Experimental report

21/05/2024

Proposal: 5-51-591 **Council:** 10/2022

Title: Magnetic structure and spin density determination at the new organic Honeycomb biradical F4BIPBNN

Research area: Physics

This proposal is a resubmission of 5-51-585

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Samples: C26H28F4N4O4
Cs[Mn(HCOO)3]

Instrument	Requested days	Allocated days	From	To
ORIENTEXPRESS	1	1	26/05/2023	27/05/2023
D9	15	15	25/05/2023	12/06/2023
D3	8	8	09/04/2023	18/04/2023
D19	10	0		

Abstract:

We have succeeded in synthesizing a new organic biradical F4BIPBNN which forms an S = 1/2 Heisenberg 3D honeycomb antiferromagnet. Alternate stacking of honeycomb layers with 4 exchange pathways is realized. Antiferromagnetic long range order has been observed below TN = 2.7 K at zero magnetic field. Static magnetic susceptibility including TN and magnetization curves are well reproduced by quantum Monte Carlo calculations with three antiferromagnetic interactions of 4.2-6.6 K.
The goal of the present experimental proposal is double. On one side our research group is interested in the exploration of the magnetic phase diagram of F4BIPBNN by the determination the magnetic structure of below 0.4K. This will help to understand the different magnetic interactions schemes proposed by the magnetometry and MO calculations.
On the other hand, the collected data at D9 will be used to determine with high accuracy the nuclear structure factors at low temperature as a previous step to proceed with the spin density determination, for which we apply to beamtime also at D3 instrument

Magnetic structure and spin density determination at the new organic Honeycomb biradical F_4BIPBNN.

1. Introduction

Purely organic magnets with π-electron spins have essentially negligibly small spin-orbit couplings and are attractive materials because they are archetypical Heisenberg spin systems in which the quantum fluctuations play an important role. The spin size and the connectivity of the network is the key factor of the novel magnetic states arising from quantum fluctuations. Among the representative stable organic radical skeleton, nitroxide (-N-O·) radical has the advantage of making antiferromagnetic spin network. The positive and negative partial charges on the N and O atoms, respectively, easily gives the intermolecular contact between the NO groups on which the singly occupied molecular orbital (SOMO), that is the molecular orbital (MO) of unpaired electron, is distributed. The intermolecular overlap between SOMO's always yields the antiferromagnetic interactions.[1,2] The stacking of planar π-conjugated molecules gives one-dimensional (1D) network. When two or more NO groups are substituted on a molecule, double spin chain with different spin size is formed.[2,3] After the extensive study on the 1D Heisenberg antiferromagnet, there is growing attention to the effect of quantum fluctuations in two- or three-dimensional (2D or 3D) Heisenberg antiferromagnets, but the experimental realization is still rare.

In order to realize a 3D spin network, we have designed an organic biradical involving two NN units which are coupled through twisted π-planes. It is F_4BIPBNN [= 2,2'-(3,3',5,5'-tetrafluorobiphenyl-4,4'-diyl)bis(4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide)] which forms a 3D honeycomb antiferromagnet with 4 magnetic exchange pathways at each site of $S = 1/2$. Each corner of a honeycomb layer is alternately connected to upper or lower layers to realize alternate stacking of honeycomb layers.

2. Previous experiments

We determined the crystal structure by single-crystal X-ray diffraction measurements [4]. On the basis of the molecular packing, two kinds of intermolecular interactions together with the intramolecular interactions form a 3D honeycomb network. The magnetic susceptibility was analyzed by quantum Monte Carlo method and the magnetic interactions were evaluated. The magnitude of the intra (J_0) and intermolecular (J_1-J_2) AF interactions is in the same order within the rage of 4.2-6.6 K. The 3D long range order was observed at $T_N = 2.7$ K, which is well reproduced by the 3D honeycomb model. The evaluation of the spin contraction factor shows the intermediate character of the present compound between 2D and 3D systems. The magnetic and thermal properties were examined in magnetic fields and the magnetic field versus temperature phase diagram is determined [4]. In the low field region, slight upward tendency of T_N for magnetic field was observed.

The heat capacity versus temperature for different magnetic fields from 0 to 14 T is shown in Fig.1. A typical λ-shaped peak was observed at $T_N = 2.7$ K for $B = 0$. It is evident that the LRO occurs in this material. The plot of T_N for each magnetic field determined from specific heat and susceptibility gives the B-T phase diagram shown in Fig.2.

Also, the *ab initio* molecular orbital (MO) calculations were performed using the package Gaussian09. UB3LYP method and broken symmetry (BS) hybrid density functional theory (DFT) calculations was applied with the basis set 6-31G. These calculations were done for the neighboring two molecules connected by J_0, J_1 or J_2, and the application of Yamaguchi's formula[5] gave the estimated values $J_0/k_B = 16$ K, $J_1/k_B = 2.7$ K, $J_2/k_B = 8.9$ K for 23 K. We must mention the overestimation of the intramolecular interaction in MO calculation. The problem is the fact that the pure singlet state is not described in unrestricted MO theory. This introduces

spin contamination especially in a biradical with large spin polarization. Although Yamaguchi's formula is the most commonly used, the overestimation of intramolecular interaction has been reported[6] whereas the intermolecular interaction is less influenced and qualitatively reliable.[7]

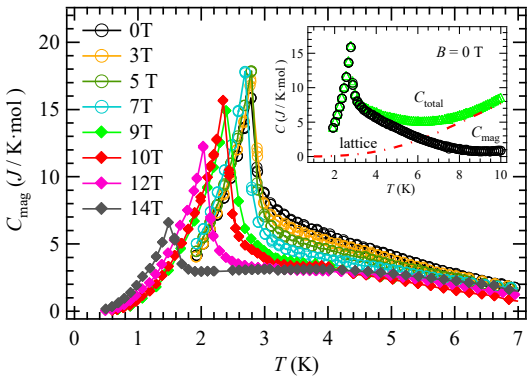

Fig. 1. Temperature dependence of magnetic specific heat of F4BIPBNN at zero field (○) and various magnetic fields B = 3T (○), 5T (○), 7T(○), 9T(◆), 10T(◆), 12T(◆), 14T(◆), respectively.

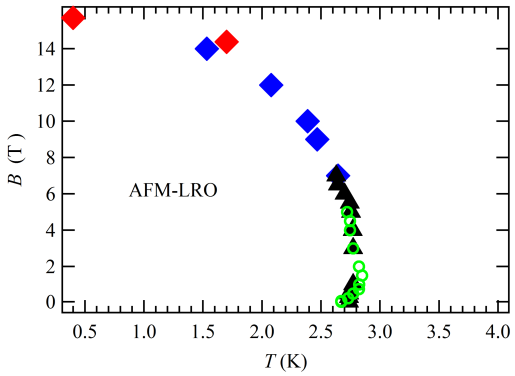

Fig. 2. B-T phase diagram of F4BIPBNN. Green circles represent TN determined by susceptibility. Black triangles and blue diamonds present TN determined by specific heat in separated measurements. Red diamonds are the saturation magnetization field observed in magnetization curves

3. References

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3) Y. Hosokoshi, K. Katoh, Y. Nakazawa, H. Nakano, and K. Inoue, J. Am. Chem. Soc., **123**, 7921 (2001).
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During the first hours we check different crystals of F4BIPBNN [= 2,2'-(3,3',5,5'-tetrafluorobiphenyl-4,4'-diyl)bis(4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide)] and unfortunately none of them had good crystallinity to start the data collection. As consequence the experiment was cancelled.