A Self-assembled Helix from 4,6-Dimethylpyrimidine and Copper(II) Bromide

Takayuki Ishida,* Liming Yang, and Takashi Nogami
Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585

(Received July 10, 2003; CL-030625)

A 1:1 polymeric complex of 4,6-dimethlpyrimidine and $\mathrm{CuBr_2}$ was spontaneously resolved to afford a 6_1 helix. Steric effects seem to play an important role for constructing a helical structure. Magnetic measurements showed a uniform $S = 1/2$ 1-D behavior. A dinuclear complex is also obtained as a precursor to the polymeric complex.

Various self-assembled structures have been developed from pyrimidines and transition metal ions, such as di- and trinuclear complexes,[1] hexagons,[2] *cis*-[3] and *trans*-zigzag chains,[4–6] and 3-D networks.[7] Lehn and co-workers exploited supramolecular approaches to helicates using oligo-bipyridines.[8] Oligo-terpyridines and -phenanthrolines have also been utilized for various helicates.[9] Peng et al.[10] and Cotton et al.[11] reported the metal wires supported by helical oligo-dipyridylamido ligands. We will report here a chiral crystal containing a 6_1 helical structure consisting of simple 4,6-dimethlpyrimidine (DMPM) and copper(II) bromide; namely, a helicate was prepared without support from pre-organization of ligands.

An ethanol solution (3 mL) containing DMPM (46 mg; 0.42 mmol) was slowly added to an ethanol solution containing $\mathrm{CuBr_2}$ (92 mg; 0.41 mmol), and the combined solution was allowed to stand in a refrigerator for a day. Black hexagonal prisms of $[\mathrm{DMPM{\cdot}CuBr_2{\cdot}(C_2H_5OH)_{\mathit{x}}}]_n$ (**1**) were precipitated. They were collected on a filter and washed with a small amount of ethanol. The yield was 66 mg (0.20 mmol; 48%). The crystals were subjected to structural and magnetic studies without further purification. Anal. Calcd.: C, 8.26; N, 22.43; H, 2.67% for **1** with $x = 0.17$. Found: C, 8.19; N, 22.98; H, 2.59%. The elemental analysis indicated that the products contained some solvent, depending on the degree of evacuation. A similar procedure using methanol as a solvent gave green blocks of a dinuclear complex $[\mathrm{DMPM_3{\cdot}(CuBr_2)_2{\cdot}(CH_3OH)_2}]$ (**2**). In some case both types of compounds were precipitated at a time, and the crystals could be separated manually based on the different shapes and colors under a microscope.

Diffraction data of a single crystal of **1** were collected on a Rigaku R-axis RAPID diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 90 K.[12] The space group was hexagonal $P6_122$. A half portion of DMPM and $\mathrm{CuBr_2}$ was crystallographically independent and $Z = 12$. The molecular structure was expanded according to the symmetry, giving a helical structure (Figure 1).

The space group of **1** is chiral, and there is no enanthiomeric helix in a crystal. Thus, spontaneous resolution took place during the crystallization, though the starting materials DMPM and $\mathrm{CuBr_2}$ are achiral.

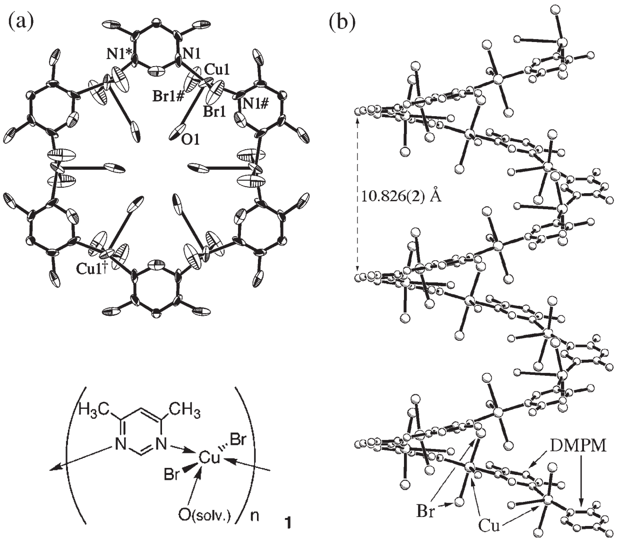

Figure 1. Crystal structure of $[\mathrm{DMPM{\cdot}CuBr_2{\cdot}(C_2H_5OH)_{\mathit{x}}}]_n$ (**1**; $x = 1$). (a) ORTEP drawing as a top view with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted. A structural formula is also shown. Only oxygen atoms are drawn for the solvent molecules.[12] Selected interatomic distances and angles are: Cu1–Br1, 2.346(2); Cu1–O1, 3.10(2); Cu1–N1, 2.02(1) Å; Br1–Cu1–Br1$^{\#}$, 168.6(2); N1–Cu1–N1$^{\#}$, 163.1(7); Br1–Cu1–O1, 84.3(1); Br1–Cu1–N1, 91.1(4); Br1–Cu1–N1$^{\#}$, 90.5(4); O1–Cu1–N1, 98.5(3)°; Cu1$\cdots$Cu1†, 12.04 Å. Symmetry operation codes for *, $^{\#}$, and † are $(-y, -x, -7/6 - z)$, $(x - y, -y, -1 - z)$, and $(-x, -y, 1/2 + z)$, respectively. (b) A side view. Three pitches are shown in an infinite helix.

The dc magnetic susceptibility of the randomly oriented polycrystalline sample of **1** was measured on a Quantum Design MPMS SQUID magnetometer at 5 kOe over a temperature range 1.8–300 K. As Figure 2 shows, the molar magnetic susceptibility of **1** was reproduced with a combined expression of a Bonner–Fisher term[13] and a small contribution of a Curie spin. The best optimized parameters were: $g = 2.16(1)$ and $2J/k_{\mathrm{B}} = -56.7(3)$ K, where the spin Hamiltonian is defined as $H = -2JS_1 \cdot S_2$. This finding indicates that the copper spins are arranged in a 1-D array with equally spacing, being consistent with the crystal structure determined. The Curie term ($C_{\mathrm{Curie}} = 0.014\,\mathrm{cm^3\,K\,mol^{-1}}$) corresponds to 3.2% of the total copper(II) spins, which is ascribable to lattice defects or other origins (e.g. staggered fields caused by the canting g-tensors of neighboring Cu ions).[5]

In **1**, pyrimidine nitrogen atoms were coordinated at the equatorial positions. The σ-type orbital overlaps between copper $\mathrm{d}_{x^2-y^2}$ and nitrogen n orbitals on both sides bring about an antiferromagnetic superexchange through the pyrimidine molecular orbitals.[3,4,14]

Steric effects seem to play an important role in forming hexagons vs zigzag chains, as previously pointed out on the crystal engineering of isophthalic acids.[15] Actually, the methyl groups in DMPM are needed for the preparation of **1**, as indicated by the following results: Complexation of unsubstituted pyrimidine

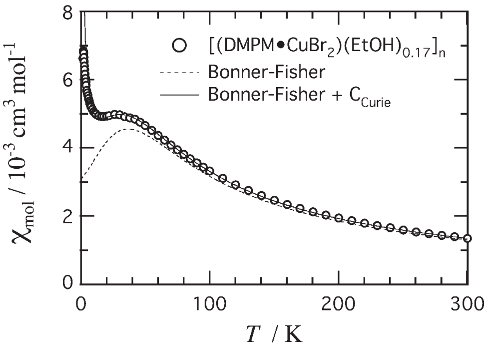

Figure 2. Temperature dependence of the molar magnetic susceptibility χ_{mol} for $[DMPM{\cdot}CuBr_2{\cdot}(C_2H_5OH)_{0.17}]_n$ (**1**). Solid and dotted lines represent calculated curves. For details, see the text.

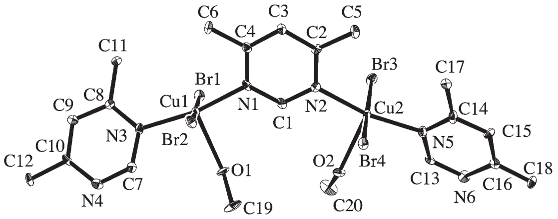

Figure 3. ORTEP drawing of $[DMPM_2{\cdot}(CuBr_2)_2{\cdot}(CH_3OH)_2]$ (**2**) with thermal ellipsoids at the 50% probability level. H atoms are omitted.

(PM) and $CuBr_2$ gave only unidentified solids, and the PM-bridged copper(II) nitrate and 1,1,1,5,5,5-hexafluoropentane-2,4,-dionate complexes have been characterized as zigzag chains.[3–6] We also have to pay attention to solvated molecules in coordination compounds.[16] To clarify driving forces of the helix formation preferable to planar cyclization, we analyzed the molecular structure of **2**[17] (Figure 3), which can be regarded as a precursor of **1**.

Each copper(II) ion in **2** possesses a methanol molecule as an axial ligand. Owing to the steric repulsion, the copper ions can not accept another axial ligand, and the *anti* configuration is favored with respect to methanol and two methyl groups (O1–C19 and C6; O1–C19 and C11). Accordingly, the two methyl groups are located in the same hemisphere of the copper surroundings, giving rise to a bent $(DMPM)_3(CuBr_2)_2$ backbone. This geometry also forces two neighboring methanol ligands close to each other (see C19 and C20), and they have to steer to opposite directions. The neighboring copper basal planes are twisted. A possible mechanism for the helix formation of **1** is as follows. Ethanol molecules are once coordinated to copper(II) ions, and a bent and twisted DMPM–$CuBr_2$ backbone is formed like **2**. After the helical polymerization, the ethanol ligands easily escape from the axial positions because of the less ligating nature than that of methanol. In fact, the X-ray crystal structure of freshly prepared **1** was solved to be a helix in a trigonal $P3_121$ space group at 90 K. Although the final R factors were rather unsatisfactory ($R = 0.083$ [$I > 2\sigma(I)$]), the electron density peaks due to the solvent could be observed more sharply than the analysis on evacuated samples.

We thank Dr. D. Hashizume and Prof. F. Iwasaki for kind assistance in the X-ray crystal structure analysis.

References and Notes

1 T. Kogane, K. Kobayashi, M. Ishii, R. Hirota, and M. Nakahara, *J. Chem. Soc., Dalton Trans.*, **1994**, 13; M. Nakagawa, Y. Ishikawa, T. Kogane, T. Ishida, M. Yasui, F. Iwasaki, and T. Nogami, *Mol. Cryst. Liq. Cryst.*, **286**, 29 (1996).
2 J. Omata, T. Ishida, D. Hashizume, F. Iwasaki, and T. Nogami, *Inorg. Chem.*, **40**, 3954 (2001); L. C. Tabares, J. A. R. Navarro, and J. M. Salas, *J. Am. Chem. Soc.*, **123**, 383 (2001).
3 M. Yasui, Y. Ishikawa, N. Akiyama, T. Ishida, T. Nogami, and F. Iwasaki, *Acta Crystallogr., Sect. B*, **57**, 288 (2001); T. Ishida, K. Nakayama, M. Nakagawa, W. Sato, Y. Ishikawa, M. Yasui, F. Iwasaki, and T. Nogami, *Synth. Met.*, **85**, 1655 (1997).
4 F. Mohri, K. Yoshizawa, T. Yamabe, T. Ishida, and T. Nogami, *Mol. Eng.*, **8**, 357 (1999).
5 R. Feyerherm, S. Abens, D. Günther, T. Ishida, M. Meissner, M. Meschke, T. Nogami, and M. Steiner, *J. Phys.: Condens. Matter*, **12**, 8495 (2000); R. Feyerherm, T. Ishida, T. Nogami, and M. Steiner, *Mol. Cryst. Liq. Cryst.*, **335**, 235 (1999).
6 T. Ezuhara, K. Endo, K. Matsuda, and Y. Aoyama, *New J. Chem.*, **24**, 609 (2000).
7 K. Nakayama, T. Ishida, R. Takayama, D. Hashizume, M. Yasui, F. Iwasaki, and T. Nogami, *Chem. Lett.*, **1998**, 497; K. Zusai, T. Kusaka, T. Ishida, R. Feyerherm, M. Steiner, and T. Nogami, *Mol. Cryst. Liq. Cryst.*, **343**, 127 (2000); S. W. Keller, *Angew. Chem., Int. Ed.*, **36**, 247 (1997); H. Cai, H.-M. Hu, W.-Z. Chen, H.-G. Zhu, and X.-Z. You, *Chem. Lett.*, **1999**, 221.
8 R. Kämer, J.-M. Lehn, and A. Marquis-Rigault, *Proc. Natl. Acad. Sci. U.S.A.*, **90**, 5394 (1993); B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, and D. Fenske, *Angew. Chem., Int. Ed.*, **35**, 1838 (1996).
9 C. Piguet, G. Bernardinelli, and G. Hopfgartner, *Chem. Rev.*, **97**, 2005 (1997).
10 S.-M. Peng, C.-C. Wang, Y.-L. Jang, Y.-H. Chen, F.-Y. Li, C.-Y. Mou, and M.-K. Leung, *J. Magn. Magn. Mater.*, **209**, 80 (2000).
11 F. A. Cotton, L. M. Daniels, T. Lu, C. A. Murillo, and X. Wang, *J. Chem. Soc., Dalton Trans.*, **1999**, 517.
12 Selected crystallographic data for **1**: $C_3H_4Br_1Cu_{0.5}N_1O_{0.5}$, hexagonal $P6_122$, $a = 14.162(3)$, $c = 10.826(2)$ Å, $V = 1880.4(7)$ Å^3, $Z = 12$, $D_{calc} = 1.852$ g cm^{-3}, μ(Mo Kα) $= 8.10$ mm^{-1}, $R = 0.058$ ($I > 2.0\sigma(I)$), $R_w = 0.147$ (all data), $T = 90$ K for 749 unique reflections. An appreciable electron density was found at an axial position of Cu1, and tentatively assigned as an oxygen atom. However, the ethanol skeleton could not be determined owing to disorder.
13 J. C. Bonner and M. E. Fisher, *Phys. Rev. A*, **135**, 640 (1964).
14 T. Ishida, T. Kawakami, S.-i. Mitsubori, T. Nogami, K. Yamaguchi, and H. Iwamura, *J. Chem. Soc., Dalton Trans.*, **2002**, 3177.
15 J. Yang, J.-L. Marendaz, S. J. Geib, and A. D. Hamilton, *Tetrahedron Lett.*, **35**, 3665 (1994).
16 H. Abourahma, B. Moulton, V. Kravtsov, and M. J. Zaworotko, *J. Am. Chem. Soc.*, **124**, 9990 (2002).
17 Selected crystallographic data for **2**: $C_{20}H_{32}Br_4Cu_2N_6O_2$, monoclinic Cc, $a = 10.187(1)$, $b = 53.072(5)$, $c = 7.1953(8)$ Å, $\beta = 134.797(4)°$, $V = 2760.5(5)$ Å^3, $Z = 4$, $D_{calc} = 2.01$ g cm^{-3}, μ(Mo Kα) $= 7.38$ mm^{-1}, $R = 0.040$ ($I > 2.0\sigma(I)$), $R_w = 0.117$ (all data), $T = 90$ K for 3607 unique reflections.

Published on the web (Advance View) October 6, 2003; DOI 10.1246/cl.2003.1018