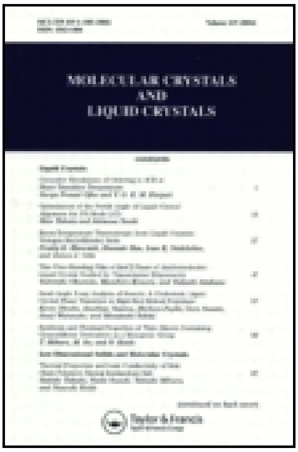

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Magnetic Phase Transition of FE^{II}, CO^{II} and NI^{II} Complexes Bridged by Pyrimidine and Dicyanamide

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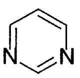
X-Ray diffraction study reveals that complexes $M^{II}[N(CN)_2]_2$-(pyrimidine) (M = Fe, Co, Ni) have an isomorphous 3-D network, in which $N(CN)_2^-$ and pyrimidine contribute μ-1,5-bridged 2-D and μ-1,3-bridged 1-D structures, respectively. Magnetic measurements indicate that the Fe, Co, and Ni complexes behave as weak ferromagnets below the transition temperatures of 3.2, 1.8, and 8.3 K, respectively.

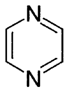
Keywords: weak ferromagnet, canted antiferromagnet, X-ray diffraction, magnetic phase transition

INTRODUCTION

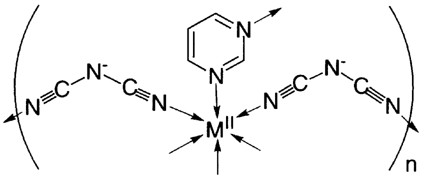
Magnetism of transition-metal complexes with a 3-dimensional network is of current interest for developing high T_C magnets. Various magnets have been reported containing polycyano-anion bridges such as $C(CN)_3^-$ [1] and $N(CN)_2^-$ anions [2]. We have reported the magnetism of pyrimidine-bridged transition metal complexes [3,4,5]. Ternary systems are also intensively studied and the peculiar crystal and magnetic structures of $Mn[N(CN)_2]_2(pz)$ [6] have been reported for an instance. Very recently we reported the crystal structure and magnetic phase transition of $M^{II}[N(CN)_2]_2(pm)$ [M = Fe (**1**), Co (**2**); pm = pyrimidine] containing both μ-1,5-$N(CN)_2^-$ and μ-1,3-pm bridges [5]. We report here the crystal structure and magnetic properties of a nickel(II) analogue, Ni[N(CN)$_2$]$_2$(pm) (**3**). In contrast to antiferromagnetism of Mn[N(CN)$_2$]$_2$(pz) containing similar μ-1,5-N(CN)$_2^-$ bridges [6], **1** - **3** show spontaneous magnetization below their transition temperature.



pm



pz



1: M = Fe, **2**: M = Co, **3**: M = Ni

EXPERIMENTAL

An EtOH-H$_2$O solution containing pm and NaN(CN)$_2$ with a 1/2 molar ratio was added to an aqueous solution of FeCl$_2$• 4H$_2$O which was equimolar of pm. The mixture was allowed to stand for several days to give yellow single crystals of **1**. Similar procedures using CoCl$_2$•6H$_2$O and NiCl$_2$•6H$_2$O in place of FeCl$_2$•4H$_2$O gave red and blue crystals of **2** and **3**, respectively. Elemental analyses (C, H, N) of **1** - **3** on a Fisons EA-1108 by a usual combustion method revealed that the crystals contained 0.5-1.0 molar of EtOH as a crystal solvent.

X-Ray diffraction data were collected on a Rigaku Raxis-Rapid IP diffractometer with monochromated Mo*K*α and Cu*K*α radiations. 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.

RESULTS AND DISCUSSION

X-Ray crystal structure analysis

Table 1 summarizes the X-ray crystallographic data for **1** - **3**. The crystals of **1** - **3** are isomorphous, belonging to a space group orthorhombic *Pnma*. Figure 1 shows the crystal structure of **3**. Following features are common to **1** - **3**: 1) M^{II} and two N(CN)$_2^-$ ions construct two-dimensional network parallel to the *ac*-plane. 2) Pm molecules bridge inter-sheet M^{II} ions along the *b*-axis, forming a pm-M *trans* zigzag chain. 3) Crystallographically independent units contain one metal ion. 4) Each octahedral M^{II} ion resides at an inversion center and is coordinated by four nitrile N atoms at the equatorial sites [7] and by two pm N atoms at the axial sites [8]. 5) The $N(CN)_2^-$ moiety was disordered into two positions. The amide nitrogen atom does not act as an N-donor. 6) The M···M separation across the pm bridge is shorter than that across the $N(CN)_2^-$ bridge. The pm bridge may afford a principal magnetic exchange pathway. 7) Crystal solvent molecules are disordered with the occupancy smaller than unity.

TABLE 1 Selected X-ray crystallographic data of **1** - **3**.

compound	**1**	**2**	**3**
Formula	$FeC_8N_8•C_2H_5OH$	$CoC_8N_8•C_2H_5OH$	$NiC_8N_8•H_2O$
Space group	*Pnma*	*Pnma*	*Pnma*
a / Å	12.917(1)	12.8586(4)	12.676(2)
b / Å	12.0440(6)	11.9268(4)	11.898(1)
c / Å	9.2575(8)	9.2126(2)	9.297(2)
V / Å^3	1440.2(2)	1412.86(7)	1402.0(3)
Z	4	4	4
D_{calc} / g cm^{-3}	1.449	1.491	1.283
T / K	100	100	296
R ($I > 2\sigma(I)$)	0.059	0.067	0.046
Reflections	1663	1699	1344
Reference	[5]	[5]	this work

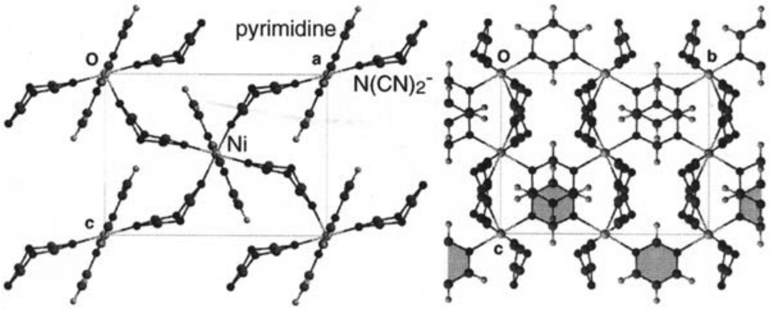


FIGURE 1 Crystal structure of $Ni[N(CN)_2]_2(pm)$ (**3**), viewed along the b (left) and a axes (right). Disordered solvent molecules are omitted for the sake of clarity. A one-dimensional Ni-pm chain is shaded.

Magnetic properties

Figure 2 shows the temperature dependence of the product of magnetic susceptibility and temperature ($\chi_{\mathrm{mol}}T$) for **1** - **3** together with those of $Mn[N(CN)_2]_2(pm)$ and $Cu[N(CN)_2]_2(pm)_{0.75}$ measured at 5 kOe. Although the decreases in $\chi_{\mathrm{mol}}T$ with a decrease of temperature are partly attributed to effects of the orbital angular momentum in metal ions, dominant antiferromagnetic interactions are assumed for all of the complexes, because the following magneto-structure relationship can be pointed out. In the crystals of **1** - **3**, every pm nitrogen atom is coordinated at an equatorial position, where a magnetic $d_{x^2-y^2}$ orbital of a high-spin Fe^{II}, Co^{II}, or Ni^{II} ion overlaps with a nitrogen lone pair. Their high-spin states are confirmed by the $\chi_{\mathrm{mol}}T$ values at 100 K. Thus, the role of an antiferromagnetic coupler is rationalized in terms of the superexchange mechanism similarly to the case of the pm-bridged copper(II) complexes [9]. Small peaks are found for **1** - **3** in Figure 2. We focus discussion on the magnetism of **3** here, since the detailed magnetic studies on **1** and **2** have been described elsewhere [5].

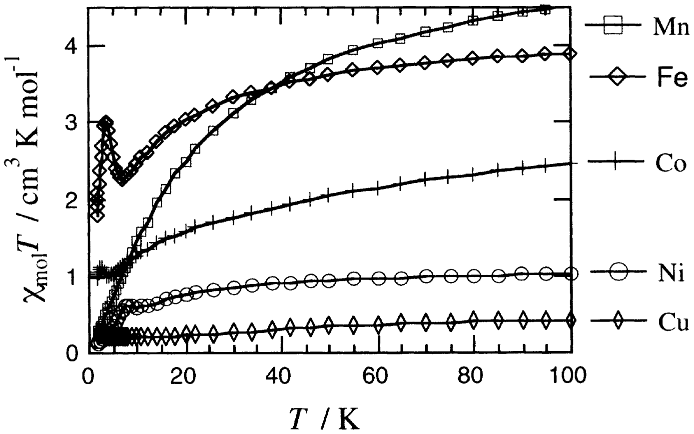


FIGURE 2 Temperature dependence of $\chi_{\mathrm{mol}}T$ for $M[N(CN)_2]_2(pm)$ complexes measured at 5 kOe.

In order to clarify the occurrence of magnetic phase transition of **3** around the peaking temperature of $\chi_{\mathrm{mol}}T$ (8 K), field-cooled magnetization (FCM), remnant magnetization (RM), and zero-field-cooled magnetization (ZFCM) were measured (Figure 3(a)). The FCM measured at an applied field of 5 Oe started to diverge at 8.5 K. The RM decreased and disappeared at 8.3 K, which we define as a transition temperature. The ZFCM, measured on heating at an applied field of 5 Oe, showed a maximum at 8.2 K and coincided with FCM above 8.2 K. Figure 3(b) shows the magnetization curve of **3** measured at 4 K. The magnetization varied linearly up to 70 kOe, owing to strong antiferromagnetic interaction. This finding is compatible with the dominant antiferromagnetic behavior of **3** observed in the $\chi_{\mathrm{mol}}T$ vs T plot (Figure 2). However, the spontaneous magnetization extrapolated to $H \rightarrow 0$ Oe was found to be 70 erg Oe^{-1} mol^{-1} (the inset of Figure 3(b)).

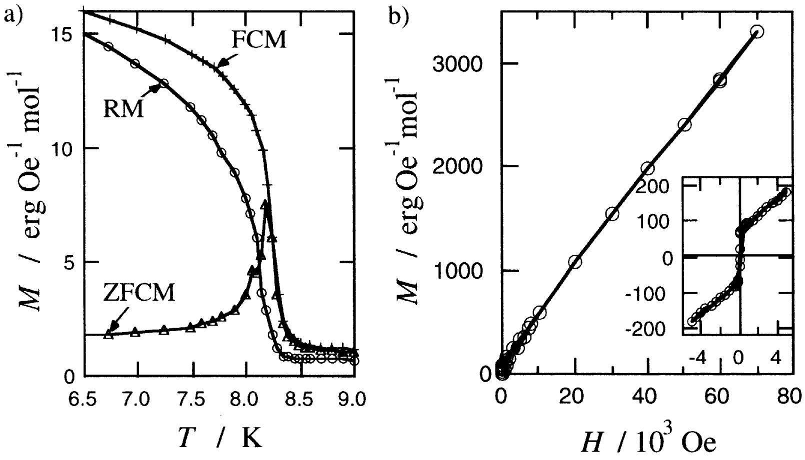


FIGURE 3 (a) Field-cooled magnetization (FCM, 5 Oe), remnant magnetization (RM), and zero-field-cooled magnetization (ZFCM, 5 Oe) for Ni[N(CN)$_2$]$_2$(pm) (**3**). (b) Magnetization curve of **3** measured at 4 K. An M-H loop near $H = 0$ Oe is magnified in the inset. The solid lines are shown as a guide to the eye.

The magnetic behavior of **3** is typical of a weak ferromagnet (canted antiferromagnet). Thus, the isomorphous series of **1** - **3** were all proved to be weak ferromagnets. The spontaneous magnetization of **1** and **2** are 5.8×10^3 and 2.5×10^3 erg Oe^{-1} mol^{-1} at 2.0 and 1.8 K, respectively [5], which are much larger than that of **3** at 4 K in spite of practically the same crystal structure. The transition temperatures (T_N's) of **1** - **3** were 3.2, 1.8 [5], and 8.3 K, respectively. We have recently reported that another isomorphous series of $MCl_2 \bullet (pm)_2$, whose T_N's are 6.1, 4.4, and 16 K for M = Fe, Co, and Ni, respectively [4]. Interestingly, the dependence of T_N upon metal ion species is parallel to each other. Furthermore, the transition temperatures of $M[N(CN)_2]_2$ (M = Fe: T_N = 18.5 K [2b]; M = Co: T_C = 9.2 K [2c]; M = Ni: T_C = 20.6 K [2c]) show a similar tendency of the metal ion dependence.

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[7] The interatomic distances between M and N(nitrile): **1**, 2.138(4), 2.142(4) Å; **2**, 2.103(4), 2.105(4) Å; **3**, 2.060(3), 2.061(2) Å.

[8] The interatomic distances between M and N(pyrimidine): **1**, 2.202(4) Å; **2**, 2.154(4) Å; **3**, 2.113(3) Å.

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