The crystal structure and magnetic properties of an organic verdazyl biradical.

K Iwase$^a$, H Yamaguchi$^a$, H Nojiri$^b$, A Matsuo$^c$, K Kindo$^c$, and Y Hosokoshi$^a$

$^a$Department of Physical Science, Osaka Prefecture University, Gakuen-cho 1-1, Naka-ku, Sakai, Osaka 599-8531, Japan

$^b$Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai, Miyagi 980-8577, Japan

$^c$The Institute for Solid State Physics, The University of Tokyo, Kashiwanoha 5-1-5, Kashiwa, Chiba 277-8581, Japan

E-mail: yhoso@p.s.osakafu-u.ac.jp

Abstract. The crystal structure and magnetic properties of metaphenylenebisverdazyl biradical ($m$-Ph-V$_2$) are presented. The temperature dependence of the product of the magnetic susceptibility and temperature, which is proportional to the square of the effective magnetic moment, shows a round maximum at about 40 K and a stationary behaviour at half the value of the room temperature in the temperature range of 4-7 K. In the crystal structure, the dimeric structure of molecules is noticeable and the susceptibility data were analysed by the four-spin cluster model with an $S = 1/2$. The intramolecular ferromagnetic interaction was estimated to $J_1/k_B = -40$ K.

1. Introduction

Recently, research of quantum spin system by using organic radicals has been interested. Because organic radicals have hardly magnetic anisotropy, they form ideal Heisenberg spin systems. Synthetic strategy to overcome weak intermolecular interactions is required. We are interested in verdazyl radicals which have widely distributed spin densities on the extended $\pi$-conjugation[1]. Although verdazyl radicals are one of the well-known radical species, systematic study with their crystal structures and magnetic properties is still limited. In this paper, we report the crystal structure and magnetic properties of metaphenylenebisverdazyl biradical ($m$-Ph-V$_2$). This compound was first synthesized by R. Kuhn et al.[2] and preliminary magnetic susceptibility measurements were reported by N. Azuma et al.[3] We succeeded in solving the crystal structure for the first time. Magnetic measurements down to low temperatures were made with high accuracy. The results were analyzed by the magnetic model based on the crystal structure.

2. Experimental

The verdazyl radical, $m$-Ph-V$_2$, was prepared by the method of Kuhn et al.[2]. Dark green single crystals of $m$-Ph-V$_2$ were grown by slow evaporation of the concentrated solution of CH$_2$Cl$_2$ at 253 K.
Figure 1. (a) Molecular structure of m-Ph-V₂. A verdazyl radical employing an S = 1/2 is marked by a broken circle. Between two radicals, the intramolecular ferromagnetic interaction (J₁ < 0) exists. (b) ORTEP drawing of an m-Ph-V₂ molecule. (c) Magnetic model of an m-Ph-V₂ molecule. An open circle and a line correspond to an S = 1/2 and the intramolecular interaction (J₁), respectively.

In the crystal structure, two kinds of intermolecular contacts shorter than the sum of van der Waals radii were observed. The one is the contact between the nitrogen atom of a verdazyl and the carbon atom of a phenyl ring between the molecules connected by an inversion symmetry (N…C 3.4 Å). Another is the contact between the carbon atoms of phenyl rings between the molecules connected by a translational symmetry (C…C 3.4 Å). The former makes a dimeric structure of molecules which results in the magnetic model of a four-spin cluster with S = 1/2 as is shown in Fig. 2 (a), where a bold and dashed line represents the intra- and intermolecular interactions, respectively. The latter gives a chain structure as is shown in Figure 2(b).

Figure 2. Schematic diagrams of two types of molecular contacts and corresponding magnetic models. A m-Ph-V₂ molecule is represented by the same definition used in Fig.1 (c). A broken line corresponds to the intermolecular contact. (a) A four-spin cluster model and (b) an alternating chain model with an intermolecular interaction J₂ and J₃, respectively.
3.2 Magnetic properties

The temperature dependences of the magnetic susceptibility ($\chi_p$) and the product of $\chi_p$ and temperature ($\chi_pT$) are shown in Fig.3(a) and (b), respectively. The value of $\chi_pT$ at 300 K is 0.77 emu K/mol, which suggests the existence of 2 mol of $S = 1/2$ species. In fact, the plot of $\chi_p^{-1}$ vs. $T$ above 200 K is reproduced by the Curie-Weiss law with the Curie constant $C = 0.752 \pm 0.003$ emu•K/mol and the Weiss constant $\Theta_W = 8 \pm 1$ K (Figure is not shown.). The positive Weiss constant is consistent with the increase of $\chi_pT$ below 300 K as decreasing $T$, and the dominant ferromagnetic interaction is attributable to the intramolecular one. The intramolecular ferromagnetic interaction is roughly estimated to $J_1/k_B = -32$ K from the relation $|J_1|/k_B = 3k_B\Theta_W/(S(S+1))$ which is consistent with the estimation for the oxoverdazyl analogue[5]. Although Azuma et al. reported a very strong intramolecular ferromagnetic interaction, we think that our result is accurate because we use crystals with high purity.

The value of $\chi_pT$ takes a maximum at about 60 K, and gradually decreases as decreasing $T$ below 60 K. This behavior suggests that there are additional antiferromagnetic intermolecular interactions. At least, two kinds of magnetic interactions exist in this system and the one is intramolecular one and another is intermolecular one. Then, we analyze the susceptibility behavior by using magnetic models considered from the crystal structure. In the crystal structure, we can see two kinds of intermolecular contacts. Consideration only one of the intermolecular contacts gives the magnetic model of a four-spin cluster (Fig.2(a)) or an alternating chain (Fig.2(b)) where the Hamiltonians is written in eq.(1) or (2), respectively.

$$H = J_1(S_1 \cdot S_2 + S_3 \cdot S_4) + J_2(S_2 \cdot S_3)$$

(1)

$$H = \sum_{i=1}^{N-1} [J_1 S_{2i} \cdot S_{2i+1} + J_3 S_{2i} \cdot S_{2i-1}]$$

(2)

In this case, the ferromagnetic interaction is assigned to $J_1(< 0)$ and $J_2$ or $J_3$ is antiferromagnetic interaction. The susceptibility behavior was analyzed by the four-spin cluster model[6] and the ferromagnetic and antiferromagnetic alternating chain model[7] and both models well reproduce the experimental results above 15 K. By the least-square-fitting, we obtained the parameter sets of $J_1/k_B = -40$ K, $J_2/k_B = 32$ K for the four-spin cluster model and $J_1/k_B = -39$ K, $J_3/k_B = 17$ K for the ferromagnetic and antiferromagnetic alternating chain model. The calculation of two models is compared with experiments in Fig.3 (a) and (b) plotted in the form of $\chi_p$ and $\chi_pT$, respectively.

Figure 3. (a) Temperature dependence of the magnetic susceptibility ($\chi_p$) of $m$-Ph-V$_2$. (b) Temperature dependence of $\chi_pT$. Open circles represent the experimental data. The solid and broken curves represent the calculated values for the four-spin cluster model with $J_1/k_B = -40$ K and $J_2/k_B = 32$ K and the ferromagnetic and antiferromagnetic alternating chain model with $J_1/k_B = -39$ K, $J_3/k_B = 17$ K, respectively.
The discrepancy below 10 K suggests that intermolecular interactions more than two should be considered. When we compare the calculation of two models with the experiment below 20 K, the calculation of the four-spin cluster model qualitatively reproduces the stationary behavior around 10 K in $\chi_p T$ vs $T$. Therefore, we consider that the first approximation of the magnetic model of $m$-Ph-V$_2$ is the four-spin cluster model shown in Fig. 2 (a). It is reasonable that the intermolecular contact between the verdazyl and phenyl ring yields stronger magnetic interaction than the one between the phenyl rings. The magnetization at 1.8 K gradually increases as increasing fields and reaches a quarter of the full saturation at 5 T. In order to elucidate the magnetic model and intermolecular interactions, observation of the full saturation in magnetization curves would be essential.

4. Summary

We have succeeded in solving the crystal structure of $m$-Ph-V$_2$ for the first time. From the result of crystal structure analysis, the magnetic system were considered to be a four-spin cluster model or an alternating chain model with ferromagnetic and antiferromagnetic interactions. Then, we analyzed the magnetic data above 15 K by using two kinds of magnetic models derived from the crystal structure. As a result, we succeeded in reproducing the observed data above 15 K by both models. Since both models give the same magnitude of the intramolecular interaction, we conclude that the intramolecular ferromagnetic interaction in $m$-Ph-V$_2$ is $J_1/k_B = -40$ K. The stationary behavior in the temperature dependence of $\chi_p T$ is qualitatively reproduceable by the four-spin cluster model with intermolecular antiferromagnetic interaction $J_2/k_B = 32$ K. The observed susceptibility below 10 K suggests that there are at least two kinds of intermolecular interactions. For the elucidation of the magnetic model, the complementary analysis of magnetization is useful. Magnetization measurements in high magnetic fields are now in underway.

5. Acknowledgement

The authors thank Mr. T. Shimokawa, Dr. H. Nakano, and Dr. T. Sakai for their helpful discussions. This research was partly supported by KAKENHI (21605010). A part of this work was performed under the interuniversity cooperative research program of the Institute for Materials Research, Tohoku University and the joint-research program of ISSP, the University of Tokyo.

References

[1] Azuma N 1982 Bull. Chem. Soc. Jpn., 55, 1357
[2] Kuhn R, Neugebauer F A, and Trischmann H 1964, Angew. Chem., 76, 691
[3] Azuma N, Ishizu, and Mukai K 1974 J. Chem. Phys., 61, 2294
[4] G. M. Sheldrick 2008 Acta. Cryst. A64,112
[5] Gilroy J B, McKinnon S D J, Kennespolh P, Zsombor M S, Ferguson M J, Thompson L K, and Hicks R G 2007 J. Org. Chem., 72, 8062
[6] Shiomi D, Tamura M, Sawa H, Kato R, Kinoshita M, 1993 J. Phys. Soc. Jpn., 62, 289
[7] Borras-Almenar J J, Coronado E, Curely J, Georges R, and Gianduzzo J C, 1994 Inorg. Chem., 33, 5171