Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: Takaharu Kusaka, Takayuki Ishida & Takashi Nogami (2003): Solvated Magnets of Fe[N(CN) 2] 2 (pyrimidine): Transition Phenomena Tuned by Guests, Molecular Crystals and Liquid Crystals, 379:1, 259-264

To link to this article: http://dx.doi.org/10.1080/713738599

Mol. Cryst. Liq. Cryst., Vol. 379, pp. 259-264

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090570

Solvated Magnets of $Fe[N(CN)_2]_2$(pyrimidine): Transition Phenomena Tuned by Guests

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Low-temperature magnets derived from $Fe[N(CN)_2]_2$(pyrimidine) have guest molecules incorporated in the clearance of the 3-D framework. The ac and dc magnetic susceptibility measurements reveal that the temperature of magnetic phase transition (T_N) depends on the guest molecules. They are characterized as weak ferromagnets below T_N. The compound containing uncoordinated pyrimidine molecules as a guest showed the highest T_N of 5.6 K in this family.

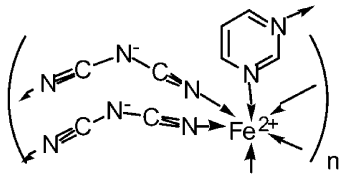
Keywords: host-guest compound; weak ferromagnet; X-ray diffraction; magnetic phase transition

INTRODUCTION

Magnetism of transition-metal complexes with 3-dimensional networks is of current interest for developing high T_C magnets[1]. Self-assembled complexes also attract attention for porous materials affording potential application in many areas (gas absorption for instance)[2]. Porous magnets enable us to examine possible control of the magnetism by means of supramolecular techniques[3]. Recently we reported the crystal structure and magnetic phase transition of

$M^{II}[N(CN)_2]_2(pm)$ (M = Fe[4], Co[4], Ni[5]; pm = pyrimidine) containing both μ-1,5-$N(CN)_2^-$ and μ-1,3-pm bridges. The specimen prepared from an ethanol solution was revealed to contain ethanol molecules as a guest[4]. Magnetic measurements indicate that the Fe complex behaves as a weak ferromagnet below the transition temperature (T_N) of 3.2 K[4]. We report here the solvent-effect on the magnetic properties of solvated magnets of $Fe[N(CN)_2]_2(pm)$ since preparation from various solvents gave isomorphous compounds with only slight structural modification.

pm



$Fe[N(CN)]_2(pm)$

EXPERIMENTAL

The following synthetic procedure is typical. An aqueous solution containing pm and $NaN(CN)_2$ with a 1/1 molar ratio was added to an aqueous solution of a half molar amount of $FeCl_2 \cdot 4H_2O$. The mixture was allowed to stand for several days to give yellow single crystals (**1**). The polycrystalline samples of **2**, **3**, and **4** were prepared similarly from EtOH-H_2O (1/2), PrOH-H_2O (1/4), and BuOH-H_2O (1/15) mixed solutions, respectively, by using the pm/$NaN(CN)_2$/$FeCl_2$ ratio of 1/2/1. Elemental analysis (C, H, N), X-ray crystallographic analysis, and magnetic measurements of these compounds were done immediately after the isolation on a filter. The elemental analysis revealed that the composition formulae were $Fe[N(CN)_2]_2(pm)(guest)_n$, where $(guest)_n$ = $(pm)_1$, $(EtOH)_1$, $(PrOH)_1$, and $(BuOH)_{0.5}$ for **1** - **4**, respectively.

X-Ray diffraction data were collected on a Rigaku Raxis-Rapid IP diffractometer with monochromated Mo*K*a radiation. Structures were solved by direct methods and the atomic positions were refined by full-matrix least-squares methods using all of the reflections.

Magnetic properties were measured on Quantum Design MPMS SQUID and PPMS ac/dc magnetometers. Diamagnetic contribution of

the sample itself was estimated from Pascal's constant.

RESULTS AND DISCUSSION

X-Ray Crystal Structure Analysis

The crystals of **1** - **4** are isomorphous, belonging to a space group orthorhombic *Pnma*. Figure 1 shows the crystal structure of **1**. The guest molecule in **1** was characterized to be an uncoordinated pm. The hydrogen atoms in the guest pm were experimentally determined; the orientation of the six-membered ring shows no disorder. There is only one Fe ion in an asymmetric unit. Each octahedral Fe ion resides at an inversion center and is coordinated by four nitrile N atoms at the equatorial sites and by two pm N atoms at the axial sites. The Fe and two $N(CN)_2^-$ ions construct a two-dimensional network parallel to the *ac*-plane. The pm molecules bridge inter-sheet Fe ions along the *b*-axis. The $N(CN)_2^-$ and pm moieties contribute μ-1,5-bridged 2-D and μ-1,3-bridged 1-D structures, respectively, forming a 3-D framework.

The $Fe[N(CN)_2]_2$(pm) skeletons are essentially the same among **1** - **4**, except for the small change of the cell lengths (Table 1) and the presence of disorder of the $N(CN)_2^-$ positions in **2** - **4**. The crystal structure of **2** was published elsewhere[4]. The solvent molecules in **2** - **4** were found in difference Fourier maps but their positional and thermal displacement parameters could not be completely determined owing to disorder.

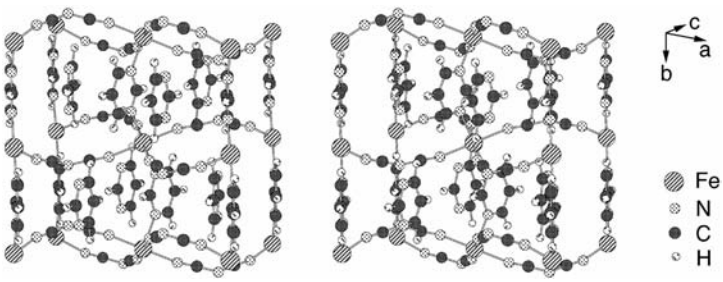


FIGURE 1 Stereo-view of the crystal structure of **1**.

TABLE 1 Selected crystallographic parameters of **1** - **4**.[a)]

Compound	**1**	**2**	**3**	**4**
Guest	pyrimidine	ethanol[b)]	propanol[b)]	1/2 butanol[b)]
a / Å	13.0061(5)	12.9378(7)	12.597(5)	12.9486(7)
b / Å	12.3550(4)	12.0279(6)	12.001(6)	12.2052(6)
c / Å	9.2235(4)	9.2456(4)	9.461(4)	9.4499(6)
V / Å^3	1482.1(1)	1438.8(1)	1430(1)	1493.5(2)
D_{calc} / g cm^{-3}	1.560	1.450	1.523	1.584

[a)] Measured at 90 K. The space groups are orthorhombic *Pnma* and $Z = 4$. [b)] Determined by elemental analysis (C, H, N).

Magnetic Properties

We measured field-cooled magnetization, remnant magnetization, and zero-field-cooled magnetization of **1** - **4**. The temperature dependence of the field-cooled magnetization at 5 Oe showed clear upsurges at about 5.6, 3.7, 4.6, and 3.6 K for **1** - **4**, respectively, and, after the applied field was removed, the remnant magnetizations were disappeared at the same temperatures. As Figure 2 shows, the ac magnetic susceptibility (χ_{ac}') measurements (100 Hz) exhibited peaks at 5.6, 3.3, 4.4, and 3.6 K, respectively, supporting the occurrence of magnetic phase transition.

Although the μ-1,3 pm bridge is supposed to work as a major exchange coupler in veiw of the Fe···Fe distances[4], we could find no relation between the transition temperatures and the b lengths. The transition temperature may be ruled also by secondary exchange couplings in the 3-dimensional network. Furthermore, the magnetic interaction is susceptible to the local geometry such as bond angles around Fe ions. Accordingly it is difficult to find relationship between the cell constants and transition temperatures. The magnetic ordering seems to be affected by crystallographic disorders, since **1** has no disorder of $N(CN)_2^-$ or of guest molecules and showed the highest transition temperature in spite of the relatively large cell volume.

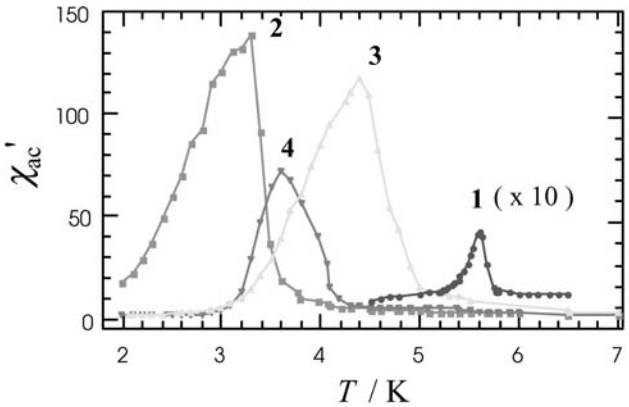


FIGURE 2 Temperature dependence of χ_{ac}' for **1** - **4**.

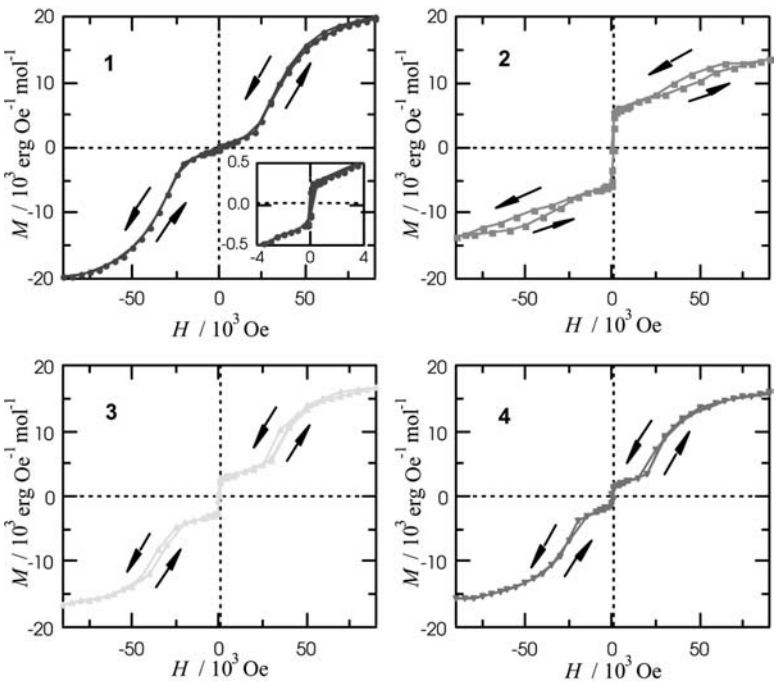


FIGURE 3 Hysteresis curves of **1** - **4** measured at 2.0 K. The solid lines are shown for a guide to the eye.

In order to clarify the nature of magnetism below the transition temperature, we measured *M-H* curves for **1** - **4**. Figure 3 shows that **1** - **4** behave as weak ferromagnets, as indicated by spontaneous magnetizations (M_S) in a low field region. Stepwise saturation behavior was observed, the origin of which has been proposed as spin-flip transition from a canted antiferromagnetic phase to a ferromagnetic phase[4]. The smaller M_S implies a smaller cant angle in a canted antiferromagnetic phase, and after a possible spin-flip transition the saturation magnetization should be larger in a canted ferromagentic phase. This interpretation is supported by comparison of the *M-H* curve of **1** with those of **2** - **4**. The M_S of **1** was the smallest and the strong antiferromagnetic nature seems responsible for the small χ_{ac}' peak of **1**.

In conclusion, we found that the molecular guests were incorporated in the clearance of the $Fe[N(CN)_2]_2(pm)$ skeleton. The T_N change of ca. 2 K is relatively large in the liquid He temperature region. The deformation of unit cells as well as the disorder of components may affect the magnetic phase transition phenomena.

Acknowledgments

This work was supported by Grants-in-Aid for Scientific Research on Priority Areas of "Metal-Assembled Complexes" (No. 401/11136212) and "Molecular Conductors and Magnets" (No. 730/11224204) and by a Grant-in-Aid for Scientific Research (No. 13640575) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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