$Cu_2(C_3H_2N_3O_3)_2(C_{10}H_8N_2)$: A Hydrogen-bonded Assemblies Supermolecule Containing 1D Channels and Novel Two-coordinated Linear N–Cu–N Configurations

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The title compound was successfully synthesized by the simple hydrothermal route. Interestingly, the title compound exhibits a rare two-coordinated linear N–Cu–N configuration around cuprous ions. Furthermore, the title compound is stacked via hydrogen-bond assembly in three dimensions to form the supermolecule with a channel of 3.98(5) × 8.81(1) Å along the *b* axis, which may be useful in studying the porous coordination materials.

It is well known that the low-coordinated copper(I) compounds are very important in biological systems, playing an important role in living organisms.[1] It is involved in biochemical oxidation–reduction processes, in electron transfers, as well as in the reversible binding of small gaseous molecules such as O_2 (Hemocyanin) or the plant hormone ethylene.[2] Therefore, the coordination chemistry of low-coordinate copper(I) compounds is important to understand the metal reactivity. The early assumption of species such as $[Cu(NH_3)^2]^+$ suggested that two-coordination would be common for Cu^I ions, but subsequent studies have proved that two-coordinated copper(I) compounds are rather rare among their inorganic complexes.[3] Up to date, two-coordination copper(I) complexes have been prepared only with anionic ligands such as halide, cyanide, and neutral ligands including NH_3 and amines.[4] With these ligands, the factors that determine the low-coordination number appear to be electronic, although spatial factors may also be important in some cases. Therefore, many researchers try their best to prepare the two-coordination of copper(I) via a simple method. Fortunately, we use a simple hydrothermal rout to synthesize the title compound.

Meanwhile, the self-assembly of supramolecular structures, which are directed by metal ions, have attracted more attention due to the range of potential applications in electrical, magnetic, and optical devices and porous zeolite mimics.[5] Among the investigations of supramolecules, cyanuric acid (CA) has been prominently featured in studies of self-assembly hydrogen-bonded arrays because it can form multiple hydrogen bonds.[6]

In this communication, we have successfully applied a simple hydrothermal method to synthesize copper(I)-bonded CA supramolecule which features 4,4′-bipyrindine (4,4′-bipy) bridging two unites of $Cu^I{\cdot}CA$.[7] Very interestingly, this compound contains novel two-coordinated linear N–Cu–N configurations and is self-assembled to form the supermoleculese via hydrogen bonds with a channel of 3.98(5) × 8.81(1) Å along *b* axis.

Reaction of $CuCl_2{\cdot}4H_2O$ with CA and (4,4′-bipy in the presence of the tributylamine gives good yieds of the copper(I) complexes $Cu_2(C_3H_2N_3O_3)_2(C_{10}H_8N_2)$. The most notable feature of the title compound is that the copper(I) is two-coordinate with an essentially linear (N1–Cu1–N4 173.79°) as shown in Figure 1. The deviation from the perfect structure (180°) is result from the electric interaction of the Cu···O1a (2.77 Å) as shown in Figure 1. The distance of the Cu–N1,4 is 1.878(3) and 1.882(3) Å, respectively, which is good agreement with the distance of Cu–N of the reported compounds $Cu_2(PhN_3)_2$[8] and $\{[3,5(CF_3)_2Pz]Cu\}_3$.[9] Although the title compound only contains one copper dimer, the length of the title compound gets up to 22.6 Å through the bridging of bipy over two $Cu^I{\cdot}CA$ units. As can be seen from Figure 1, the crystal structure of the title compound is centro-symmetric, whose center is sited at the middle point of C6–C6a. Meanwhile, the CA anion plane is not exactly perpendicular to the bipy plane, and the dihedral angle is about 86.5°, resulting from both the space effect and stacking fashion. In order to evaluate the copper valence, magnetic susceptibility measurement proves the cuprous Cu^I state because the title compound shows Pauli-paramagnetism which is consistent with the absence of free spins in the structure. Also Cu^I state is proved by EPR spectra, as no signal was detected from solid title compound at room temperature. According to the electronic neutral theory, CA must present negative charge. Hence, another notable feature is that the organic spacer itself is the anion. The site of deprotonation on the cyanuric anion was unambiguously identified during refinement. There is no significant difference between the three C–O bond lengths in either independent cyanuric anion, or between the C–N bonds in the ring, indicating that the negative charge is delocalized.

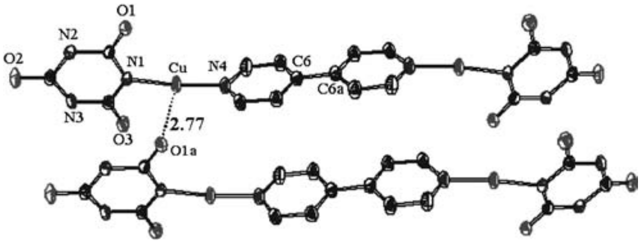

Figure 1. Molecular structure of the title compound, hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bonded distances (Å) Cu1–N1 1.878(3), Cu1–N4 1.882(3); and angles (°): N1–Cu1–N4 173.79(14). x, y, z; $-x+1/2, y+1/2, -z+1/2$; $-x, -y, -z$; $x-1/2, -y-1/2, z-1/2$.

In the *bc* plane, the unites are connected by hydrogen bonds (O2–N3) to form 2D sheet shown in Figure 2. The N–O distance corresponding to N–H···O bonds is about 2.803 Å, which is in the range of H-bond distance of approximately 3.0 Å.[10] In the sheet, the shortest Cu···Cu distances are 4.51 Å, which is much longer than that of the Cu–Cu bond in metallic copper (2.56 Å), indicat-

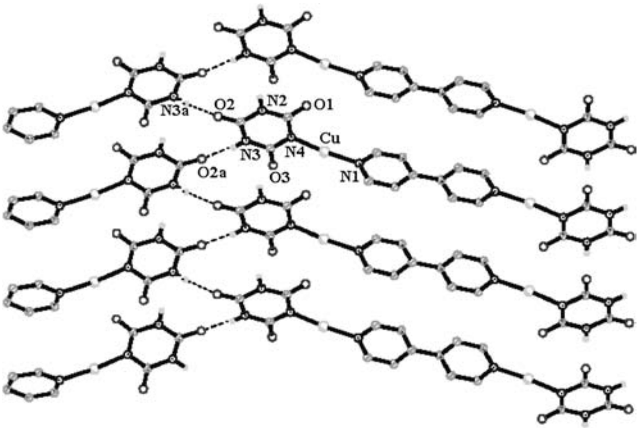

Figure 2. 2D layer structure along the *bc* plane connected by hydrogen bonds. The hydrogen atoms of the crystallization have been removed for clarity.

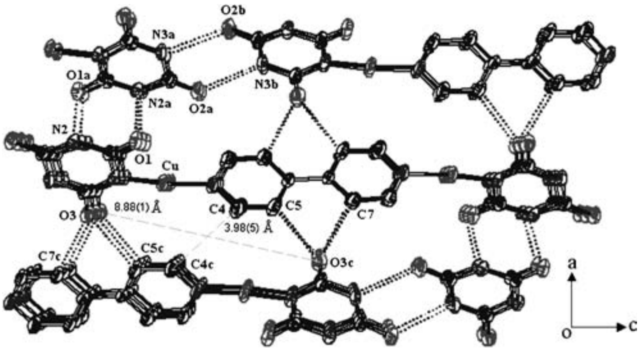

Figure 3. 3D arrangements of the title compound forming channels along the crystallographic *b* axis. The hydrogen atoms have been removed for clarity.

ing that there is no interaction between copper(I) ions. In addition, the distance of 3.99 Å between the 2D sheet motifs of the nearest-neighbor bipy ligands indicates the presence of face-to-face π–π stacking interaction.[11]

Packing analysis shows that the title compound is held together hydrogen bonds of N–H···O and O···H–N yielding 3D sheet structure shown in Figure 3. The N···O distances corresponding N–H···O and O···H–N bonds are the same 2.79 Å, indicating that there are hydrogen bonds in the nearest layers.[12] By close observation, the cyanuric anions are arranged in one dimension to form the linear tape by N–H···O and O···H–N hydrogen bonds, as is predicted by Whitesides et al.[13] Interestingly, the plane sheets are stacked in three dimensions to give channels along the *b* axis with a cross section of 3.98(5) × 8.81(1) Å, which may be useful in studying the porous coordination materials.

In summary, we have successfully synthesized the CA-coordinated-Cu^{I} superamolecule via hydrogen-bonded interaction by simple hydrothermal route. The title compound features following novel structure: (i) a rare two-coordinated linear N–Cu–N configuration around cuprous ions, (ii) a limited 1D structure of as long as 22.6 formed through the bridging of 4,4′-bipy over two cyaunric anions, and (iii) containing 1D channels along *b* axis with a cross section of 3.98(5) × 8.81(1) Å like those of zeolites and opening up a new field in porous coordination materials.

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7 A platelike yellow single crystal for the title compound was selected and mounted on a Enraf–Nonius CAD4 diffractometer with the graphite-monochromatized Mo Kα radiation source ($\lambda = 0.7103$ Å). Intensity data were collected in the $\omega < 2\theta$ scan mode with $2.74 < 2\theta < 25.96°$ at 293 and corrected in the Lorentz-polarization as well as for absorption by SADABS program. A total of 1732 independent reflections were collected, in which 1593 reflections were viewed as observed ($I > 2\sigma(I)$) and used in subsequent structural determination and refinements. The structure was solved by the direct methods and refined by full-matrix least-squares filling on on F^2 by SHELX-97. All non-hydrogen atoms were located by a series of least-squares cycles and difference Fourier syntheses and refined anisotropically. Hydrogen atoms were located at geometrically calculated positions. Crystal data: $Cu_2(C_3H_2N_3O_3)_2(C_{10}H_8N_2)$, $M_r = 539.42$, monoclinic, space group $P2_1/n$, $a = 13.458(3)$, $b = 4.5104(9)$, $c = 15.457(3)$ Å, $\beta = 105.65(3)°$, $V = 903.5(3)$ Å^3, $Z = 2$, $R = 0.0562$, $wR = 0.1697$.

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14 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html. Experimental procedures; X-ray crystallographic data for the title compound 1 (CIF), IR, NMR.

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