Studies for Direction Dependences of Magnetizations and Magnetic Structure of Chiral Molecule-based Metamagnet, $[Mn(hfac)_2]\cdot BNO^*$

Youhei Numata[1,2] and Katsuya Inoue*[2,3]
[1]*Department of Structural Molecular Science, The Graduate School for Advanced Studies, Myodaiji, Okazaki 444-8585*
[2]*Department of Chemistry, Graduate School of Chemistry, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526*
[3]*Institute for Advanced Materials Research, Facility of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8530*

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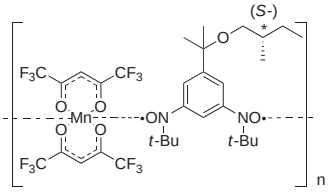
We measured angular dependences of single-crystal magnetization for the chiral structural molecule-based metamagnet $[Mn(hfac)_2]\cdot BNO^*$ (**1**). This crystal shows remarkable crystal direction dependences of spin flip transition in all crystallographic *a*, *b*, and *c* axes and the transitions are observed at different critical magnetic fields ($H \parallel a$: 640 Oe, $H \parallel b$: 1000 Oe, and $H \parallel c$: 1250 Oe at 2 K). These results mean that **1** has independent antiferromagnetic multi-sublattices. We calculated its possible magnetic structure from magnetic data and constructed magnetic structural model.

Constructions and investigations of chiral magnets are attracting, because of its novel and interesting magnetic and optical properties. For example, helical or conical magnetic structure,[1] canted antiferromagnetism,[2] nonlinear magneto-optical effects[3] and magneto chiral dichroism (MChD) effect[4] are expected in such materials. We designed chiral structural molecule-based magnets by means of the structural chirality inducing from chiral substituents. In such structurally chiral magnets, asymmetric electronic dipole moments survive. And the asymmetric dipole fields stabilize ferroic Dzyaloshinsky–Moriya (DM) vectors.[2b,5] Results of these situations, the chiral magnetic structures are expected. Now, many chiral structural magnets are prepared and its magnetic, optical, and other physical properties are investigated.[6]

On the other hand, low-dimensional ferro- or ferrimagnetic systems frequently show metamagnetic behaviors. The spin structures of metamagnets are understood as the antiferromagnetic orderings of ferro- or ferrimagnetic one-dimensional chains or two-dimensional sheets. In such case, these materials show spin flip transition at a critical magnetic field. In the single crystal of meta- and antiferromagnets, magnetization curves show the angular dependent behaviors. These behaviors depend on the angles between the direction of spins and applied magnetic field. If the direction is parallel ($H_{\parallel}$), a spin flip transition is observed (easy axis). If the direction is perpendicular (H_{∞}), magnetization values increase gradually and then, saturate (hard axis) (Figure S5).[7] However, the chiral structural molecule-based metamagnet **1** shows the spin flip transitions for all crystallographic axes. In this paper, we report temperature dependences of zero-field-cooled and field-cooled magnetization and magnetization processes of single crystal of **1**. And the magnetic structure of **1** is considered from these magnetic data.

Preparation, crystal structure, and magnetic properties of polycrystalline sample of **1** are already reported.[6a] $[Mn(hfac)_2]$ and chiral bisnitroxide radical molecules form alternate one-dimensional helical chain along to crystallographic *c* axis (Scheme 1). Space group of this compound is chiral triclinic *P*1 (No. 1). Interchain Mn–Mn distances are more than 11.0 Å and intrachain Mn–Mn distances are shorter than 8.9 Å. The Mn–Mn distances are presented in Figures S1[9] and S2[9]. This magnet undergoes antiferromagnetic phase at $T_N = 5.4$ K. Below 5.4 K, spin flip transition is observed. The observed saturated magnetization value, M_S corresponds to expected value of Mn^{II} ($S = 5/2$) and two aminoxyl groups ($S = 1$) are interacted antiferromagnetically. The ratio of inter- and intrachain magnetic interaction is estimated as ca. 10^{-3} for this complex.[8]



Scheme 1.

Single crystal of **1** was grown according to literature method.[6a] Magnetic measurements were done using Quantum Design MPMS-5S SQUID magnetometer and all data were corrected by Pascal's constants. The single crystal of **1** was mounted in the straw with Apiezon-M grease. Crystal dimension was $750 \times 600 \times 450\,\mu m^3$ and weight was 0.2346 mg. Figure S3[9] shows schematic drawing of the shape and size of this crystal.

Figure 1 shows the temperature dependences of *M* values measured in different crystallographic axes under 100 Oe. All magnetization curves show sharp peaks at 5.4 K and decrease by further cooling. These behaviors suggest that the all axes are antiferromagnetic easy axis. At 2 K, *M* values are 53 ($H \parallel a$), 148 ($H \parallel b$), and 223 ($H \parallel c$) emu mol^{-1} under 100 Oe.

Figure 2 shows the direction dependent *M*–*H* plots measured at 2 K. At 2 K, spin flip transitions were observed in every axis at 640 Oe ($H \parallel a$), 1000 Oe ($H \parallel b$), and 1250 Oe ($H \parallel c$), respectively. These results indicate that crystallographic *a*, *b*, and *c* axes correspond to magnetic easy axes for metamagnet. *M* values in all axes rise sharply at different critical field (Figure 2 inset). These results are evidence of existence of antiferromagnetic multi-sublattices in this single crystal. This multi-sublattice structure is understood as that some canted spins are interacted ferro- and antiferromagnetically, and total *M* values become zero. The driving force of spin canting is considered with DM interaction, which is generated from its asymmetric electronic dipole field based on its chiral structure.[2b,5]

Figure 3 shows the relationship among observed *M* values, the directions of applied magnetic field and spin orientations in metamagnet. We calculated the angles between antiparallel spin couples and each crystallographic axes using magnetic data and the equation, $\Delta|M| = 2|s|\cos\theta$. ΔM corresponds to the

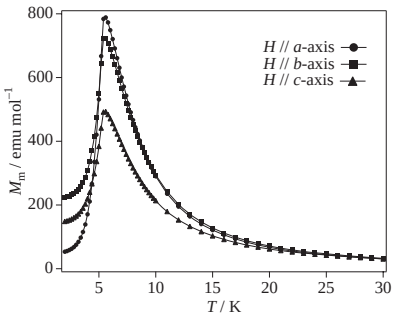


Figure 1. Temperature dependences of magnetization values measured under 100 Oe (field cooled).

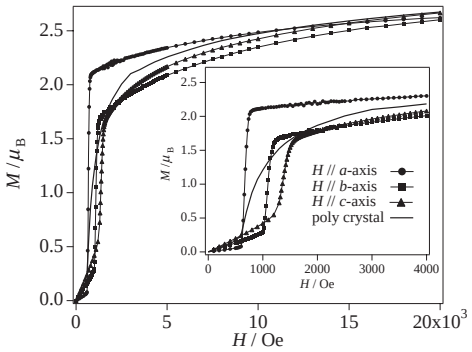


Figure 2. Magnetization curves of **1** measured at 2 K (inset is magnified).

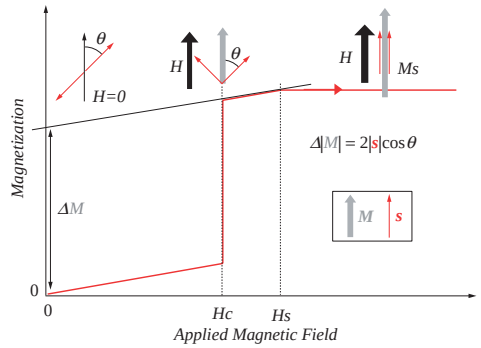


Figure 3. The relationship between the directions of antiparallel spin couples and applied magnetic field.

value of intersection with vertical axis (Figure 3). Calculated angles are 51° (from *a* axis), 67° (from *b* axis), and 74° (from *c* axis), respectively. These angles correspond to the projection angles of spin components to each crystallographic plane and spin orientations can be calculated from these angles. We draw possible magnetic structure of **1** and its projections in Figure 4. Further accurate research and neutron diffraction measurement are needed to reveal its magnetic structure and relationship with magnetic structure and chirality. These measurements are in progress.

In conclusion, we observed metamagnetic spin flip phenomena in all crystallographic axes in chiral molecule-based magnet **1**. The crystal direction dependences of critical field were measured in its single crystal. It is considered that these

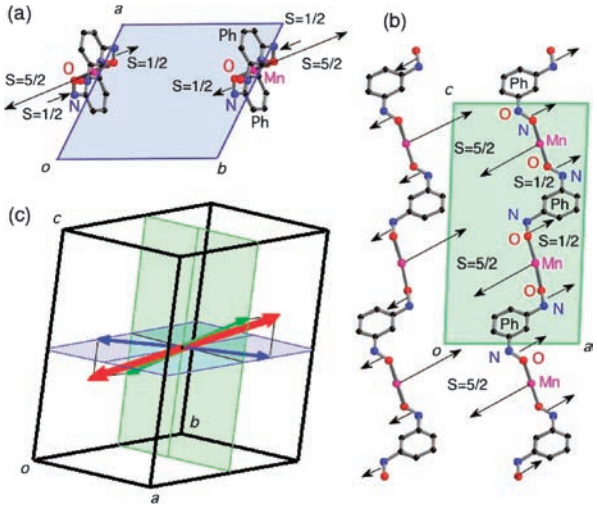


Figure 4. Projections of calculated magnetic structure of **1** down to a; *ab*-plane, b; *ac*-plane c; schematic drawing of spin structure with unit cell. Red = total spin, Blue = *ab*-plane component, and Green = *ac*-plane component.

results are come from chiral spin arrangement in asymmetric electronic dipole field. We calculated spin angles and possible magnetic structure.

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9 Supporting Information is available electronically on the CSJ-Journal Web site. http//www.csj.jp/journals/chem-lett/index.html.

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