Strong Magnetocrystalline Anisotropy in MnTPP-TCNE Charge Transfer Complex

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Magnetic properties of one-dimensional charge transfer complex between manganese *meso*-tetraphenylporphyrin (MnTPP) and tetracyanoethylene (TCNE) were investigated as its plate crystals. Strong magnetocrystalline anisotropy was observed in the field and the temperature dependences of magnetization. Magnetic phase transition was observed at 24 K and 27 K under 0.5 T of magnetic field along a- and b-axes, and c-axis, respectively. Either temperature was higher than that (18 K) of powder sample reported previously.

Recently, remarkable progress has been made in development of molecule-based magnets with their deep understanding.[1, 2] Great significance is always placed on structural dimensionality in material design of the molecule-based magnets, similar to researches of organic conductors and superconducting materials.[3-6] Although recent studies have concluded that higher-order dimensionality of spin-spin interaction should be crucial to design a magnet with higher magnetic transition temperature,[7] a one-dimensional system is still one of the most foundamental targets to be studied due to easy adaptability of theories and clear correlation between anisotropic properties and crystal structures.[8] Here is a one-dimensional molecule-based magnet, charge transfer complex (MnTPP-TCNE) of manganese *meso*-tetraphenylporphyrin (Fig. 1) and tetracyanoethylene which has been investigated by J. S. Miller et al..[9] This powder sample shows a magnetic phase transition at 18 K with a magnetic hysterisis loop. However, no information on magnetic properties of its single crystals has been given although its crystallographic study was successful. In this paper we report strong magnetocrystalline anisotropy in the crystals of MnTPP-TCNE charge transfer complex and higher magnetic transition temperatures along three orthogonal directions.

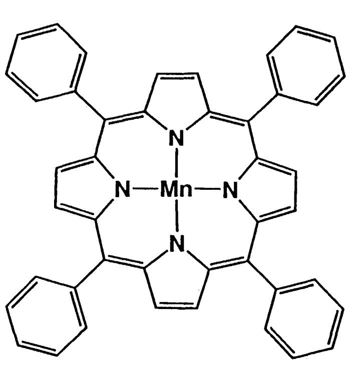

Figure 1. Manganese meso-tetraphenylporphyrin.

The charge transfer complex, MnTPP-TCNE, was prepared according to the method reported by Basolo and co-workers.[10] Mixing of Mn(II)TPP pyridine solution and TCNE toluene solution immediately gave a precipitate, which was identical a powder sample reported previously.[9,10] According to the crystallographic study,[9] MnTPP is linked along axial direction by TCNE radical anion through weak coordination of the *trans*-cyano groups to manganese as a bidentate ligand, to form one dimensional polymer chain with alternate arrangement. The plate crystals were obtained through slow crystallization from the resulting toluene filtrate at room temperature for a few days. The plate crystals showed optical dichroism, implying that one-dimensional MnTPP-TCNE chain would lie on the planar plate and along the long axis of the crystal. One of the plate crystals studied here was 1.2 mm x 0.2 mm x 0.6 mm in size where the directions of three sides of the crystal were defined as a-, b-, and c-axes, respectively. The magnetic properties were measured by a superconducting quantum interference device magnetometer (Quantum Design, MPMS-5S).

Strong magnetocrystalline anisotropy was observed in the field dependences of magnetization at 1.7 K (Fig. 2). The curve along a-axis, probably as an easy axis, was almost saturated over 1 T. This saturation magnetization corresponds to 4.3 Bohr magneton, in reasonably agreement with a simple sum of S = 2 for high-spin state of manganese atom and S = 1/2 for TCNE radical anion, assuming ferromagnetic exchange coupling between them. On the contrary, the crystal resisted magnetizations along b- and c-axes under the same field. Even at 5 T no saturation was achieved, so that both directions may be hard axes.

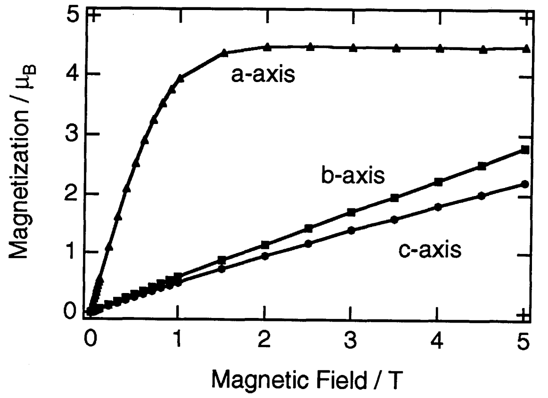

Figure 2. Field dependences of magnetization along three orthogonal directions at 1.7 K

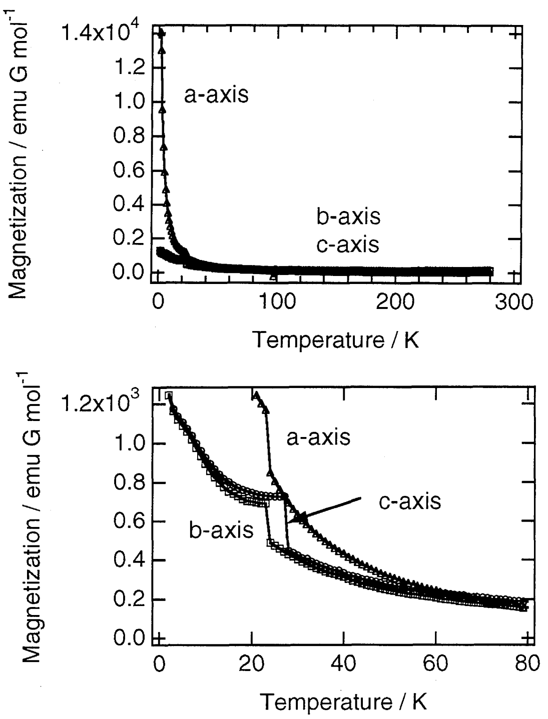

Figure 3. Temperature dependences of magnetization along three orthogonal directions (a) and its enlarged figure around magnetic phase transitions (b).

On decreasing temperature, a conventional field-cooled magnetization curve at 0.5 T gave no distinct break indicating magnetic phase transition. Magnetization at 0.5 T was recorded with increasing temperature from 1.7 K to 280 K. The magnetization curve displayed a drastic decrease under 0.5 T of external field along a-axis and gentle curves under the same field applied to b- and c-axes (Fig. 3a). Careful attention should be drawn on small abrupt breaks at 24 K for a- and b-axes, and 27 K for c-axis, indicating anisotropic magnetic phase transition (Fig. 3b). The small but reproducible difference in temperature of the phase transition may result from anisotropic crystal structure with easy and hard axes for magnetization. Note that all these temperatures are higher than the magnetic phase transition (18 K) of powder sample reported previously.[9]

Temperature dependences of susceptibility in the paramagnetic region were analyzed by Curie-Weiss formula. The plots for a-, b-, and c-axes gave Weiss temperatures of 64 K, -1.7 K, and -12 K, respectively. The first positive value for a-axis suggests strong ferromagnetic exchange interaction which is consistent with the result that the a-axis saturation magnetization (Fig. 2) was described by a simple sum of S=2 for manganese atom and S=1/2 for TCNE radical anion. This a-axis magnetization may result from intrachain interaction between MnTPP and TCNE. The other Weiss temperatures imply weak antiferromagnetic interactions between the polymer chains. Curie-Weiss analysis on powder sample in the present study and the previous report by J. S. Miller et al.[9] suggested both ferromagnetic and antiferromagnetic interactions with 61 K and -15 K of Weiss temperature. One can reasonably find almost the same temperatures to the present anisotropic Weiss temperatures of the crystal.

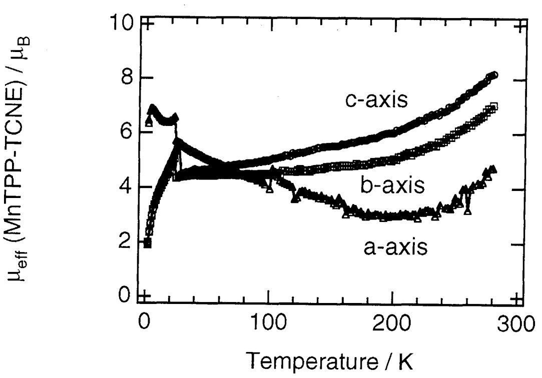

Figure 4. Temperature dependences of effective magnetic moment for MnTPP-TCNE along three orthogonal directions.

In addition to these anisotropy, the features of individual spin-spin interactions as a function of temperature can not be well explained, as Fig. 4 shows. For example, the paramagnetic behaviors above 200 K look different from those in the range between 200 K and the phase transitions to which the Curie-Weiss law was applied. These behaviors have not been observed in the powder sample of MnTPP-TCNE. A detailed interpretation will require crystallographical data, especially considering the possibility of any structural changes or phase transitions in the temperature range studied here, which is under investigation.

In conclusion, clear magnetocrystalline anisotropy was revealed in the field dependence of magnetization, the magnetic phase transition, and the spin-spin interaction of the MnTPP-TCNE charge transfer complex by using its plate crystal. These features can be attributed mainly to coexistence of both intrachain ferromagnetic interaction and interchain antiferromagnetic one, and does be characteristic of a one-dimensionally molecule-based magnet. Further analysis on the magnetocrystalline anisotropy will provide significant insight to engineer molecule-based magnets with higher performances.

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