Deprotonated Copper(II) Complex with a Tripod Ligand Involving Three Imidazole Groups: A Two-Dimensional Chiral Honey-Comb Structure Made by Hydrogen Bonds

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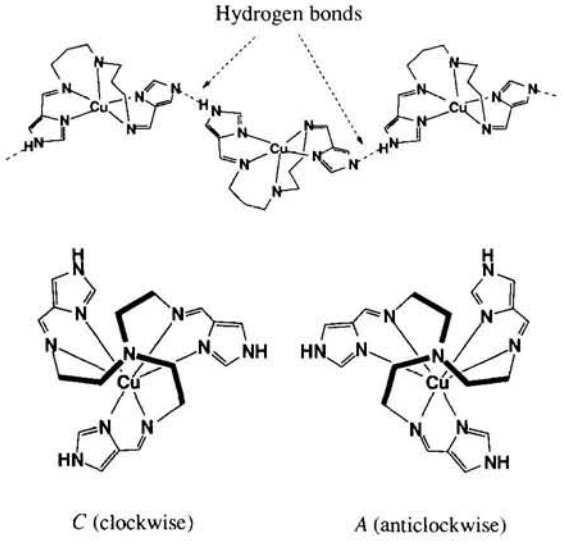
Synthesis and X-ray crystal structure of the deprotonated complex with a tripod hexadentate ligand involving three imidazole groups were reported. The deprotonated complex assumed a chiral two-dimensional quasi-honey-comb structure made by the network of hydrogen bonds.

The design and synthesis of hydrogen-bonded molecular architecture have attracted much attention in the fields of new functional materials and crystal engineering.[1] In the previous paper,[2] we reported an enantioselective self-assembly behavior of the copper(II) complex with the linear pentadentate Schiff-base ligand, *N,N'*-bis(2-methyl-imidazol-4-yl)methylene)-3,3'-diaminopropylamine, (Scheme 1). The mono-deprotonated complex assumes enantiomers of *C* (clockwise) and *A* (anticlockwise) due to the spiral arrangement of the strand ligand and functions as a chiral building component. They aggregate due to the hydrogen bond between the imidazole group of a unit and the imidazolate group of the adjacent unit to give a one-dimensional zigzag-chain with homochirality described as *CCC*... and *AAA*... As our continuing interest to create new hydrogen-bonded functional materials, we investigated the copper(II) complex of a tripod hexadentate ligand involving three imidazole groups, *N,N',N''*-tris(imidazol-4-ylmethylideneethyl)amine (H_3L), **1**. We report the chiral two-dimensional quasi-honey-comb structure made by the hydrogen bonds of the deprotonated complex **1'**.

Scheme 1.



Molecular structure of 1.

The tripod hexadentate ligand H_3L was prepared by mixing 4-formylimidazole and tris(2-aminoethyl)amine with the 3:1 molar ratio in methanol and the resulting solution was used without the isolation of the ligand for the synthesis of the copper(II) complex. The protonated copper(II) complex **1** was prepared by mixing the ligand solution and copper(II) nitrate trihydrate in methanol with the 1 : 1 molar ratio. **1** was obtained as green plates in 42% yield. The C, H, and N microanalysis agreed with the formula $[Cu(H_3L)](NO_3)_2 \cdot 0.5H_2O$. Treatment of **1** with 2 equivalent amounts of triethylamine gave the deprotonated complex **1'** as green microcrystals in 78% yield. The elemental analysis agreed with $[Cu(H_{1.5}L)](NO_3)_{0.5} \cdot 0.5H_2O \cdot 0.5CH_3OH$, indicating that 1.5 proton per Cu dissociated.[3] The IR spectrum of **1'** showed the characteristic bands assignable to the C=N stretching vibration of the Schiff-base ligand at 1640 – 1615 cm^{-1}, the N–O vibration of the nitrate ion at 1385 cm^{-1}, and the broad absorption bands with fine structures in the region 2700 – 2300 cm^{-1} which suggest the presence of the stretching vibration of N–H groups associated with H-bonding interaction.[4] The magnetic susceptibility on the powdered sample was measured in the range of 2.0 – 300 K. The magnetic moment was practically constant in the temperature range 10 – 300 K and showed a slight decrease from 1.76 μ_B at 10 K to 1.59 μ_B at 2 K. The magnetic data indicated that the magnetic interaction through the hydrogen bonds is presumed to be very weak.

The circular dichroism (CD) spectrum of a piece of crystal **1'** was measured as a KBr disc. The spectrum showed a positive CD band at 316 nm. Another crystal showed an enantiomeric CD pattern. These results indicate that spontaneous resolution took place in the process of crystallization, and this was confirmed by the X-ray crystal structure analysis.

The crystal structure of a piece of crystal **1'** was determined by the single-crystal X-ray analysis.[5] **1'** crystallizes in a noncentrosymmetric trigonal space group *P*321. The asymmetric unit consists of 1/3[$Cu(H_{1.5}L^1)$], 1/6NO_3^- and 1/3CH_3OH. The copper and the central nitrogen atom of the tripod ligand are found at the special positions and lie on the three-fold rotation axis. The nitrate ions as the counter anion and the methanol molecules as the crystal solvent are located in the hexagonal hole, in which no short contacts suggesting hydrogen bond were observed. As shown in Figure 1, the copper(II) ion is coordinated octahedrally by the N_6 donor atoms of the tripod ligand, and the Cu–N(2) and Cu-N(3) distances are 2.142(7) and 2.101(8) Å, respectively. The distance of Cu–N(1) is 3.188(9) Å, indicating that the central nitrogen atom does not participate in coordination. The parameter representing the deviation from octahedron to trigonal prism is α = 47.1(4)°, where the α values of ideal octahedron and trigonal prism are 60° and 0°, respectively. There are two possible configurations for the metal complex with the tripod-ligand,

clockwise (*C*) and anticlockwise (*A*) configurations. The Frack parameter, that is used to determine the absolute configuration, indicated that the crystal consists of a molecule with *A* configuration. Each copper(II) complex is linked intermolecularly by the hydrogen-bond between the imidazole group of a molecule and the imidazolate group of the adjacent molecule with the N···N distance of 2.72(2) Å. As the result, a two-dimensional quasi-honey-comb layer structure is formed, as shown in Figure 2. The layers are stacked along the *c* axis. The noteworthy character of the crystal structure is that the unit molecule functions as a chiral building component and the molecules with homochirality aggregate due to the hydrogen bonds described as *AAA*... to give the chiral crystal with noncentrosymmetric space group.

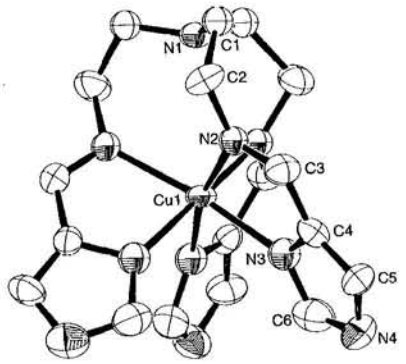


Figure 1. An ORTEP view of the deprotonated copper(II) complex with the tripod-type ligand, showing 30 % probability ellipsoids.

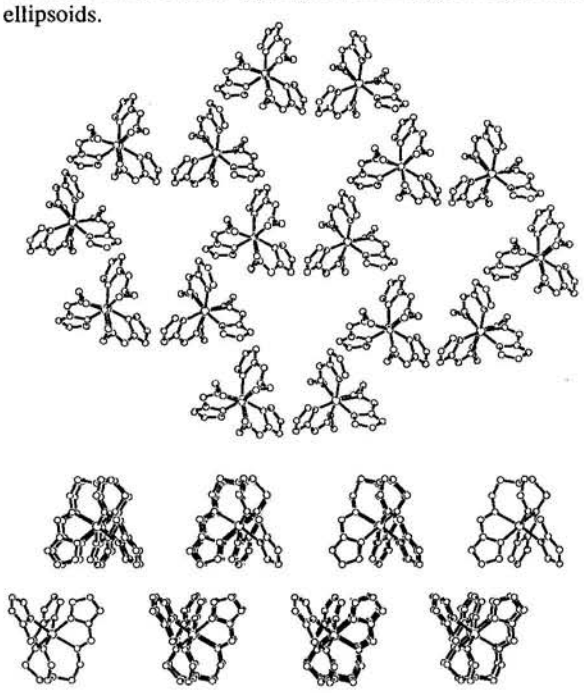


Figure 2. Chiral two-dimensional quasi-honey-comb structure made by hydrogen bonds. The nitrate ion and methanol molecule are omitted. (top) quasi-honey-comb structure, (bottom) a side-view showing layer structure.

The results provide a promising way for a pH-dependent host-guest chemistry and construction of chiral multi-dimensional architecture by modifying this system.

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References and Notes

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2 a) H. Miyasaka, S. Okamura, T. Nakashima, and N. Matsumoto, *Inorg. Chem.*, **36**, 4329 (1997). b) Y. Shii, M. Mimura, T. Matsuo, Y. Motoda, F. Kai, T. Nakashima, and N. Matsumoto, to be submitted.

3 The selected analytical data for **1** and **1'**: **1**: Found: C, 37.47%; H, 4.43%; N, 28.96%. Calcd for $C_{18}H_{25}N_{12}O_{6.5}Cu$: C, 37.46%; H, 4.37%; N, 29.14%. IR(KBr): $\nu_{N\text{-}H}$, 3125; $\nu_{C=N}$, 1640; $\nu_{N\text{-}O}$, 1380 cm^{-1}. UV/vis in H_2O [λ_{max}/nm (ε/dm^3 cm^{-1} mol^{-1})]: 728(132). $\Lambda_M(H_2O)$: 218 S mol^{-1} cm^2. Mp: > 280°C. **1'**: Found: C, 44.54%; H, 5.20%; N, 29.42%. Calcd for $C_{18.5}H_{25.5}N_{10.5}O_{2.5}Cu$: C, 44.57%; H, 5.16%; N, 29.51%. IR(KBr): $\nu_{N\text{-}H}$, 3120; $\nu_{C=N}$, 1640 – 1620; $\nu_{N\text{-}O}$, 1390 cm^{-1}. Mp: > 280°C.

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5 Single crystal of **1'** was obtained from slow evaporation of the methanol solution. Crystal data: $C_6H_{7.5}N_{3.5}O_{0.83}Cu_{0.33}$, FW = 162.95, green crystal with 0.2 × 0.2 × 0.3 mm^3, trigonal, space group *P*321, a = 12.065(2), c = 9.629(1) Å, V = 1213.9(4) Å^3, Z = 6, D_{calc} = 1.337 g cm^{-3}, absolute structure parameter[6] x = 0.04, S = 1.50, R = 0.054 and R_w = 0.043, 589 reflections with $I > 3\sigma(I)$. The hydrogen atom bonded to imidazole nitrogen atom N(4) is placed at the calculated positions and the population was set to be 0.5.

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