two

¹ The article is published in the original.

Table 1. Crystallographic data and details of the experiment and refinement of structures **I**

Parameter	Value
Crystal system	Orthorhombic
Space Group	$Pca2_1$
a , Å	17.3071(3)
b , Å	9.86630(10)
c , Å	15.4404(2)
V , Å ³	2636.56(6)
Z	4
μ , mm ⁻¹	0.976
ρ_{calcd} , g/cm ³	1.450
Size, mm	0.55 × 0.40 × 0.35
Color	Blue
θ range, deg	3.395–27.485
Measured/independent reflections	57262/5808
Goodness of fit on F^2	1.018
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0390$
R indices (all data)	$R_1 = 0.0658$, $wR_2 = 0.1042$
Residual electronic density (max/min), $e \text{ \AA}^{-3}$	0.864 and -0.712

Table 2. Selected bonds (Å) and angles (deg) for **I**

Bond	d , Å	Bond	d , Å
Cu(1)–N(1)	1.969(3)	Cu(1)–N(2)	2.139(3)
Cu(1)–N(3)	1.974(3)	Cu(1)–N(4)	2.204(3)
Cu(1)–N(5)	2.051(4)	N(5)–N(6)	1.188(5)
Cu(1)–N(2)	2.139(3)	N(6)–N(7)	1.167(6)
Cu(1)–N(4)	2.204(3)		
Angle	ω , deg	Angle	ω , deg
N(1)Cu(1)N(3)	177.42(14)	N(1)Cu(1)N(4)	97.65(12)
N(1)Cu(1)N(5)	90.93(14)	N(3)Cu(1)N(4)	80.98(12)
N(3)Cu(1)N(5)	91.63(14)	N(5)Cu(1)N(4)	113.00(13)
N(1)Cu(1)N(2)	81.71(13)	N(2)Cu(1)N(4)	118.86(12)
N(3)Cu(1)N(2)	97.02(12)	N(6)N(5)Cu(1)	120.9(3)
N(5)Cu(1)N(2)	128.13(13)	N(7)N(6)N(5)	178.1(5)

sharp strong bands are assignable to the azido asymmetric $\nu_{as}(\text{N}_3)$ stretching mode and symmetric $\nu_s(\text{N}_3)$ stretching mode.

Crystals for X-ray structural study were picked from the reaction mixture. The experiment was carried out on a Bruker–Nonius Kappa CCD diffractometer at room temperature (296(2) K). Crystal data and details of experiment are listed in Table 1. All calculations were performed with the SHELX–97 program package [9]. Selected bonds and angles are given in Table 2.

RESULTS AND DISCUSSION

Molecular structures and crystal packing are illustrated in Figs. 1 and 2, respectively. Each Cu^{2+} ion is planar coordinated by three N atoms (two of piperidine rings and one of azido ligand) and axially bonded by two N atoms of pyridine ring. The Cu–N bond lengths are situated in a common range from 1.969 to 2.204 Å that are comparative to other azido copper complexes [10]. Interestingly, there are shorter axial bonds Cu–N(1) and Cu–N(3) (1.969 to 1.974 Å, respectively) and longer equatorial plane bonds Cu–N(5), Cu–N(2), and Cu–N(4) (2.051, 2.139, and 2.204 Å, respectively).

Thus, the coordination geometry of Cu^{2+} ion can be illustrated as a compressed trigonal bipyramid CuN_5 due to the Jahn–Teller effect of the copper ion (d^9). The length differences of the equatorial plane bonds Cu–N may derive from the steric effects of the coordinating N atoms. While the two L ligands are both acting in chelating fashion, the azido ligand just serves as a monodentate one. As a result, the complex $[\text{Cu}(\text{C}_{11}\text{H}_{16}\text{N}_4)_2(\text{N}_3)]$ units have been formed into cations, which are countered by perchlorate ions. To the azido group, the N(5)–N(6) distance is 1.188(5) Å, thus it's a double bond; the N(6)–N(7) distance is 1.167(6) Å, its bond order lies between two and three. However, the azido group is nearly linear with an angle of 178.1(5)° for N(5)N(6)N(7). There is an angle of 120.9(3)° between the azide ion and the coordinative bond Cu–N(5). The formation of this angle may give access to the existence of hydrogen bond O(5)–H...N(5) (O...N 2.910 Å, OHN angle 162°) between solvent water and azide ion, and the inclusion of solvent water in the crystal packing.

Furthermore, the complex cations $[\text{Cu}(\text{C}_{11}\text{H}_{16}\text{N}_4)_2(\text{N}_3)]^+$, the perchlorate anions, and solvent water molecules are joined into two-dimensional

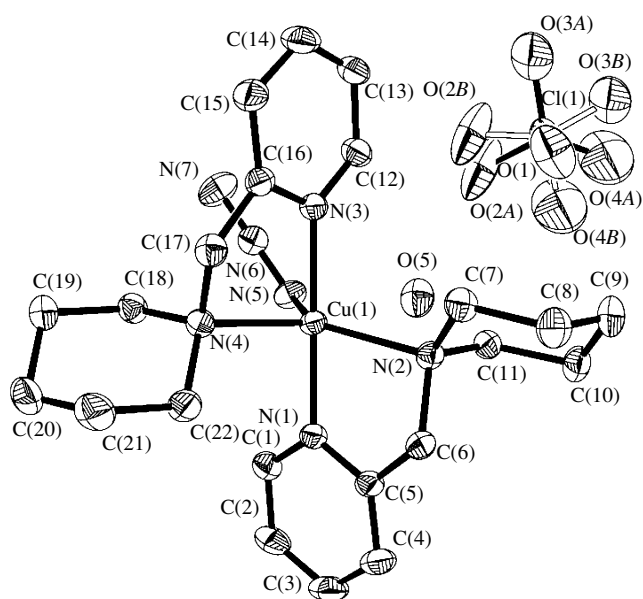


Fig. 1. The molecular structure of **I**, showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and all H atoms were omitted.

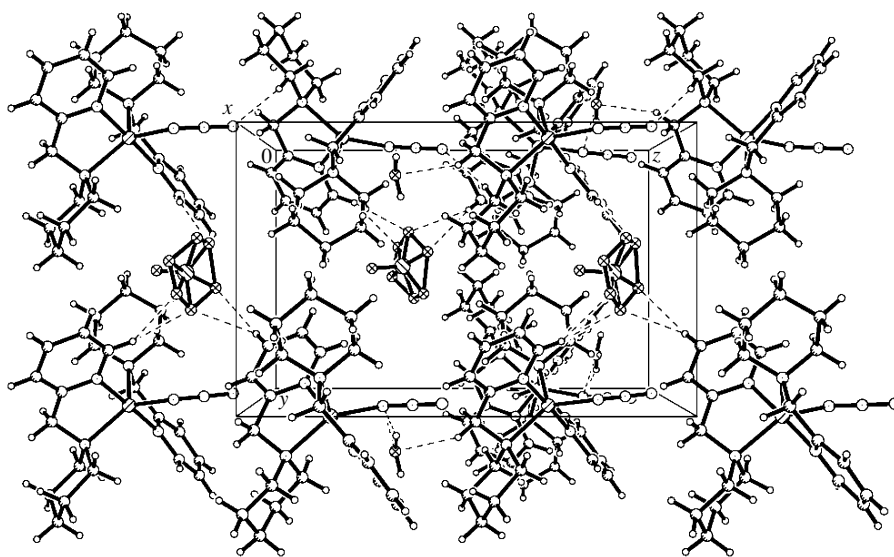


Fig. 2. A view of the packing down the z axis for structure **I**. Hydrogen bonds are shown as dotted lines.

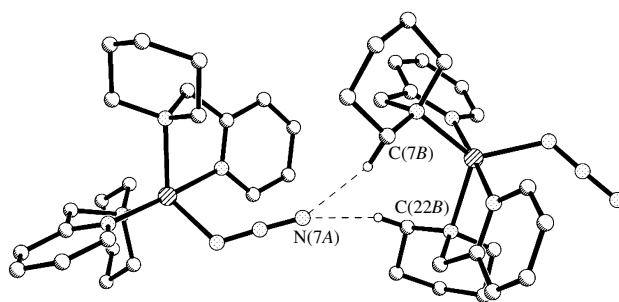


Fig. 3. A view down the y axis for **I**. Hydrogen bonds are shown as dotted lines.

supramolecular networks by both strong hydrogen bonds O(5)–H···N(5) (between solvent water and azide ion) and O(5)–H···O(2) (O···O 2.715 Å, OHO angle 163°) (between solvent water and perchlorate ion), and weak hydrogen bonds C(1)–H···O(1) (C···O 3.505 Å, CHO angle 162°). Then by another weak bifurcated hydrogen bonds C(7)–H/C(22)–H···N(7) (C···N 3.460 Å, CHN angle 130°; 3.555 Å, 126°, respectively) in which N atom of azide ion serves as bifurcated acceptor and two piperidine C–H groups as donors (Fig. 3). Therefore, a three-dimensional supramolecular networks has been built.

REFERENCES

1. Schubert, U.S. and Eschbaumer, C., *Angew. Chem. Int. Ed.*, 2002, vol. 41, p. 2892.
2. Zhou, M. and Roovers, J., *Macromolecules*, 2001, vol. 34, p. 244.
3. Oh, M. and Mirkin, C.A., *Nature*, 2005, vol. 438, p. 651.
4. Oh, M. and Mirkin, C.A., *Angew. Chem. Int. Ed.*, 2006, vol. 45, p. 5492.
5. Rakitin, Y.V. and Kalinnikov, V.T., *Russ. Chem. Bull. Int. Ed.*, 2004, vol. 53, p. 766.
6. Halcrow, M.A., Huffman, J.C., and Christou, G., *Angew. Chem. Int. Ed.*, 1995, vol. 8, p. 889.
7. Ribas, J., Escuer, A., Monfort, M., et al., *Coord. Chem. Rev.*, 1999, vol. 193–195, p. 1027.
8. Bai, S.Q., Fang, C.J., and Yan, C.H., *Chin. J. Inorg. Chem.*, 2006, vol. 12, p. 2123.
9. Sheldrick G.M., *SHELX-97, Release 97-1*, Göttingen (Germany): Univ. of Göttingen, 1997.
10. Aronica, C., Jeanneau, E., El Moll, H., et al., *Chem. Eur. J.*, 2007, vol. 13, p. 3666.