

Communication

2D Hydrogen Bonded Copper (II) Coordination Network Constructed by the Combination of Flexible and Rigid Ligands

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Complex $[\text{Cu}(2,2'\text{-bipy})(\text{H}_2\text{L}^1)](\text{ClO}_4)_2$ (**1**) has been synthesized by the self-assembly of $\text{Cu}(\text{ClO}_4)_2$ with a rigid ligand 2,2'-bipyridine and a flexible potential tetradentate ligand *N,N'*-bis(hydroxyethyl)ethylenediamine (H_2L^1). Crystal analyses reveal that the potentially tetradentate ligand H_2L^1 acts in a tridentate mode by the coordination of one hydroxyl oxygen atom and two amino nitrogen atoms. The Cu(II) atom coordinates additionally with two bipyridyl nitrogen atoms, giving a distorted square pyramidal geometry. Each complex molecule is connected with four surrounding molecules along the *ac* plane by multiple hydrogen bonds, leading to 2D sheets constituted with $0.7874 \text{ nm} \times 1.0891 \text{ nm}$ metallomacrocyclic rectangles. Each vertex of the rectangle is occupied by a copper atom, and the four sides are comprised of multiple hydrogen bonds.

Keywords Self-assembly, hydrogen bonds, copper(II) complex, 2D networks

The self-assembly of metal coordination supramolecular structures is one of the most active topics of current chemistry due to their potential applications in catalysis,¹ host-guest chemistry² and molecular electronics.³ Combination of metal ions and ordered hydrogen-bonding to build a variety of architectures has caused growing interests.⁴⁻⁷ Conformational rigid ligands, such as 4,4'-bipyridine, are commonly utilized in these cases in order to reduce the unfavorable entropic factors⁸ in the process of constructing supramolecular assemblies with predictable structures. In contrast to this, the application of flexible ligand to build metal-containing hydro-

gen-bonded network still remains relatively unexplored.⁹⁻¹¹ Whereas, self-assemblies of flexible components driven together by weak interactions, including hydrogen bonds, are essential in many biological processes.⁸ The relationships between the structures of the flexible ligands and the supramolecular coordination structures need further investigations.

In this work, a mixed ligands complex $[\text{Cu}(2,2'\text{-bipy})(\text{H}_2\text{L}^1)](\text{ClO}_4)_2$ (**1**) has been self-assembled from the reaction system of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with a rigid ligand 2,2'-bipyridine and a flexible potentially tetradentate ligand *N,N'*-bis(2-hydroxyethyl)ethylenediamine (H_2L^1) which has complementary groups as donors and acceptors for hydrogen bonding. X-ray structure reveals that **1** forms a 2D supramolecular structure through the multiple hydrogen-bonding connections. $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.148 g, 0.40 mmol), H_2L^1 (0.0593 g, 0.40 mmol), 2,2'-bipyridine (0.0625 g, 0.40 mmol) and aqueous NaOH (0.20 mL 4.0 mol/L, 0.80 mmol) were added to 100 mL of methanol. The resulting solution was refluxed for 3 h, and concentrated *in vacuo*. The resulting green powder was collected, washed with ether and dried. Yield 97%, 0.22 g. Crystals suitable for X-ray analysis were grown by slow evaporation of a methanol solution of the complex. The structure of **1** was established by X-ray analysis.¹² Selected bond lengths and angles for **1** are listed in Table 1. The copper center adopts a distorted square pyramidal geometry (Fig. 1) by coordinating to two bipyridyl nitrogen

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atoms, N(1) and N(2), two amino nitrogen atoms, N(3) and N(4), and one hydroxyl oxygen atom O(2) from the ligand H_2L^1 . The Reedijk distortion index τ^3 ($\tau = 0$ for a square pyramid, and $\tau = 1$ for a trigonal bipyramid) value for Cu(1) is 0.28. The nitrogen atoms N(1), N(2), N(3) and N(4) constitute the base of the pyramid with Cu—N distances in the range of 0.2006—0.2049 nm, consistent with other basal distances of square pyramidal copper complexes;¹⁴ whereas O(2) occupies the apical position with a Cu—O distance of 0.2255(3) nm. Each ring of the bipyridyl ligand is nearly coplanar; the angle between the two pyridyl rings is extremely high,¹⁵ with a value of 23.8(1)°. It is worth noting that the symmetrical potential tetradentate ligand H_2L^1 acts as an unsymmetrical tridentate ligand by the coordination of the two nitrogen atoms and one hydroxyl oxygen atom O(2) to the copper(II) atom, leaving the other oxygen atom O(1) to form the outer-sphere hydrogen-bonding.

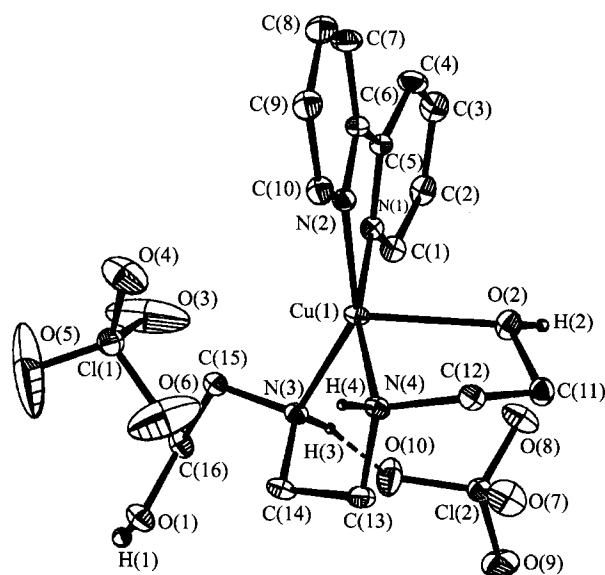


Fig. 1 View of $[Cu(2,2'\text{-bipy})(H_2L^1)](ClO_4)_2$ (**1**) molecular structure showing the numbering scheme at the 30% probability level with the H atoms omitted for clarity.

Table 1 Selected bond lengths (nm) and angles (deg) for **1**

Cu(1)—N(1)	0.2016(3)	Cu(1)—N(2)	0.2027(3)
Cu(1)—N(3)	0.2049(3)	Cu(1)—N(4)	0.2006(3)
Cu(1)—O(2)	0.2255(3)		
N(4)—Cu(1)—N(1)	164.82(12)	N(4)—Cu(1)—N(2)	101.81(12)
N(1)—Cu(1)—N(2)	81.34(13)	N(4)—Cu(1)—N(3)	85.87(13)
N(1)—Cu(1)—N(3)	99.27(13)	N(2)—Cu(1)—N(3)	148.28(12)
N(4)—Cu(1)—O(2)	79.21(12)	N(1)—Cu(1)—O(2)	85.66(11)
N(2)—Cu(1)—O(2)	98.01(12)	N(3)—Cu(1)—O(2)	113.68(12)

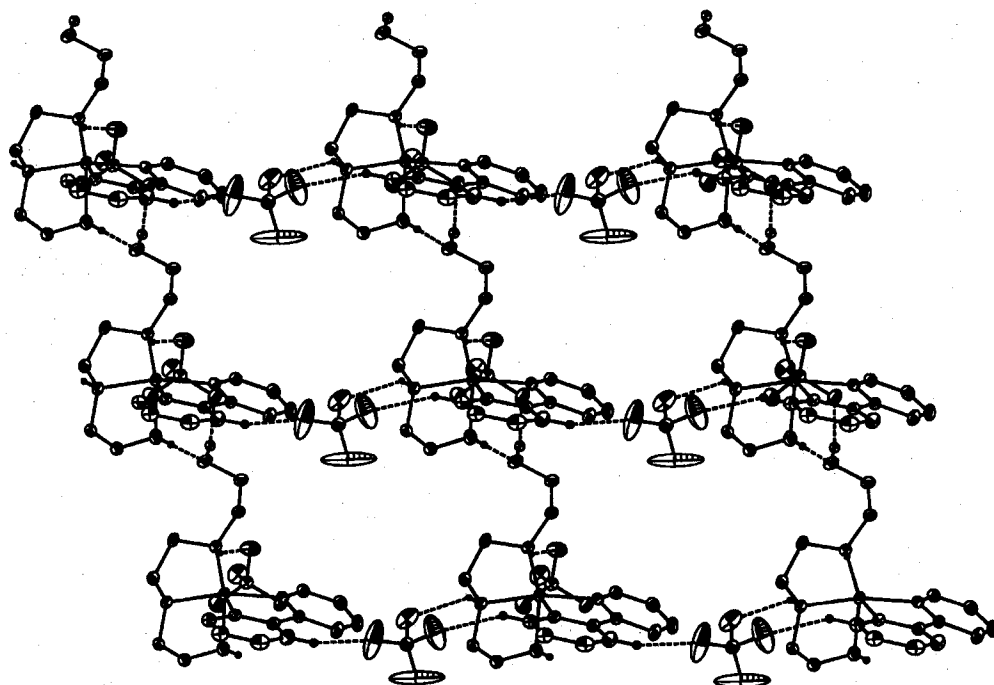
Approximately along the *ac* plane of the crystal structure, each complex molecule is connected with four surrounding molecules by multiple hydrogen bonds¹⁶ (Table 2), leading to 2D sheets constituted with 0.7874 nm × 1.0891 nm metallomacrocyclic rectangles (Fig. 2). Each vertex of the rectangle is occupied by a copper ion. The four sides are comprised of multiple hydrogen bonds, *i. e.*, N(3)—H, N(4)—H and pyridyl C—H groups act as proton donors; the perchlorate anions act as proton acceptors; and the uncoordinated O(1)—H groups act as both donors and acceptors at the same time. The pyridyl rings in one sheet are exactly fitted in the rectangles of a neighboring sheet. The unfavorable

entropic factors for the flexible ligand in the process of forming the ordered supramolecular structure can be overcome by the extra stability contributed by the multiple hydrogen bonds.

In conclusion, it has been shown that the copper(II) complex of the rigid ligand 2,2'-bipyridine and the flexible ligand H_2L^1 forms an ordered supramolecular structure of metallomacrocyclic rectangles. The hydrogen bonding interaction involved here is important in construction of the supramolecular structure. H_2L^1 is a good organic ligand which can afford multiple donors and acceptors for hydrogen bonding to build various supramolecular structures.

Table 2 Hydrogen-bonds for **1** (nm and deg)

D—H	d (H···A)	∠DHA	d (D···A)	A (symmetry operations)
O(1)—H(1)	0.2154	169.91	0.2882	O(8) [x+1, y, z]
O(2)—H(2)	0.1897	177.32	0.2758	O(1) [x-1, y, z]
N(3)—H(3)	0.2492	153.60	0.3121	O(10)
C(7)—H(7A)	0.2551	145.89	0.3362	O(3) [-x+1, -y+1, -z+1]
C(15)—H(15B)	0.2528	139.19	0.3323	O(3)
N(4)—H(4)	0.2511	138.05	0.3176	O(4) [-x+1, -y+2, -z]
C(10)—H(10A)	0.2581	140.02	0.3347	O(6) [-x+1, -y+2, -z]

**Fig. 2** 2-D sheet of complex **1** consisted of metallomacrocylic rectangles approximately along the ac plane.**References and notes**

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- [Cu(2,2'-bipy)(H₂L¹)](ClO₄)₂ (**1**) IR (KBr) *v*: 3443br, 3245s, 2937, 1606, 1500, 1479, 1444, 1321, 1251, 1087, 925, 887, 767, 733. Anal. calcd for C₁₆H₂₄Cl₂CuN₄O₁₀: C 33.90, H 4.27, N 9.88; found C 34.14, H

- 4.66, N 10.00. Crystal data for **1**: $C_{16}H_{24}Cl_2CuN_4O_{10}$, $M_r = 566.83$, monoclinic, space group $P2(1)/n$, $a = 0.78740(16)$, $b = 2.7174(5)$, $c = 1.0891(2)$ nm, $\beta = 105.64(3)^\circ$, $V = 2.2441(8)$ nm³, $Z = 4$, $T = 293(2)$ K, $\mu(\text{Mo } K_\alpha) = 1.272$ mm⁻¹. Goodness-of-fit on F^2 was 1.145. $R_1[\text{for } I > 2\sigma(I)] = 0.0637$, $wR_2 = 0.1644$. All measurements were made on a Rigaku RAXIS-IV image plate area detector. The structure was solved by direct methods using SHELXTL-97.
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- The occurrence of the hydrogen bonds (D—H \cdots A) can be inferred from the atom distances. For all the listed hydrogen bonds in this work, the A \cdots H distances are at least 0.01 nm less than the Van der Waals contact distances, and the A \cdots D distances are less than 0.34 nm apart.

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