Chemistry

1B/2006P015

Pressure effect on a structure and magnetic property of Fe(II)-Fe(III) alternate single chain magnet.

Takashi KAJIWARA*[1,2], Masahiro YAMASHITA[1]
[1]Tohoku Univ., Aza-Aoba, Aramaki, Sendai 980-8578, Japan
[2]Nara Wemen's Univ., Nara 630-8506, Japan

Introduction

One of the major advantages of molecular based magnets is their controllability in structures, which could affect on a magnetic behavior. We have reported a single-chain magnet (SCM), *catena*-[$Fe^{II}(ClO_4)_2\{Fe^{III}(bpca)_2\}$]-$ClO_4$ (Hbpca = bis(2-pyridylcarbonyl)amine) [1], in which two spin carriers Fe(II) (S = 2) and Fe(III) (S = 1/2) are alternately arranged in a ferrimagnetic manner. The magnetic easy-axis arises from the twisted arrangement of easy-plane of high-spin Fe(II) ion; high-spin Fe(II) ion in elongated octahedron possesses positive D, or easy-plane anisotropy, and mutual orthogonal arrangement of the easy-plane along the chain axis resulted in an easy axis anisotropy for the whole chain. This complex shows a reversible enhancement of its SMM character under the presence of the pressure up to 5 kPa [2]. This reversible changing of magnetism might be attributed to the small change of crystal structure of **1**, especially for the bonding distances around Fe ions. To discuss the detail of magnetism, single crystal X-ray diffraction analysis was carried out under the pressure of 2.1 kPa and 5.0 kPa.

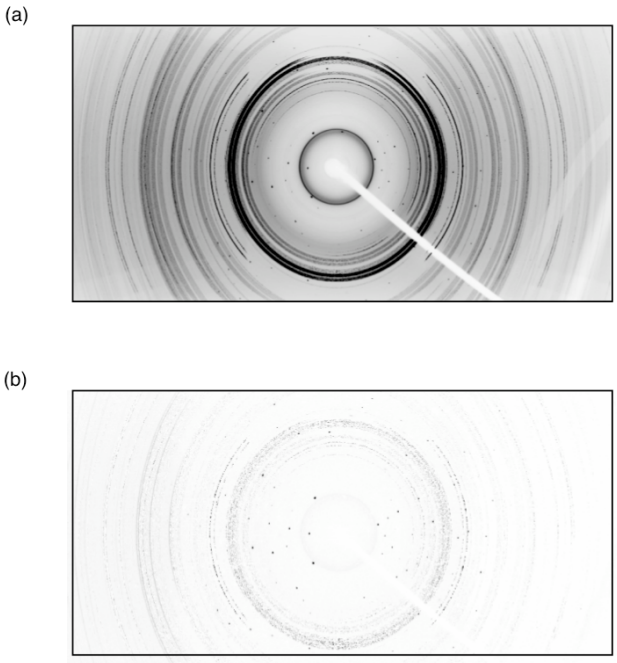

Figure 1. Observed (top) and processed (bottom) reflection images of **1**.

Results

A single crystal of **1** was located in the Be-Cu cell and pressure was applied using 1:1 mixture of Florinate 70 and 77 as a pressure medium.

It was hard to remove the diffractions from the Be pipe in a complete manner (Figure 1), and the structural analysis was impossible to be carry out. However, the unit cell parameters under each pressure were estimated with a sufficient quality (Table 1). Unit cell volume linearly changes along the applied pressures, and the volume loss leaches up to 2.1 % and 4.3 %, respectively. These large volume changes may be related to the shrink of inter-chain separation as well as to the shrink of chain itself along the chain axis, the latter may induce the changing of the SMM character of **1**. **1** remains its SMM character under these conditions, indicating that the each chain is spatially separated and inter-chain interaction is negligibly small under the applied pressures. The shrink of the unit cell is anisotropic, being more significant for a and c axes compared for b axis. Since the chain complex is lying along a–c vector, the shrink along this vector may cause the enhancement of magnetic interactions among Fe ions through bridging $bpca^-$ ligands, and then it resulted into the formation of higher energy barrier for spin flipping of Fe(II) ions which leads to an enhancement of SMM behavior of **1**.

Table 1: Unit cell parameters observed under different pressures.

	0 kbar	2.1 kbar	Dev. from 0 kbar	5 kbar	Dev. from 0 kbar
a/Å	13.811(7)	13.707(5)	-1.04	13.566(8)	-0.255
b/Å	18.523(4)	18.434(7)	-0.89	18.372(8)	-0.151
c/Å	15.473(7)	15.330(5)	-1.43	15.20(1)	-0.27
β/°	90.21(5)	90.38(4)	+0.17	91.22(6)	+1.01
V/Å^3	3958(4)	3873(3)	-85	3787(5)	-171

References

[1] T. Kajiwara *et al.*, J. Am. Chem. Soc., **127**, 10150 (2005).
[2] M. Mito, private communication.

* kajiwara@cc.nara-wu.ac.jp