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.

On the other hand, each $\text{[Cr(CN)\textsf{\textit{6}}]}^{3-}$ ion utilizes all cyanide moieties to connect between adjacent strands via cyanide bridges to Mn$^{\text{II}}$ 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$^{\text{III}}$ and two Cr$^{\text{III}}$ ions) and four cyanide groups as a repeating unit characterized by a reverse 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, $\mu$SR (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](image1.png)

**Figure 1.** a) Coordination geometry of the heptanuclear unit of \([\text{Cr}^{III}(\text{CN})_{6}]\)[Mn\(^{II}\) L-NH\(_2\)ala\(_3\)](3H\(_2\)O) (1). b) Overall view of crystal structure of \([\text{Cr}^{III}(\text{CN})_{6}]\)[Mn\(^{II}\) L-NH\(_2\)ala\(_3\)](3H\(_2\)O) (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](image2.png)

**Figure 2.** Capped sticks models of a left-handed and a right-handed triple strands in \([\text{Cr}^{III}(\text{CN})_{6}]\)[Mn\(^{II}\) D- or L-NH\(_2\)ala\(_3\)](3H\(_2\)O) (1). Mn atoms are shown in purple, C in gray N in blue and O in red.

![Figure 3](image3.png)

**Figure 3.** \(\chi_{mol} T\) versus \(T\) plot at 5000 G of \([\text{Cr}^{III}(\text{CN})_{6}]\)[Mn\(^{II}\) D or L-NH\(_2\)ala\(_3\)](3H\(_2\)O) (1). Inset: Plot of effective magnetic moment versus \(1/T\).

![Figure 4](image4.png)

**Figure 4.** Temperature dependence of magnetization of \([\text{Cr}^{III}(\text{CN})_{6}]\)[Mn\(^{II}\) D- or L-NH\(_2\)ala\(_3\)](3H\(_2\)O) (1). The FC (triangle) and ZFC (circle) magnetizations at 5 G are shown. Inset: Field dependence of magnetization of \([\text{Cr}^{III}(\text{CN})_{6}]\)[Mn\(^{II}\) D- or L-NH\(_2\)ala\(_3\)](3H\(_2\)O) (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, \([\text{Cr}(\text{CN})_{6}]\)[Mn(S)-phH(H\(_2\)O)](H\(_2\)O) (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 $P2_12_1'$, 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 $[\text{Cr(CN)}_6][\text{Mn(S)-pnH(H}_2\text{O)}]$ ($\text{H}_2\text{O}$). 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 $[\text{Cr(CN)}_6]$ $[\text{Mn(S)-pnH(H}_2\text{O)}]/\text{H}_2\text{O}$) 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 depen-
dence of the intensity ratio of the 020 magnetic Bragg
reflection to the 002 nuclear Bragg one, I020/I002.