

## Synthesis, Crystal Structure, and Magnetic Properties of Polymeric Iron(III) Hexacyanide Complex Linked by Copper(II) Macrocycle

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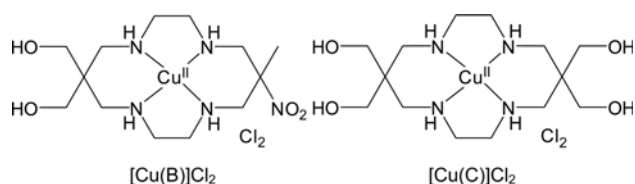
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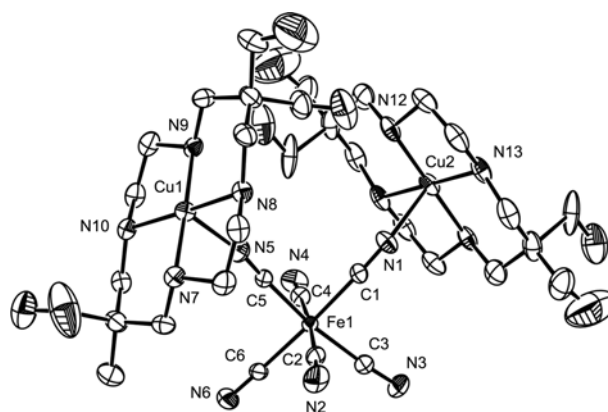
**Key Words** : Coordination polymer, Copper(II) complex, Iron(III) hexacyanide, Crystal structure, Magnetic properties

Self-organization of multidimensional coordination materials containing metal cyanide complexes has been attracted much interest in the development of functional magnetic materials, because of their potential applications such as data recording and electronic sensors.<sup>1</sup> Metal cyanides have been extensively used and studied for coordination polymer networks because they are good building blocks to make extended network structures and show efficient superexchange interactions through cyanide ions between paramagnetic metal ions.<sup>2</sup> For example,  $[\text{Cu}^{\text{II}}(\text{cyclam})]_3[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$  (cyclam = 1,4,8,11-tetraazacyclotetradecane) displays a rope-ladder 1D chain structure assembled by copper(II) macrocycle and hexacyanochromate(III) and it also shows a moderate ferromagnetic interaction.<sup>3</sup> Furthermore, many copper(II) complexes as linkers have been used for constructing multidimensional frameworks which show extensive magnetic interactions.<sup>4</sup> However, the use of azamacrocyclic copper(II) complexes has been comparatively limited, even though they can be good building blocks.<sup>5</sup> Recently, we have reported the structure and magnetic properties of a branch-like one-dimensional cyano-bridged coordination polymer,  $[\text{Cu}(\text{A})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 8\text{H}_2\text{O}$  (A = 6,13-dimethyl-6-nitro-1,4,8,11-tetraazabicyclo[11.1.1]pentadecane),<sup>6</sup> in which it has shown a fern branch structure and a weak ferromagnetic coupling.<sup>7</sup> Thus, in the efforts to explore the structures and properties of coordination polymers including azamacrocyclic copper(II) complexes, we have synthesized a coordination polymer network including iron(III) hexacyanide complex ( $[\text{Fe}(\text{CN})_6]^{3-}$ ) and macrocyclic copper(II) complex,  $[\text{Cu}^{\text{II}}(\text{B})]\text{Cl}_2$  (included  $[\text{Cu}^{\text{II}}(\text{C})]\text{Cl}_2$ ) (B = 6-methyl-6-nitro-13-dimethylhydroxy-1,4,8,11-tetraazadecane; C = 6,13-dimethylhydroxy-1,4,8,11-tetraazadecane). Herein, we report the synthesis, crystal structure and magnetic properties of 2D  $[\text{Cu}(\text{B})]_2[\text{Cu}(\text{C})][\text{Fe}(\text{CN})_6]_2 \cdot 7\text{H}_2\text{O}$  (**1**).



The reaction of three equivalents of  $[\text{Cu}^{\text{II}}(\text{B})]\text{Cl}_2$  (included  $[\text{Cu}^{\text{II}}(\text{C})]\text{Cl}_2$ ) with two equivalents of  $\text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]$  in  $\text{H}_2\text{O}$  under aerobic conditions affords air stable two-dimensional (2D) coordination network  $[\text{Cu}(\text{B})]_2[\text{Cu}(\text{C})][\text{Fe}(\text{CN})_6]_2 \cdot 7\text{H}_2\text{O}$  (**1**) as brown crystals. The composition of **1** was determined by elemental analysis, infrared, and single crystal X-ray diffraction. From the X-ray crystallography (*vide infra*), we have identified the exact composition of copper(II) macrocycles in unit formula, *i.e.*  $[\text{Cu}(\text{B})]^{2+}:[\text{Cu}(\text{C})]^{2+} = 2:1$ . Infrared spectrum of **1** shows a sharp CN stretching band at  $2113\text{ cm}^{-1}$ , which is slightly lower than that of  $\text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]$  ( $\nu_{\text{CN}} 2118\text{ cm}^{-1}$ ).<sup>8</sup> The thermogravimetric analysis (TGA) trace of **1** shows a weight loss of 6.7% at  $135\text{ }^\circ\text{C}$ , which corresponds to the loss of seven water molecules per unit formula. No chemical decomposition was observed up to  $198\text{ }^\circ\text{C}$  (Figure S1).

**1** crystallizes in the monoclinic  $C2/c$  space group, and the atom labeling ORTEP drawing of **1** is shown in Figure 1. Table 1 shows the selected bond distances and angles. The core structure of **1** is composed of two  $[\text{Cu}^{\text{II}}(\text{B})]^{2+}$  cations, one  $[\text{Cu}^{\text{II}}(\text{C})]^{2+}$  cation, two  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  anions, and seven water molecules as lattice solvent. The Cu1 and Cu2 centers show distorted octahedral geometry with the four nitrogen atoms of macrocyclic ligand and the two nitrogen atoms of

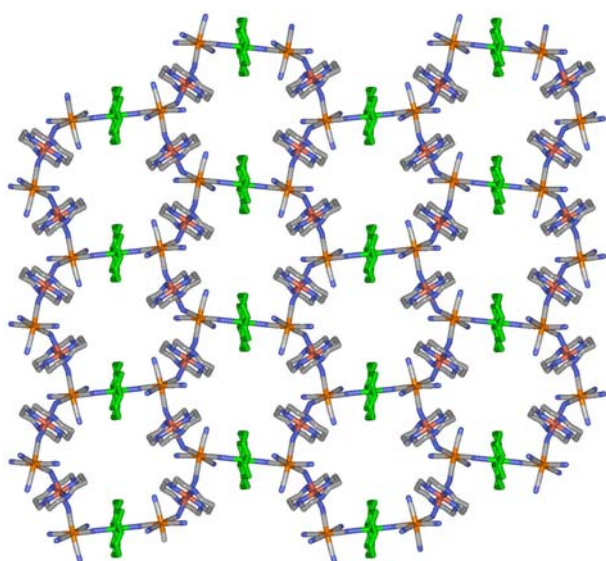
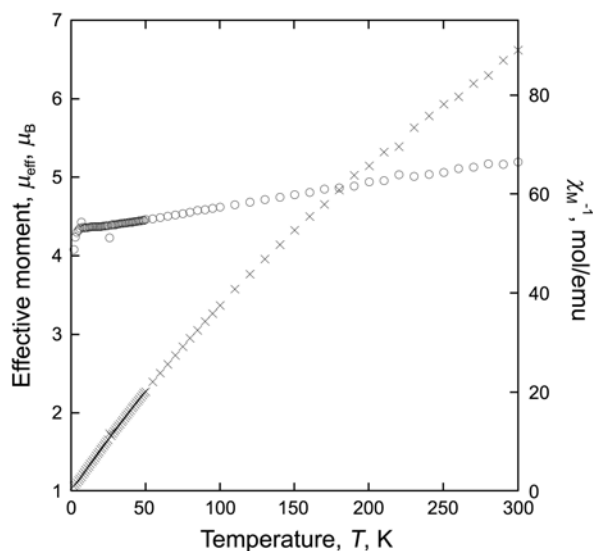


**Figure 1.** ORTEP (30% probable thermal ellipsoid) view of **1**. Cu1 and Cu2 are coordinated by two ligands B and C, respectively. H atoms and  $\text{H}_2\text{O}$  are omitted for clarity.

**Table 1.** Selected bond distances (Å) and angles (°) for **1**

Cu1-N5	2.358(4)	Cu1-N10	2.029(4)
Cu1-N7	2.020(4)	Cu2-N1	2.454(5)
Cu1-N8	2.011(4)	Cu2-N12	2.025(5)
Cu1-N9	2.002(4)	Cu2-N13	2.005(4)
Fe1-C1	1.931(5)	Fe1-C4	1.941(5)
Fe1-C2	1.913(5)	Fe1-C5	1.929(5)
Fe1-C3	1.935(6)	Fe1-C6	1.937(5)
N5-Cu1-N7	95.12(18)	N1-Cu2-N12	88.40(18)
N5-Cu1-N8	96.88(18)	N1-Cu2-N13	90.40(17)
N5-Cu1-N9	87.65(17)	C1-Fe1-C2	94.9(2)
N5-Cu1-N10	86.48(17)	C1-Fe1-C3	86.9(2)
N7-Cu1-N9	177.22(17)	C1-Fe1-C4	89.6(2)
N8-Cu1-N10	176.58(17)	C1-Fe1-C5	84.1(2)
N12-Cu2-N13	85.6(2)	C1-Fe1-C6	176.9(2)

$[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ . The average Fe1-C bond length is 1.931(2) Å. Four secondary nitrogens of azamacrocyclic ligand bind to the copper(II) ions with the average Cu-N distances of 2.016(2) Å for Cu1 and 2.013(2) Å for Cu2, respectively. Two nitrogen atoms of the bridging cyanide ligands axially bind to the copper(II) ions with the Cu-N distances of 2.479(3) Å for Cu1 and 2.454(2) Å for Cu2, respectively. The copper(II) ions are 0.053(2) Å for Cu1 and 0.0 Å for Cu2 out of the square-coordination  $\text{N}_4$  plane.<sup>9</sup> The deviation of Cu1 is slightly larger than that of Cu2, because the Cu2 ion has the inversion center. The bridging CN ligands bind to the copper(II) ions mostly in a bent fashion with the Cu-N-C bond angles ranging from 133.9(5) to 163.5(4)°. The adjacent Fe...Cu distances are 5.340(1) Å for Cu1...Fe1, 5.105(1) Å for Cu2...Fe1, and 5.197(1) Å for Cu1...Fe1 (0.5-x, -0.5+y, 0.5-z), respectively. The shortest intersheet

**Figure 2.** Extended 2D structure of **1**. The pendant groups of macrocyclic ligand are removed for clarity.  $[\text{Cu}(\text{C})]^{2+}$  units are indicated as different color, in order to differentiate between  $[\text{Cu}(\text{B})]^{2+}$  and  $[\text{Cu}(\text{C})]^{2+}$ .**Figure 3.** Temperature dependence of  $\mu_{\text{eff}}$  (o) and  $\chi_M^{-1}$  (x) for **1** at 1000 Oe.

metal-metal separation is 7.343(1) Å for Fe1...Cu1(0.5-x, -0.5-y, -z). As shown in Figure 2, the  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  anion (Fe1) uses three facial  $\text{CN}^-$  groups to connect with three *trans*  $[\text{Cu}^{\text{II}}(\text{B})]^{2+}/[\text{Cu}^{\text{II}}(\text{C})]^{2+}$  cations (Cu1, Cu2), whereas the three remaining  $\text{CN}^-$  groups are monodentate. The coordinated  $[\text{Cu}^{\text{II}}(\text{B})]^{2+}/[\text{Cu}^{\text{II}}(\text{C})]^{2+}$  cations (Cu1, Cu2) link to other  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  anions, which display distorted octahedral geometries, thus, the framework does extend to form two-dimensional structure. Finally **1** forms a honeycomb-like two-dimensional coordination polymer network and extends parallel to the *a* + *c* axis (Figure 2).

The magnetic susceptibility,  $\chi$ , of **1** was measured on powdered sample in an applied field of 1000 Oe between 2 and 300 K, and is plotted as  $\chi_M^{-1}(T)$  and  $\mu_{\text{eff}}(T)$  ( $\mu_{\text{eff}}(T) = [8\chi T]^{1/2}$ ), Figure 3. At 300 K the effective magnetic moment is 5.20  $\mu_B$ , and it is gradually decreased with decreasing temperature until 7 K. Below 7 K,  $\mu_{\text{eff}}(T)$  decreases to 4.08  $\mu_B$  at 2 K. This exceeds the 3.87  $\mu_B$  expected for independent  $g = 2$ ,  $S = 1/2$ ,  $\text{Fe}^{\text{III}}$  and  $S = 1/2$ ,  $\text{Cu}^{\text{II}}$  spins and is attributed to a high effective Landé *g* value typical of  $\text{Cu}^{\text{II}}$ .<sup>10</sup> Above 2 K,  $\chi^{-1}(T)$  can be fit to the Curie-Weiss expression  $\chi_M = C/(T-\theta)$  with  $\theta = -11.5$  K ( $C = 3.289$  emu K/mol).<sup>11</sup> The magnetic properties show a weak antiferromagnetic coupling between the copper(II) and Fe(III) ions (Figure 3). The antiferromagnetic behavior can be attributed to the magnetic interaction within the two-dimensional sheet. This weak interaction might be due to a long distance between the copper(II) and iron(III) ions (Cu1, Cu2, Fe1) and/or the deviation of orthogonality between them.

In conclusion, we have prepared a 2D coordination polymer network,  $[\text{Cu}(\text{B})]_2[\text{Cu}(\text{C})][\text{Fe}(\text{CN})_6]_2 \cdot 7\text{H}_2\text{O}$  (**1**), from the reaction of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and macrocyclic copper(II) complex,  $[\text{Cu}^{\text{II}}(\text{B})]\text{Cl}_2$  (included  $[\text{Cu}^{\text{II}}(\text{C})]\text{Cl}_2$ ) in  $\text{H}_2\text{O}$ . **1** has formed a 2D sheet with distorted hexagon shape by self-assembly from three copper(II) macrocyclic complexes (two  $[\text{Cu}^{\text{II}}(\text{B})]^{2+}$  and one  $[\text{Cu}^{\text{II}}(\text{C})]^{2+}$ ) and two  $[\text{Fe}(\text{CN})_6]^{3-}$  units. **1**

**Table 2.** Crystallographic data and structure refinement for **1**

Compound	<b>1</b>
Empirical formula	C <sub>52</sub> H <sub>104</sub> Cu <sub>3</sub> Fe <sub>2</sub> N <sub>26</sub> O <sub>19</sub>
Formula weight	1699.94
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	27.627(3)
<i>b</i> (Å)	15.469(2)
<i>c</i> (Å)	17.991(1)
$\beta$ (°)	104.35(1)
<i>V</i> (Å <sup>3</sup> )	7448.6(11)
<i>Z</i>	4
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.516
$\lambda$ (Å)	0.71073
<i>T</i> (K)	293(2)
$\mu$ (mm <sup>-1</sup> )	1.305
<i>F</i> (000)	3556
Collected	7290
Unique	6914
Observed	5448
Parameters	475
GOF	1.056
<i>R</i> <sub>1</sub> <sup>a</sup> (4 $\sigma$ data)	0.0638
<i>wR</i> <sub>2</sub> <sup>b</sup> (4 $\sigma$ data)	0.1993

$${}^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, {}^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

shows weak *antiferromagnetic* interactions through the cyanides.

## Experimental

**Measurements.** All chemicals used in the synthesis were of reagent grade and used without further purification. [Cu(B)]Cl<sub>2</sub> (included [Cu(C)]Cl<sub>2</sub>) was prepared according to literature procedure.<sup>12</sup> In the preparation of [Cu(B)]Cl<sub>2</sub>, [Cu(C)]Cl<sub>2</sub> is contained inevitably. Infrared spectra were recorded with a Thermo Fisher Scientific IR200 spectrophotometer ( $\pm 1$  cm<sup>-1</sup>) using KBr disk. Elemental analyses were carried out using a Fisons/Carlo Erba EA1108 instrument. Magnetic susceptibilities were measured in applied field of 1000 Oe between 2 and 300 K on a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were made ( $925.5 \times 10^{-6}$  (1) emu/mol) by using Pascal's constants. Thermogravimetric analysis (TGA) was performed at a scan rate of 5 °C/min using a Seiko TG/DTA 320 & SSC 5200H Disk Station system.

**Preparation of 1.** K<sub>3</sub>[Fe<sup>III</sup>(CN)<sub>6</sub>] (14 mg, 0.043 mmol) was dissolved in H<sub>2</sub>O (3 mL) in a test tube at room temperature. An aqueous solution (3 mL) of [Cu(B)]Cl<sub>2</sub> (included [Cu(C)]Cl<sub>2</sub>) (30 mg, 0.066 mmol) was added dropwise to the top of the above iron(III) solution without agitating it. After two days brown crystals were formed as the diffusion proceeded. These brown crystals were filtered, washed with water, and dried in air. Yield; 15 mg (42%). Brown block-shaped crystals of **1** suitable for X-ray diffraction were obtain-

ed by layering of a methanol solution of [Cu(B)]Cl<sub>2</sub> (included [Cu(C)]Cl<sub>2</sub>) into an aqueous solution of K<sub>3</sub>[Fe<sup>III</sup>(CN)<sub>6</sub>]. FT-IR (KBr, cm<sup>-1</sup>):  $\nu = 3577, 3396, 3266, 2941, 2883, 2113, 1550, 1458, 1351, 1078, 1051, 988$ . Anal. Calcd for C<sub>52</sub>H<sub>104</sub>Cu<sub>3</sub>Fe<sub>2</sub>N<sub>26</sub>O<sub>19</sub>: C, 36.74; H, 6.17; N, 21.42. Found: C, 36.35; H, 5.99; N, 22.00.

**Crystal Structure Determination.** Single crystal of **1** was mounted on a Bruker SMART APEX CCD-based diffractometer (Korea Basic Science Institute, Chonju Branch). X-ray data for **1** was collected at 293(2) K and using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å, graphite monochromator). The raw data were processed to give structure factors using the Bruker SAINT program and corrected for Lorentz and polarization effects.<sup>13</sup> No absorption correction was made. The crystal structure was solved by direct methods,<sup>14</sup> and refined by full-matrix least-squares refinement using the SHELXL97 computer program.<sup>15</sup> All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except for H<sub>2</sub>O were positioned geometrically and refined using a riding model. The crystallographic data and the result of refinements are summarized in Table 2.

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**Supporting Information.** TGA trace for **1**. CCDC 898762 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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