RESEARCH ACTIVITIES V
Department of Applied Molecular Science

V-A Synthesis of Chiral Molecule-Based Magnets

Construction of molecule-based multifunctional materials is now becoming a challenging target. Especially, magnetic materials which have additional optical and electronic properties in the same crystals are increasing interests. Specific goals aimed for these molecule-based magnets include: i) the ability to design the molecular building blocks and to organize them in the solid for desired dimensionality, ii) the optical transparency. The physical characteristic of current interest involves optical properties, particularly with respect to natural optical activity. When a magnet has optical transparency and chiral structure, the magnetic structure of crystal expects to be a chiral spin structure. These magnets will show an asymmetric magnetic anisotropy and magneto-chiral dichroism. This category of materials don't only have scientific interest but also have the possibility for use in new devices. When we construct chiral molecule-based magnets, chirality must be controlled not only in the molecular structure, but in the entire crystal structure. As a consequence of this difficulty, only few examples of this type of magnet exist. Up to the present reported chiral magnets have low dimensional magnetic structures, the magnetic ordering temperatures are below 10 K. To afford a high-T_C magnet, dimensionality of magnetic structure must be extended in two or three dimension. When we introduce magnetic bricks, which have more than three connections for the construction of magnets, we can expect to make two or three-dimensional magnets. To make high dimensionality molecule-based magnets, we recently discovered using cyano bridged complex with chiral organic ligands.

V-A-1 Synthesis of a Novel Three-Dimensional Chiral Molecule-Based Ferrimagnet with Triple-Helical Strand Structure

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Dark orange, hexagonal prism crystals of $[Cr(CN)_6][Mn\ D\text{- or }L\text{-}NH_2ala]_3\cdot(3H_2O)$ were obtained by slow diffusion of $MnCl_2\cdot4H_2O$ (1.7 mmol), D- or L-aminoalanine hydrochloride (D- or L-$NH_2alaH\cdot HCl$, 2.6 mmol), and KOH (5.2 mmol) in H_2O into $K_3[Cr(CN)_6]$ (1.5 mmol) in H_2O/*iso*-propanol (1:1) mixture under argon atmosphere after several weeks. X-ray crystal structure analyses of D- and L-isomers at 100 K reveal that compounds (**1**) crystallize in the chiral space group, hexagonal $P6_3$, and consist of left- and right-handed helical structures of Mn^{II} ions, respectively (Figure 1). Each aminoalanine ion employs two types of functional groups to bridge between two adjacent Mn^{II} ions (Mn–Mn separation is 5.923 Å.). Two amino moieties and one carboxyl group within the aminoalanine ion are coordinated to two Mn^{II} ions in monodentate and bidentate coordination mode, respectively. This unique coordination leads to the construction of two differing chelating rings around the Mn^{II} ion: five- and six-membered rings. These rings align alternately resulting in the generation of extended helical chains along the *c*-axis. As expected, self-assemblies are formed between helical chains to aggregate three helical chains (Figure 2), in which the shortest Mn–Mn separation between chains is 6.517 Å. The channel structure is generated and disordered water molecules exist in the center of the triple helical strand structure (on the screw axis).

On the other hand, each $[Cr(CN)_6]^{3-}$ ion utilizes all cyanide moieties to connect between adjacent strands *via* cyanide bridges to Mn^{II} ions; as a result, a three-dimensional cyanide network is formed. The shortest and longest adjacent Cr–Mn distances through cyanide bridges are 5.490 and 5.508 Å, respectively, which are slightly longer than those in the previous crystals. The cyanide bridged network also displays basic units comprised of a helical strand structure. Each cyanide-bridged helical strand, which is composed of four metal centers (two Mn^{II} and two Cr^{III} ions) and four cyanide groups as a repeating unit characterized by a reverse turn within the helical strand of Mn^{II} and NH_2ala ions along the *c*-axis, shares the apex of the helical strand (Cr^{III} ion) between three adjacent helical strands (Figure 1).

This compound exhibits ferrimagnetic behavior essentially below 35 K. The magnetic transition temperature of this compound is relatively low despite formation of a three-dimensional cyanide network. This phenomenon is probably attributable to the comparatively long cyanide-bridged distance in this crystal. In addition, it may result consequent to the occurrence of spin frustration between manganese ions within the triple helical strand at high temperature. Below 35 K, the spin on manganese alone survives due to the ferrimagnetic coupling between manganese and chromium ions. From a physical standpoint, this phenomenon is the focus of interesting research, as the spin structure of this compound is also expected to possess triple helical nature. Some chiral molecule-based magnets have been prepared previously; however, at present, a chiral helical spin structure has not been documented. It is one of the reasons affording an explanation as to why a crystal forming a helical structure has never been synthesized. Thus, it is certain that this molecule is a suitable candidate for this endeavor. Magnetization measurements, μSR (muon spin resonance) spectroscopy and neutron diffraction of a single crystal will lead to characterization of the details of magnetic structure in this compound.

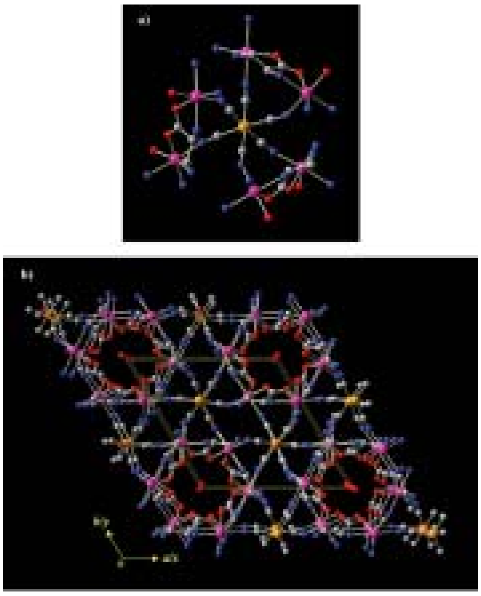

Figure 1. a) Coordination geometry of the heptanuclear unit of $[Cr^{III}(CN)_6][Mn^{II}\ L\text{-}NH_2ala]_3\cdot(3H_2O)$ (**1**). b) Overall view of crystal structure of $[Cr^{III}(CN)_6][Mn^{II}\ L\text{-}NH_2ala]_3\cdot(3H_2O)$ (**1**) along the *c*-axis. Cr atoms are shown in yellow brown, Mn in purple, C in gray N in blue and O in red. The hydrogen atoms are omitted for simplicity.

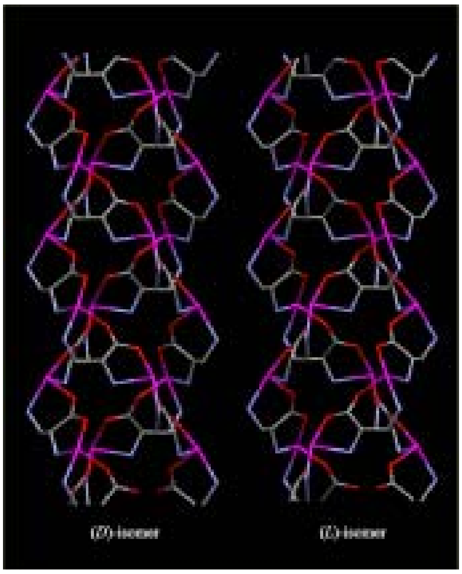

Figure 2. Capped sticks models of a left-handed and a right-handed triple strands in $[Cr^{III}(CN)_6][Mn^{II}$ D or $L\text{-}NH_2ala]_3\cdot(3H_2O)$ (**1**). Mn atoms are shown in purple, C in gray N in blue and O in red.

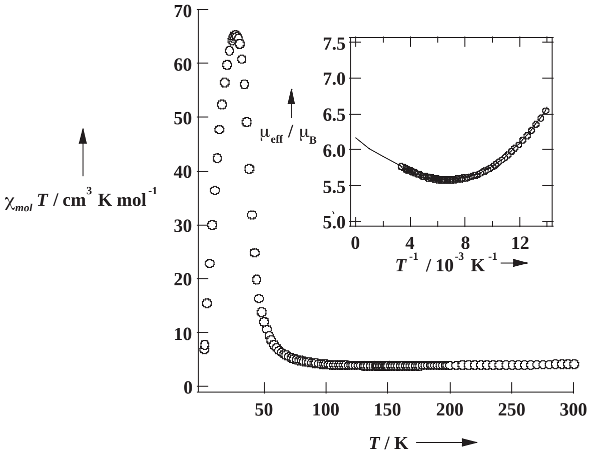

Figure 3. $\chi_{mol}T$ *versus* T plot at 5000 G of $[Cr^{III}(CN)_6][Mn^{II}$ D or $L\text{-}NH_2ala]_3\cdot(3H_2O)$ (**1**). Inset: Plot of effective magnetic moment *versus* $1/T$.

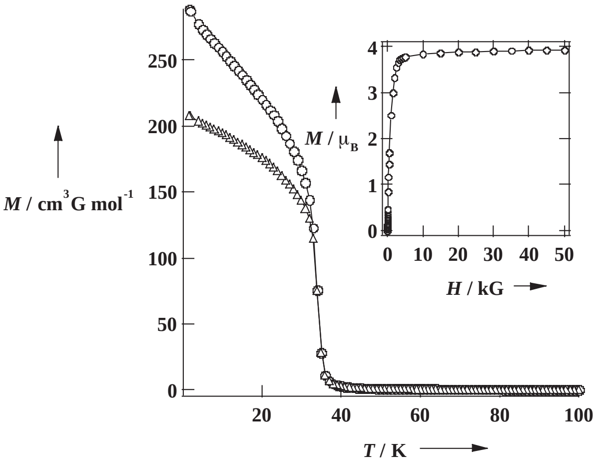

Figure 4. Temperature dependence of magnetization of $[Cr^{III}(CN)_6][Mn^{II}$ D- or $L\text{-}NH_2ala]_3\cdot(3H_2O)$ (**1**). The FC (triangle) and ZFC (circle) magnetizations at 5 G are shown. Inset: Field dependence of magnetization of $[Cr^{III}(CN)_6][Mn^{II}$ D- or $L\text{-}NH_2ala]_3\cdot(3H_2O)$ (**1**) at 2 K.

V-A-2 TOF Neutron Powder Diffraction Studies on a Chiral Two-Dimensional Molecule-Based Magnet

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The magnetic structure of a chiral molecule-based magnet, $[Cr(CN)_6][Mn(S)\text{-}pnH(H_2O)](H_2O)$ (Space group = $P2_12_12_1$, Figure 1), has been studied by neutron powder diffraction as a function of temperature from 4 K to 300 K. The 020 and 022 magnetic reflections were clearly observed below T_C = 38 K (Figure 2). From the intensity analysis of magnetic reflections, it was concluded that the magnetic structure is non-collinear ferrimagnetic with the magnetic (Shubnikov) space group $P2_12_1'2_1'$, and magnetic moments of Cr and Mn atoms are mutually antiparallel along a direction near the *a*-axis. Our result implies that the long-period magnetic structure, if exists, is not a helical structure but a conical one.

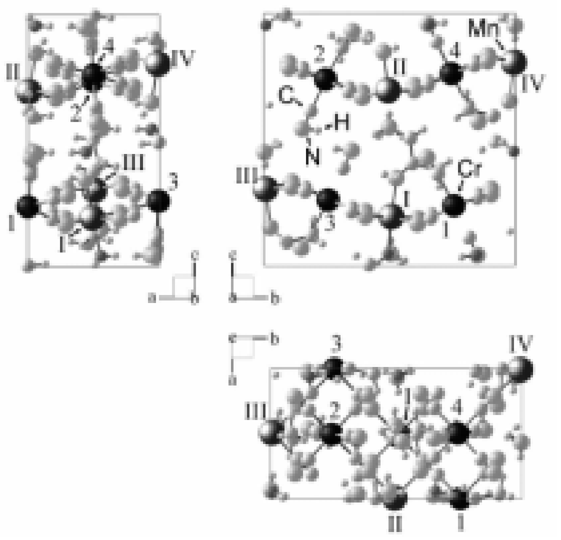

Figure 1. Crystal structure of $[Cr(CN)_6][Mn(S)\text{-}pnH(H_2O)](H_2O)$. Magnetic atoms Cr and Mn are marked with the Arabic and Roman numerals, respectively.

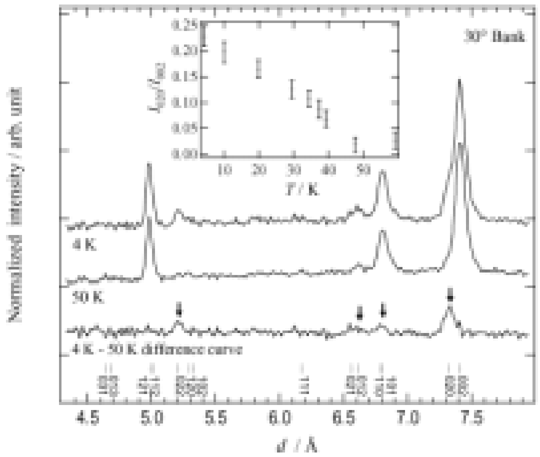

Figure 2. The neutron diffraction patterns at 4 K (below T_C) and 50 K (above T_C), and their difference pattern of $[Cr(CN)_6][Mn(S)\text{-}pnH(H_2O)](H_2O)$ obtained by the 30 degree bank of the Vega diffractometer. The difference pattern shows the magnetic contribution only. Intensities are normalized by the incident spectrum. The inset shows the temperature dependence of the intensity ratio of the 020 magnetic Bragg reflection to the 002 nuclear Bragg one, I020/I002.