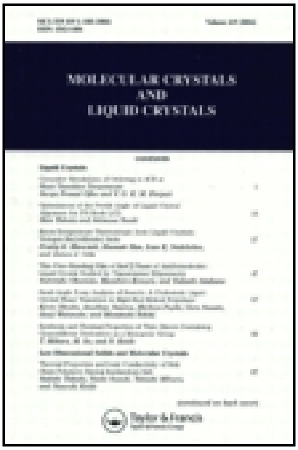

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Masaaki Ohba [a] & Hisashi Ōkawa [a]
[a] Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka, 812, Japan

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SYNTHESIS AND MAGNETISM OF NEW BIMETALLIC ASSEMBLIES, $[Ni(diamine)_2]_2[Fe(CN)_6]X$, EXTENDED BY Fe^{III}-CN-Ni^{II} LINKAGES

MASAAKI OHBA AND HISASHI ŌKAWA*
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Fukuoka 812, Japan.

Abstract Bimetallic assemblies of the general formula, $[Ni(diamine)_2]_2$-$[Fe(CN)_6]X$ (diamine = en, pn, 1,1-dmen (1,1-dimethylethylenediamine); X^- = ClO_4^-, BF_4^- or PF_6^-) have been prepared as anhydrides for the en compounds and di- or trihydrates for the pn and 1,1-dmen compounds. The X-ray crystallography for $[Ni(pn)_2]_2[Fe(CN)_6]ClO_4 \cdot 2H_2O$ has proved a 2-D network of a square structure extended by Fe-CN-Ni linkages. All the compounds show a ferromagnetic spin-exchange interaction between the adjacent Fe(III) and Ni(II) ions through cyanide bridge. The pn and 1,1-dmen compounds show a long-range magnetic ordering over the lattice (metamagnet). The en compounds probably have a network differing from the 2-D network of the pn and 1,1-dmen compounds and show no magnetic ordering over the lattice.

INTRODUCTION

Recently there has been an increasing interest in the design of molecular-based magnetic material using paramagnetic complexes as constituents.[1-3] Bimetallic assemblies derived from hexacyanometallate ions $[M(CN)_6]^{n-}$ and simple metal ions form a family of magnetic materials exhibiting spontaneous magnetization and high T_C or T_N is reported for some of the assemblies such as $CsMnCr(CN)_6$ (T_C = 90 K)[4], $CsNiCr(CN)_6$ (T_N = 90 K)[5], $Cs_2MnV(CN)_6$ (T_N = 125 K)[6], $Cs_{0.75}[Cr^{II}_{1.125}Cr^{III}(CN)_6]$ (T_C = 190 K)[7], $Cr^{II}_3[Cr^{III}(CN)_6]_2$ (T_C = 240 K).[7] However, magnetostructural correlation for those high T_C or T_N compounds remains to be studied. With the aim to gain an insight into the origin for high T_C or T_N of those bimetallic assemblies, we have initiated the study on bimetallic assemblies derived from $[M(CN)_6]^{n-}$ and bis(diamine)nickel(II) $[Ni(diamine)_2]^{2+}$ complexes. In the previous communications we have reported a 1-D chain compound of a rope-ladder structure $[Ni(en)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$[8] and a 2-D compound of a square structure $[Ni(pn)_2]_2$-$[Fe(CN)_6]ClO_4 \cdot 2H_2O$.[9] Here we report the synthesis and magnetism of the bimetallic assemblies of the general formula $[Ni(diamine)_2]_2[Fe(CN)_6]X$ (diamine = en, pn or 1,1-dmen (1,1-dimethylethylenediamine); X^- = ClO_4^-, BF_4^- or PF_6^-).

PREPARATIONS AND GENERAL CHARACTERIZATION

In our preliminary study the bimetallic assemblies were obtained as microcrystals by the 1 : 2 reaction of [Ni(diamine)$_2$]X$_2$ and K$_3$[Fe(CN)$_6$] in an aqueous solution, but eventually it was found that the use of [Ni(diamine)$_3$]X$_2$ gave the same compounds as large crystals. It is likely that the slow dissociation of [Ni(diamine)$_3$]$^{2+}$ into [Ni(diamine)$_2$]$^{2+}$ in aqueous solution leads to growing large crystals of orderd network structure. By this method the following bimetallic assemblies have been obtained: [Ni(en)$_2$]$_2$[Fe(CN)$_6$]X (X$^-$ = ClO$_4$ (**1**), BF$_4$ (**2**), PF$_6$ (**3**)), [Ni(pn)$_2$]$_2$[Fe(CN)$_6$]X·2H$_2$O (X$^-$ = ClO$_4$ (**4**), BF$_4$ (**5**), PF$_6$ (**6**)), and [Ni(1,1-dmen)$_2$]$_2$[Fe(CN)$_6$]X·nH$_2$O (X$^-$ = ClO$_4$ and n = 2 (**7**), X$^-$ = BF$_4$ and n = 3 (**8**), X$^-$ = PF$_6$ and n = 2 (**9**)).

It must be emphasized that the en compounds (**1-3**) were obtained as anhydrides whereas the pn (**4-6**) and 1,1-dmen (**7-9**) compounds as hydrates (n = 2 - 3). This fact suggests that the network structure of the en compounds differs from that of the pn and 1,1-dmen complexes. The en compounds show three ν(CN) modes of cyanide group around 2140, 2130 and 2110 cm^{-1}. The vibration at 2110 cm^{-1}, well corresponding to the ν(CN) band of K$_3$[Fe(CN)$_6$] (2110 cm^{-1}), may be assigned to the cyanide group free from bridging to [Ni(en)$_2$]$^{2+}$. It is noticed that in ν(CN) modes the en compounds resemble the Ni$_3$Fe$_2$-type bimetallic assembly having a 1-D network of a rope-ladder structure.[8] Such IR spectral feature of the en complexes suggests two types of cyanide bridge existing in their network. The pn and 1,1-dmen complexes show two ν(CN) modes near 2140 and 2110 cm^{-1}, which are assigned to the bridging and non-bridging cyanide groups, respectively. The 2140 cm^{-1} vibration bears a large intensity relative to the 2110 cm^{-1} vibration.

CRYSTAL STRUCTURE

The structure of [Ni(pn)$_2$]$_2$[Fe(CN)$_6$]ClO$_4$·2H$_2$O (**4**) has been preliminarily reported.[9] The ORTEP drawing of the essential part of the crystal structure is given in Figure 1. The asymmetric unit comprises of each one-half of [Fe(CN)$_6$]$^{3-}$ and ClO$_4^-$ ions, one [Ni(pn)$_2$]$^{2+}$, and one water molecule. Hexacyanoferrate(III) ion makes bonds to four [Ni(pn)$_2$]$^{2+}$ ions through its four cyano nitrogens on a plane, providing a 2-D network extended through Fe(III)-CN-Ni(II) linkage (see Figure 2). The mean Fe-C, C-N, and N-Ni bond lengths are 1.949, 1.142, and 2.105 Å, respectively. The intrasheet Fe--Ni(1) and Fe--Ni(2) separations are 5.062(2) and 5.126(3) Å, respectively. The quadangle formed by four Fe ions shows a slight distortion to a rhombus with the interior angles of 85.0 and 95.0°. All the Ni ions assume a *trans* octahedral geometry together with two cyanide nitrogens at the axial sites. Perchlorate ion resides within each quadrangle.

In the lattice the 2-D sheets align along *c* axis with the Fe--Fe(0, 1/2, 1) separation of 8.978(5) Å. The nearest intersheet Fe--Ni(1)(x, y, z+1), Fe--Ni(2)(x, y+1, z+1) and Ni(1)--Ni(2)(x+1, y+1, z+1) separations are 9.852, 8.613, and 9.754 Å, respectively.

Based on our preliminary studies, the 1,1-dmen compounds are shown to have a 2-D network essentially the same as that of **4**. In spite of many efforts we have not yet succeeded in growing good crystals suitable for X-ray crystallography for the en compounds.

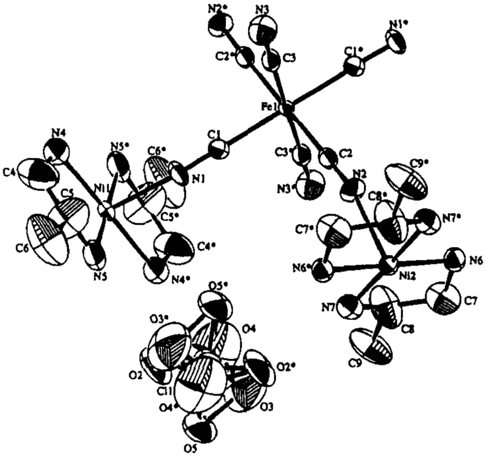

FIGURE 1 ORTEP drawing of the asymmetric unit of **4** with atom numbering scheme (water molecules are omitted for clarity).

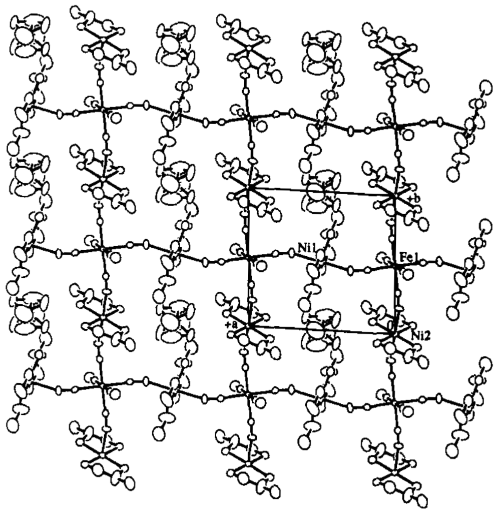

FIGURE 2 Projection of the polymeric structure of **4** onto the *ab* plane.

MAGNETIC PROPERTY

En Compounds (1 - 3)

Cryomagnetic properties of the en compounds have been studied in the temperature range of 4.2-90 K. The $\chi_M T$ *vs.* T and χ_M *vs.* T plots of **1** are exemplified in Figure 3.

The $\chi_M T$ value at room temperature is 2.90 cm^3 K mol^{-1} (4.81 μ_B) per FeNi$_2$, that is slightly larger than the value expected for one low-spin Fe(III) and two paramagnetic Ni(II) ions (2.38 cm^3 K mol^{-1}; 4.36 μ_B). The $\chi_M T$ value increases with decreasing temperature, reaches the maximum value of 6.09 cm^3 K mol^{-1} (6.98 μ_B) at 14 K, and then decreases below this temperature. The maximum $\chi_M T$ value is significantly larger than the value expected for $S_T = 5/2$ of ferromagnetically coupled Ni(II)Fe(III)Ni(II). This fact suggests an intramolecular ferromagnetic interaction through the cyanide bridge. This is supported by a large Weiss constant ($\theta = +9.5$ K) determined by the Curie-Weiss plots in the range of 13 - 90 K. The drop in $\chi_M T$ below 9 K suggests the operation of an intermolecular antiferromagnetic interaction.

The χ_M *vs.* T plot shows a maximum at 14 K and a minimum at 6 K. Below this temperature a tendency of saturation is seen. The behavior in χ_M at low temperature is typical of antiferromagnets and the non-zero χ_M value can be attributed to a residual $\chi_\perp$ component. No spontaneous magnetization occurs in **1** - **3**.

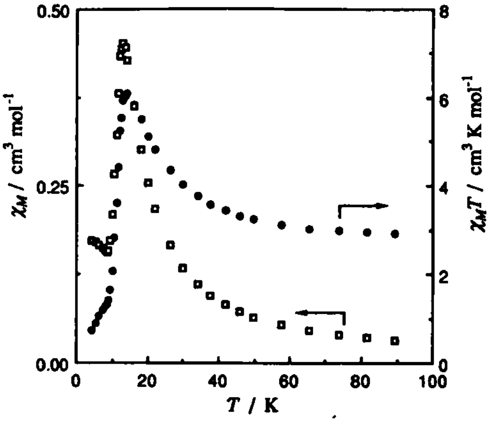

FIGURE 3 Temperature-dependences of χ_M (□) and $\chi_M T$ (●) per FeNi$_2$ unit of **1**.

Pn Compounds (4 - 6)

All the pn compounds are similar to each other in magnetic behavior. The crymagnetic property of **4** is shown in Figure 4 in the forms of $\chi_M T$ *vs.* T and χ_M *vs.* T plots. At room temperature the $\chi_M T$ value is 3.21 cm^3 K mol^{-1} per FeNi$_2$ (5.07 μ_B) which is larger than the expected value for one low-spin Fe(III) and two paramagnetic Ni(II) (2.38 cm^3 K mol^{-1}; 4.36 μ_B). With decreasing temperature the $\chi_M T$ increases up to the maximum value of 11.31 cm^3 K mol^{-1} (9.51 μ_B) near 10 K and then decreases below this temperature. The result clearly indicates a ferromagnetic ordering of spins within the 2-D sheet through the Fe-CN-Ni linkages and the drop in $\chi_M T$ below 10 K can be ascribed to an antiferromagnetic intersheet interaction. The χ_M *vs*. T curve shows a maximum at 10 K and a minimum at 6 K. The non-zero value of χ_M below 6 K can be attributed to a residual $\chi_\perp$ component of antiferromagnets.

The increasing tendency of χ_M at low temperature suggests the magnetic ordering over the lattice. To confirm this, the magnetization M was studied in the temperature range of 4.2 - 20 K under a weak applied field 3 G (Figure 4). The field-cooled magnetization (FCM) curve showed a peak near 10 K and a break for saturation near 8 K. Essentially the same FCM curve was obtained under 100 G. When the applied field was switched off at 4.2 K, a remnant magnetization (RM) was observed which decreased with increasing temperature and vanished at 8 K. The zero-field-cooled magnetization (ZFCM) curve showed two maxima at 8.0 and 9.9 K which correspond to the breaking point and the maximum in the FCM curve, respectively. Such cryomagnetic behavior is typical of metamagnetic ordering and the peak at 8.0 K implies that the applied field is too weak to move the domain walls below this temperature.

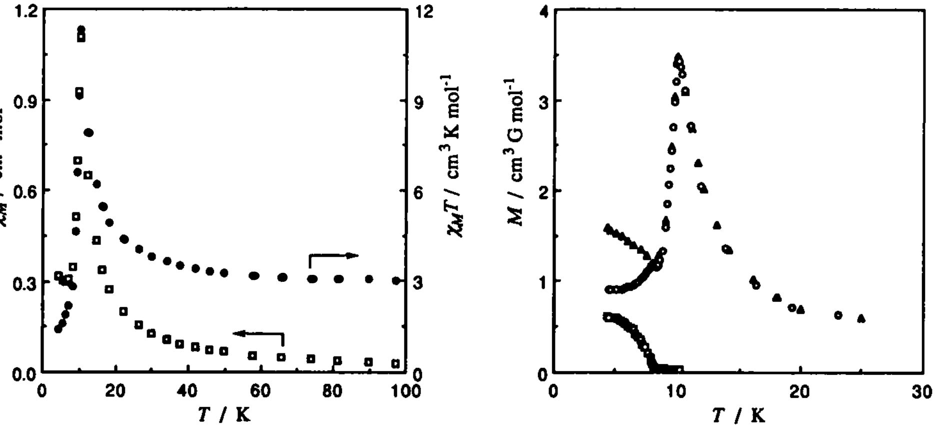

FIGURE 4 Temperature-dependences of χ_M (□) and $\chi_M T$ (●) per FeNi$_2$ unit of **4** (left) and the magnetization M for **4** under an applied field of 3 G (right): FCM (▲), RM (□), ZFCM (○).

The magnetic hysteresis loop determined at 4.2 K also adds a support to metamagnetic nature of this compound (Figure 5). The magnetization increased abruptly around 3800 G, probably due to spin flipping based on the intersheet antiferromagnetic interaction. The magnetization was 2.47 μ_B under 20 kG and was not saturated under 80 kG (3.88 μ_B). It appears that each local spin is canted and a large magnetic field is neccessary for overcoming the canting.

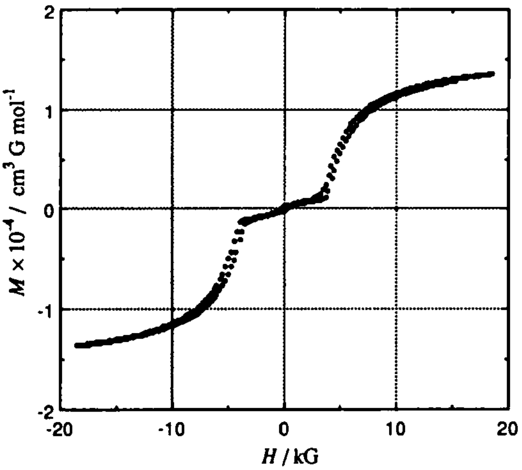

FIGURE 5 Magnetic hysteresis loop of **4** at 4.2 K.

1,1-Dmen Compounds (7 - 9)

The 1,1-dmen compounds are suggested to have a 2-D network structure like **4**, based on our preliminary X-ray crystallographic studies. In fact the 1,1-dmen compounds **7** - **9** resemble the pn complexes **4** - **6** in magnetic property. The $\chi_M T$ *vs*. T and χ_M *vs*. T curves of **7** are shown in Figure 6. The $\chi_M T$ value at 90 K is 3.38 cm^3 K mol^{-1} per Ni_2Fe (5.20 μ_B) that increases with decreasing temperature up to the maximum value of 32.58 cm^3 K mol^{-1} (16.1 μ_B) at 11 K. The χ_M *vs*. T curve shows a maximum at 11 K, a minimum at 7 K, and a trend to increase below 7 K. It appears that in **7** the intrasheet ferromagnetic interaction is strengthened whereas the intersheet antiferromagnetic interaction is weakened relative to the case of **4**. The reduced intersheet interaction in **7** may be due to the large intersheet separation relative to that of **4**, owing to the bulkyness of the diamine 1,1-dmen.

The temperature-dependence of the magnetization of **7** was studied under a weak applied field 3 G (see Figure 6). The FCM curve shows a peak at 11 K and a break for saturation near 10 K. A remnant magnetization is observed in the temperature range below 12 K. The ZFCM curve shows a maximum at 11.1 K. Thus, a long-range magnetic ordering occurs in this compound (T_C = 11.1 K). Similarly, **8** and **9** show a magnetic ordering at 14.6 and 11.0 K, respectively.

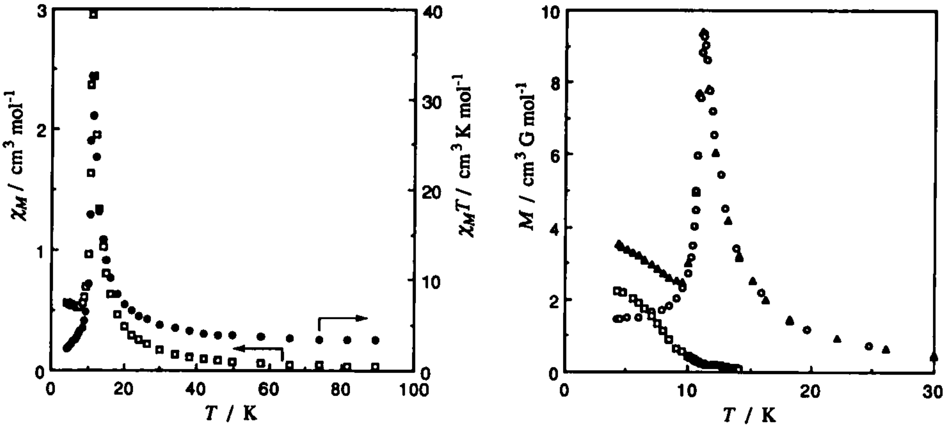

FIGURE 6 Temperature-dependences of χ_M (□) and $\chi_M T$ (●) per FeNi$_2$ unit of 7 (left) and the magnetization M for 7 under an applied field of 3 G (right): FCM (▲), RM (□), ZFCM (○).

The magnetic hysteresis loop of 7 is given in Figure 7, which shows an abrupt increase of magnetization around *ca.* 1800 G. Thus, 7 is metamagnetic in nature. The spin flipping in 7 occurs under a lower magnetic field (*ca.* 1800 G) compared with 4 (*ca.* 3800 G). The magnetization of 7 was practically saturated under 80 kG (4.96 μ_B per FeNi$_2$). It appears that the intersheet antiferromaganetic interaction is weak in 7, relative to 4, probably because of the large intersheet separation in the former. The remnant magnetization and the coercive field of 7 are 1140 cm^3 G mol^{-1} and 600 G, respectively.

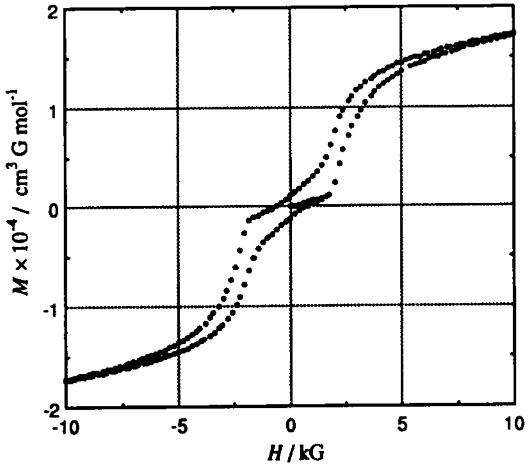

FIGURE 7 Magnetic hysteresis loop of 7 at 4.2 K.

CONCLUSION

Bimetallic assemblies of the general formula $[Ni(diamine)_2]_2[Fe(CN)_6]X$ (diamine = en, pn, 1,1-dmen); $X^- = ClO_4^-$, BF_4^- or PF_6^-) have been prepared and studied in their magnetic property. The en compounds of unknown network structure show a ferromagnetic spin-exchange between the adjacent Fe(III) and Ni(II) ions but no long-range magnetic ordering. The pn and 1,1-dmen compounds have a 2-D network of square structure and show a long-range magnetic ordering (T_C: 9.4 - 14.6 K).

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