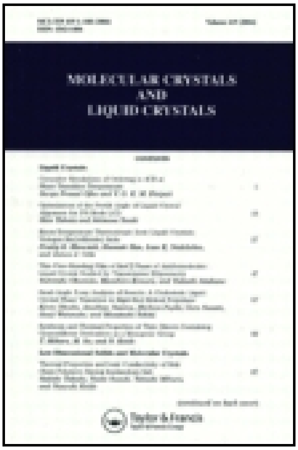

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Crystal Structure and Magnetic Properties of the S=1 Quasi-One-Dimensional Compound Ni([15]aneN$_4$)N$_3$(PF$_6$)

Yang Yu [a] , Zentaro Honda [a] , Koichi Katsumata [a] , Tachi Ohishi [b] , Toshio Manabe [b] & Masahiro Yamashita [b]
[a] The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama, 351-01, Japan
[b] Graduate School of Human Informatics, Nagoya University, Chikusaku, Nagoya, 464-01, Japan
Version of record first published: 04 Oct 2006.

To cite this article: Yang Yu , Zentaro Honda , Koichi Katsumata , Tachi Ohishi , Toshio Manabe & Masahiro Yamashita (1996): Crystal Structure and Magnetic Properties of the S=1 Quasi-One-Dimensional Compound Ni([15]aneN$_4$)N$_3$(PF$_6$), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 286:1, 121-126

To link to this article: http://dx.doi.org/10.1080/10587259608042275

Mol. Cryst. Liq. Cryst., 1996, Vol. 286, pp. 121–126
Reprints available directly from the publisher
Photocopying permitted by license only

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF THE S=1 QUASI-ONE-DIMENSIONAL COMPOUND Ni([15]aneN$_4$)N$_3$(PF$_6$)

YANG YU*, ZENTARO HONDA*, KOICHI KATSUMATA*, TACHI OHISHI**, TOSHIO MANABE** AND MASAHIRO YAMASHITA**
* The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan. **Graduate School of Human Informatics, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

Abstract A new S=1 quasi-one-dimensional compound Ni([15]aneN$_4$)N$_3$(PF$_6$) (chemical formula $NiC_{11}N_7H_{26}PF_6$, in short NPAP) has been synthesized. Both crystal structure and magnetic properties of this compound have been characterized using the single crystal samples. NPAP crystallizes in the orthorhombic system, with space group P2nn (No.34), Z=2 and unit-cell parameters a=11.332(5)Å, b=13.861(4)Å and c=6.173(2)Å, respectively. The crystal structure was solved using direct method and the refinement converged at R(R$_W$)=0.062(0.062). A superlattice along the c-axis was conformed by both X-ray Weissenberg film and powder diffraction method. In addition, a disorder of the packing sequence of the ([15]aneN$_4$) in-plane ligands along the c-axis was proposed. The temperature dependence of magnetization of a single crystal of NPAP was measured using a SQUID magnetometer. We have observed a large difference in zero field cooled and field cooled magnetizations below about 20K. We have also measured the AC susceptibility of this sample in zero static magnetic field. A cusp is observed at about 22K in the temperature dependence of AC susceptibility.

INTRODUCTION

One-dimensional Heisenberg antiferromagnetic (1DHAF) compounds become more and more interested both theoretically and experimentally due to their unique behaviour originating from quantum fluctuations. In 1983, Haldane [1] predicted that 1DHA compounds with integer spin (S=1,2,3..) exhibit an energy gap (Haldane-gap) between the singlet ground state and the first excited state, while those with half-integer spin (S=1/2, 3/2) do not have this gap. Since then, a number of 1DHAF compounds with S=1 have been synthesised and their Haldane gaps have been proved experimentally [2-6]. In addition, S=1/2 degrees of freedom have been observed in NENP doped with Cu [7], Zn, Cd and Hg [8] and even in undoped NENP [9]. A more recent work has been reported on the possibility of a spin-glass transition in a NENP crystal obtained by chance [10].

In the present work, a new S=1 quasi-one-dimensional compound Ni([15]aneN$_4$)N$_3$(PF$_6$) (NPAP) is reported, which behaves similar to the NENP crystal [10]. Its crystal structure and magnetic properties are studied. More concern is due to the structure characteristics.

SYNTHESIS AND CRYSTAL STRUCTURE OF NPAP

The synthesis of Ni([15]aneN$_4$)N$_3$(PF$_6$) was performed in two steps. First, Ni([15]aneN$_4$)(PF$_6$)$_2$ was obtained by mixing stoichiometrically Ni(PF$_6$)$_2$ aqueous solution with 1,4,8,12-tetraazacyclopentadecane ([15]aneN$_4$) methanol solution. Second, NaN$_3$ was mixed with Ni([15]aneN$_4$)(PF$_6$)$_2$ in aqueous solution and then the mixture was filtered. By slow evaporation at room temperature for two weeks, single crystals of Ni([15]aneN$_4$)N$_3$(PF$_6$) with blue-purple color were obtained.

The as-grown crystals were examined with an optical microscope and a Weissenberg X-ray camera, and one with the best quality was selected for data collection. The X-ray intensities were measured with a *MacScience* MXC18 automatic four-circle single-crystal diffractometor using graphite monochromated Mo$K\alpha$ (λ=0.71073 Å) radiation. The crystal structure of NPAP was solved by the direct method using the program SIR92. There was no solution unless one more carbon atom is added to the nominal in-plane ligand [15]aneN$_4$ (N$_4$C$_{11}$H$_{26}$). Under such circumstances, we had to "accept" this prerequisite in order to obtain the crystal structure. The final structure refinement converged at R(R$_W$)=0.062(0.062).The detail structure and its determination will be reported in a separate paper [11].

The crystal structure of NPAP, as shown in Fig.1, consists of two sets of linear chains (one through the vertices and the other through the body-center of the unit-cell), on which nickel ions and azido groups alternate following the sequence -Ni^{2+}-N$_3$-Ni^{2+}-N$_3$- in the c-direction (chain direction). The orientation of the in-plane ligands to each set of chains deviate about 12 degrees from the chain direction to each side of b-axis. PF$_6^-$ ions accommodate in the big vacancies between each chain. On the chain, a Ni^{2+} ion is surrounded pseudo-octahedrally by four nitrogen atoms of the in-plane ligand and two ones of the azido groups.

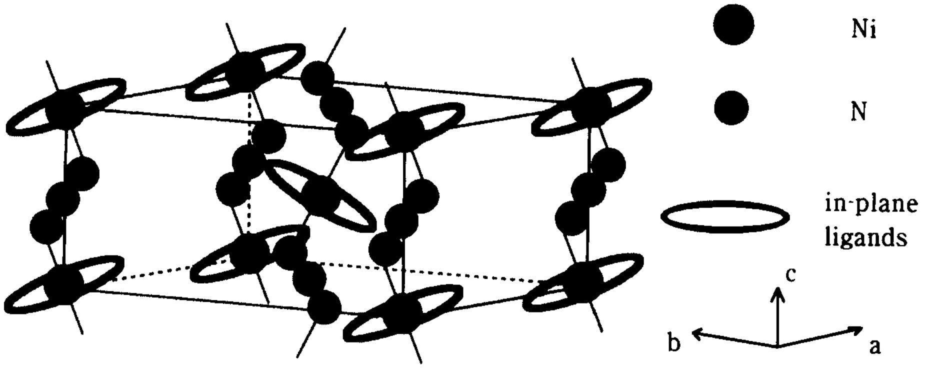

FIGURE 1 The crystal structure of Ni([15]aneN$_4$)N$_3$(PF$_6$)*.
* PF$_6^-$ atomic clusters are not indicated for simplification.
See Color Plate I.

MAGNETIC MEASUREMENTS

A DC magnetic susceptibility of a single-crystal NPAP has been measured with a SQUID magnetometer (Quantum design's MPMS2). Two modes of measurement were performed: Zero Field Cooled measurements (ZFC) and field cool measurements (FC). In ZFC measurement, the sample was cooled from high temperature to 1.8K in zero magnetic field, then a field of 100G was applied and the magnetic susceptibility was measured with increasing temperature. In the FC case, however, the measurement was performed under the applied field with decreasing temperature from room temperature. The results are shown in Fig. 2.

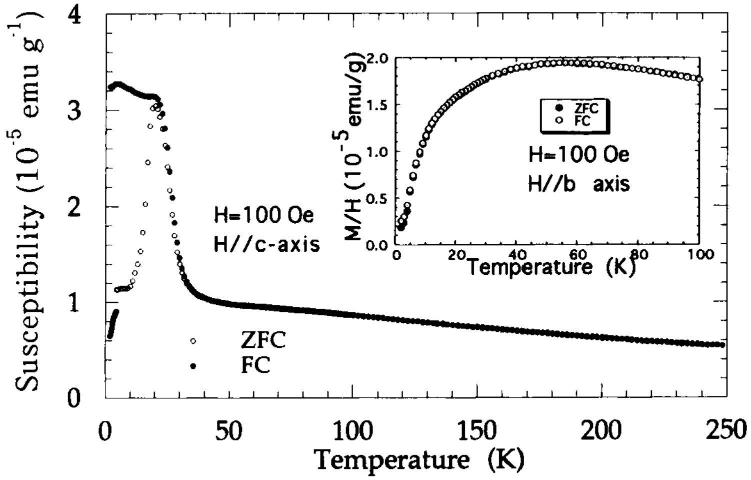

FIGURE 2 Temperature dependence of DC susceptibility of NPAP along the c-axis. Insect: temperature dependence of DC susceptibility of NENP [10].

DISCUSSION

As mentioned above, the result of our X-ray measurements suggests that the in-plan ligand contains twelve carbon atoms instead of eleven as proposed in the formula. However, a mass spectroscopy measurement of the same sample conformed that there are eleven carbon atoms included in the in-plane ligand. Therefore, the only explanation is as the following: in the "actual" structure, the orientation of the in-plane ligands has four choices, indicated 1,2,3,4 as shown in Fig. 3, in the way they pack along the chain direction. Since X-rays penetrate the whole crystal, only an "averaged structural result" can be found, i.e. the in-plane ligand looks as if it were composed of twelve carbon atoms (5 in Fig. 3). In addition, when solving the structure using the direct method, a two-fold rotational axis was found in the direction of N-Ni^{2+}-N in the in-plane ligand. Therefore, the possible orientation of the in-plane ligands is either 1&2 or 3&4, as shown in Fig. 3 where the case 1&2 is shown.

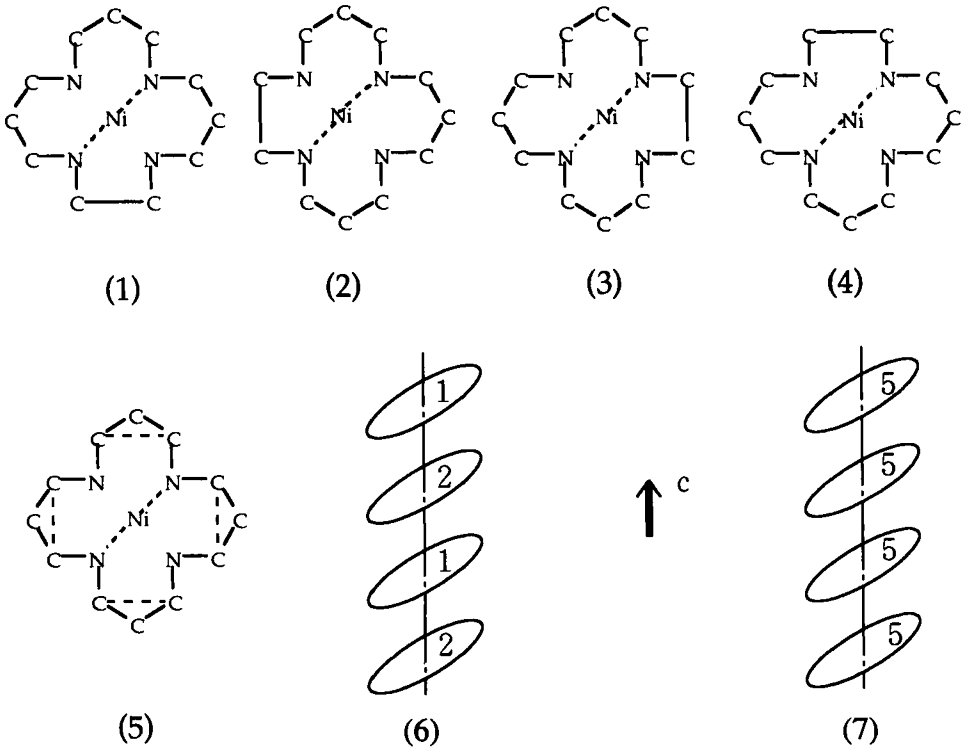

FIGURE 3 Diagrammatic configurations of the in-plan ligands in "actual" (1-4) and "ideal" (5) crystal and their packing modes along the chain direction in "actual" (6) and "ideal" (7) crystal.

Moreover, from the Weissenberg X-ray oscillation film with the oscillation axis parallel to c-axis and, as well, from the powder diffraction pattern of the same sample, a superlattice along the c-axis was found, which is about twice of c of the unit-cell. This indicates that the packing sequence of the in-plane ligands along the chain is -1-2-1-2- in the "actual" crystal instead of -5-5-5-5- in the "ideal" (as from X-ray study) crystal, as indicated 6 and 7 respectively in Fig. 3.

It should be noted that for the same Weissenberg X-ray film, the diffraction spots corresponding to the superlattice are broadened compared to those corresponding to the normal lattices. It is reasonable if we assume that a small part of the in-plane ligands do not pack in a well-ordered -1-2-1-2- sequence in the "actual" crystal. This disorder in the packing sequence of the in-plane ligands will result in a broadening of the superlattice diffraction spots.

From Fig. 2, it can be seen that the DC susceptibility of NPAP differs very much from that of the typical S=1 Haldane compound, e.g. NENP, as shown in the inset. No rounded maximum is found in NPAP as in NENP. Instead, for both ZFC and FC measurements, the susceptibility of NPAP steadily increases from room temperature down to about 30K and then drastically increases from 30K to about 20K. Whereafter, the susceptibility for ZFC measurement decreases greatly, while that for FC measurement remains almost constant with decreasing temperature.

We have also measured AC susceptibility of NPAP. A cusp has been observed in the temperature dependence and the position of which shifts to the high temperature side with increasing frequency. The temperature corresponding to the cusp at the lowest frequency (0.1Hz) is about 22K, which is slightly larger than that for the DC measurement (20K). This is reasonable because the DC measurement is a specific case of AC measurement in zero frequency limit.

It should be mentioned that all these novel behaviours of both DC and AC susceptibility measurements described above are typical what a spin-glass compound behaves [12]. However, other explanations are possible. In order to clarify the unique magnetic properties found in NPAP, further experiments are necessary. Synthesis of other batch of the NENP crystals which show spin-glass behaviour [10] has been unsuccessful. In the present case, we have obtained qualitatively the same magnetic behaviour in different crystals from different batches. This makes a systematic study of the magnetism in NPAP possible.

Finally, we would like to acknowledge Dr. I. Higashi, Ms. K. Kobayashi and Mr. Y. Iimura for their helpful discussions about the structure. Thanks are also due to Mr. Y. Esumi for his help in the mass spectroscopy experiment.

REFERENCES

1. F. D. M. Haldan, Phys. Lett., 93A, 464 (1983); Phys. Lett., 50, 1153 (1983).
2. J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkelens, J. Rossant-Mignod, J. Ribas, W. G. Striling and C. Vettier, J. Appl. Phys., 63, 8 (1988).
3. K. Katsumata, H. Hori, T. Takeuchi, M. Date, A. Yamagishi and J. P. Renard, Phys. Rev. Lett., 63 86 (1989).
4. T. Takeuchi, M. Ono, T. Yosida, A. Yamagishi and M. Date, J. Phys. Soc. Jpn., 61 3255 (1992).
5. T. Takeuchi, H. Hori, T. Yosida, A. Yamagishi, K. Katsumata, J. P. Renard, V. Gadet, M. Verdaguer and M. Date, J. Phys. Soc. Jpn., 61 3255 (1992).
6. M. Yamashita, K. Inoue, T. Ohishi, T. Takeuchi, T. Yosida and W. Mori, Mol. Cryst. Liq. Cryst., 274, 25 (1995).
7. M. Hagiwara, K. Katsumada, I. Affleck, B. I. Halperin and J. P. Renard, Phys. Rev. Lett., 65 3181 (1990).
8. S. H. Glarum, S. Geschwind, K. M. Lee, M. L. Kaplan, and J. Michel, Phys. Rev. Lett., 67 1614 (1991).
9. M. Hagiwara and K. Katsumada, J. Phys. Soc. Jpn., 61 1481 (1992).
10. M. Hagiwara, K. Katsumada S. Sasaki, N. Narita, I. Yamada and T. Yosida, J. Phys. Soc. Jpn., 64 3674 (1995).
11. Y. Yu, Z. Honda, K. Katsumata, T. Ohichi, T. Manabe and M. Yamashita, in manuscript.
12. J. A. Mydosh, Spin Glasses (Taylor & Francis, London, Washington DC, 1993).