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A Bimetallic Magnetic System Exhibiting Reversible Ferromagnetism/Metamagnetism Modulation

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A cyanide-bridged bimetallic compound, $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot 4H_2O$ (**1**) (1,1-dmen = 1,1-dimethylethylenediamine, $BPDS^{2-}$ = biphenyl-4,4′-disulfonate), has been prepared. It has a pseudo 2-D network structure based on a Fe_4Ni_4 square unit with two Fe–CN–Ni–NC–Fe and two Fe–CN⋯H_2O–Ni–NC–Fe linkages and shows a metamagnetic ordering with $T_C = 3.3$ K. The dehydration of **1** at 150 °C has afforded $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}$ (**1a**). It has a definite 2-D network structure based on a Fe_4Ni_4 square unit with four Fe–CN–Ni–NC–Fe linkages and shows essentially a ferromagnetic ordering with $T_C = 10.7$ K under weak applied field (> 250 G). **1a** is hygroscopic and adsorbed atmospheric moisture to afford $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot 2H_2O$ (**1b**), which has a pseudo 2-D network structure similar to that of **1** and shows a metamagnetic ordering with $T_C = 4.0$ K. **1a** and **1b** can be interconverted by dehydration at 150 °C and hydration in open air at room temperature, producing a unique molecular magnetic system exhibiting a reversible ferromagnetism/metamagnetism modulation.

Design of molecular-based magnetic compounds using paramagnetic metal complexes as constituents is a subject of many recent studies.[1–4] One current focus is placed on 3-D bimetallic networks that may have a bright prospect of developing high T_C magnetic materials, and we recently reported 3-D cyanide-bridged ferrimagnetic compounds, $[Mn(en)]_3[Cr(CN)_6]_2\cdot 4H_2O$ (T_C = 69 K)[5] and $[Mn(glya)]_3[Cr(CN)_6]_2\cdot 2.5H_2O$ (glya = glycineamide) (T_C = 71 K).[6] Along with the production of high T_C magnetic compounds, an important subject in the study of the "second generation" of molecular-based magnets is to produce unique magnetic systems that cannot be realized with inorganic magnetic materials in common use (metal or metal oxides). One characteristic of molecular-based magnets is the "soft" network that may be changeable by some external effect to cause a magnetic modulation. The dehydration or desolvation of low-dimensional network compounds in a hydrated or solvated form often gives rise to a magnetic modulation due to a change in the bulk structure.[7–11] By this way a magnetically-isolated system has been converted into a magnetically-condensed or a magnetically-ordered system.[8,10,11] Moreover, the dehydration and/or desolvation of 1-D or 2-D network compounds give rise to an enhancement of interchain or intersheet magnetic interaction or a change in the nature of magnetic interaction.[7,9] The reverse conversion of the dehydrated or desolvated compounds into the original forms is difficult and has not been achieved with one exception. Kahn et al. reported bimetallic compounds that show paramagnetism/ferrimagnetism magnetic modulation based on the reversible interconversion between a hydrated form and a dehydrated form.[8]

This work relates to a cyanide-bridged bimetallic compound, $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot 4H_2O$ (**1**) (1,1-dmen = 1,1-dimethylethylenediamine, $BPDS^{2-}$ = biphenyl-4,4′-disulfonate) which is converted into essentially ferromagnetic $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}$ (**1a**) by the thermal dehydration and then into metamagnetic $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot 2H_2O$ (**1b**) by the adsorption of atmospheric moisture at room temperature. A ferromagnetism/metamagnetism magnetic modulation system is produced based on the reversible interconversion between **1a** and **1b**.

Experimental

Physical Measurements. Elemental analyses of C, H, and N were obtained at the Service Center of Elemental Analysis of Kyushu University. Metal analyses were made on a Shimadzu AA-680 Atomic Absorption/Flame Emission Spectrophotometer. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR system using KBr disks. Magnetic susceptibilities were measured on a Quantum Design MPMS 5XL SQUID susceptometer. Data were corrected for the magnetization of the sample holder and capsule used. Diamagnetic corrections for the constituting atoms were made using Pascal's constants.[12] Magnetization studies were carried out on the same instrument. Thermogravimetric analyses were performed on a Perkin Elmer TGA 6.

Preparation. $[Ni(1,1\text{-dmen})_3]Cl_2$ was prepared by the literature method.[13] Sodium diphenyl-4,4′-disulfonate (Na_2BPDS) and

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$K_3[Fe(CN)_6]$ were of reagent grade and were used as purchased.

$[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot 4H_2O$ (1). $[Ni(1,1\text{-dmen})_3]Cl_2$ (40 mg, 0.1 mmol) was dissolved in water (10 cm^3). To this solution was added an aqueous solution (10 cm^3) of $K_3[Fe(CN)_6]$ (16 mg, 0.05 mmol) and Na_2BPDS (10 mg, 0.025 mmol), and the resulting brown solution was allowed to stand for few days to give brown crystals. These were separated by suction filtration and washed with water. Found: C, 36.93; H, 6.60; N, 21.55; Fe, 6.14 ; Ni, 12.70%. Calcd for $C_{28}H_{60}N_{14}FeNi_2SO_7$: C, 36.95; H, 6.65; N, 21.55; Fe, 6.14 ; Ni, 12.90%.

$[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}$ (1a). This was obtained by dehydrating **1** at 150 °C for 2 hours. The release of four water molecules was confirmed by TG study. Elemental analyses were not made for **1a** because of its highly hygroscopic nature.

$[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot 2H_2O$ (1b). This was obtained when **1a** was allowed to stand in open air at room temperature. Found: C, 38.56; H, 6.27; N, 22.50; Fe, 6.28; Ni, 13.75%. Calcd for $C_{28}H_{56}N_{14}FeNi_2SO_5$: C, 38.47; H, 6.46; N, 22.43; Fe, 6.39; Ni, 13.43%.

X-ray Structure Analyses. A single crystal of $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot 4H_2O$ (**1**) was sealed in a capillary tube and used for crystallographic measurements at 23 ± 1 °C on a Rigaku AFC-7R diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and a 12 kW rotating anode generator. The data were collected using the ω–2θ scan technique at a scan rate of 16.0°/min (in ω). The octant measured was $\pm h$, $+k$, $+l$. Three standard reflections were monitored every 150 reflections. Over the course of the data collection, the standard decreased by 0.7%. A linear correction factor was applied to the data to account for the decay phenomenon. Intensity data were corrected for Lorentz and polarization effects. Crystallographic parameters are given in Table 1.

The structures were solved by the direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation but were not refined. Computations were carried out on an IRIS O2 computer using the teXsan crystallographic software package.[14]

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 169485. The data are also deposited as Document No. 75037 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Crystal Structure of $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot 4H_2O$ (1). An ORTEP view of the asymmetric unit of **1** is shown in Fig. 1 together with the atom numbering scheme. Selected bond distances and angles are given in Table 2.

The asymmetric unit consists of one $[Fe(CN)_6]^{3-}$ anion, each one half of two crystallographically-independent $[Ni(1,1\text{-dmen})_2]^{2+}$ cations, one $[Ni(1,1\text{-dmen})_2(H_2O)]^{2+}$ cation, one half of $BPDS^{2-}$ and three water molecules. Each $[Fe(CN)_6]^{3-}$ makes bonds to one $[Ni(1,1\text{-dmen})_2(H_2O)]^{2+}$ and two $[Ni(1,1\text{-dmen})_2]^{2+}$ cations through three cyanide groups in the *mer* mode (Fig. 1). The bonding to two crystallographically-independent $[Ni(1,1\text{-dmen})_2]^{2+}$ cations (Ni(2) and Ni(3)) forms a 1-D zigzag chain extended by the –Ni(2)–NC–Fe–CN–Ni(3)–NC– linkage, and the bonding to $[Ni(1,1\text{-dmen})_2(H_2O)]^{2+}$ cation (Ni(1)) affords the terminal $\{Ni1(1,1\text{-dmen})_2(N)(H_2O)\}$ moiety attached to the 1-D chain (N is the cyanide nitrogen atom from an adjacent $[Fe(CN)_6]^{3-}$). The Fe–C bond distances fall in the range of 1.92(1)–1.96(1) Å and the Ni–N bond distances in the range of 2.059(9)–2.159(9) Å. The Ni–N–C bond angles range from 154.8(8)° to 176(1)°. The Ni(1)–O(1) bond distance is 2.198(7) Å.

The aqua ligand in the terminal $\{Ni1(1,1\text{-dmen})_2(N)(H_2O)\}$ moiety is hydrogen-bonded to a cyanide nitrogen (N(4)) of the adjacent chain, affording a pseudo 2-D network structure based on a hydrogen-bonded Fe_4Ni_4 unit with two Fe–CN–Ni–NC–Fe and two Fe–CN···H_2O–Ni–NC–Fe linkages (Fig. 2a). The separation between the two pseudo 2-D sheets is 9.880 Å. The counter anion $BPDS^{2-}$ is intercalated between two pseudo

Table 1. Crystal Parameters for **1**.

Formula	$C_{28}H_{60}N_{14}SO_7Ni_2Fe$
Formula weight	910.18
Crystal color	brown
Crystal system	monoclinic
Space group	$P2_1/c$(# 14)
a/ Å	9.880(8)
b/ Å	29.52(2)
c/ Å	14.986(6)
α/°	90
β/°	92.15(5)
γ/°	90
V/ Å^3	4368(5)
Z	4
D_c/g cm^{-3}	1.384
No. observations ($I > 3.00\sigma(I)$)	3559
R	0.063
R_w	0.073

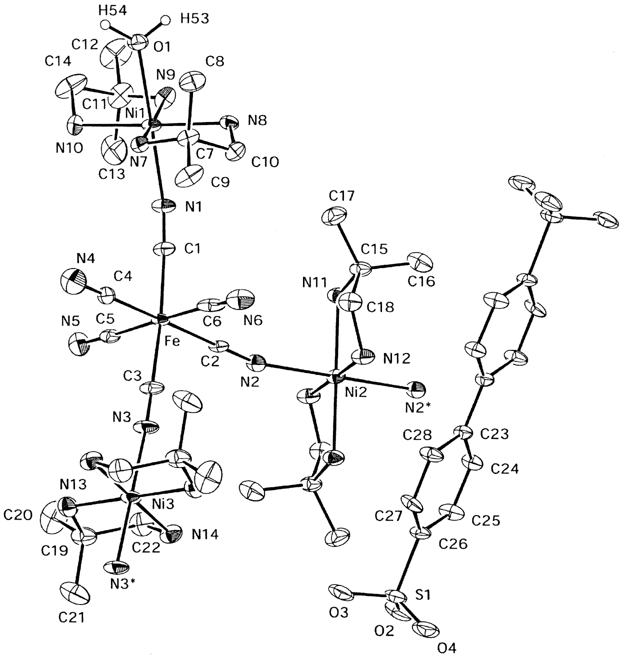


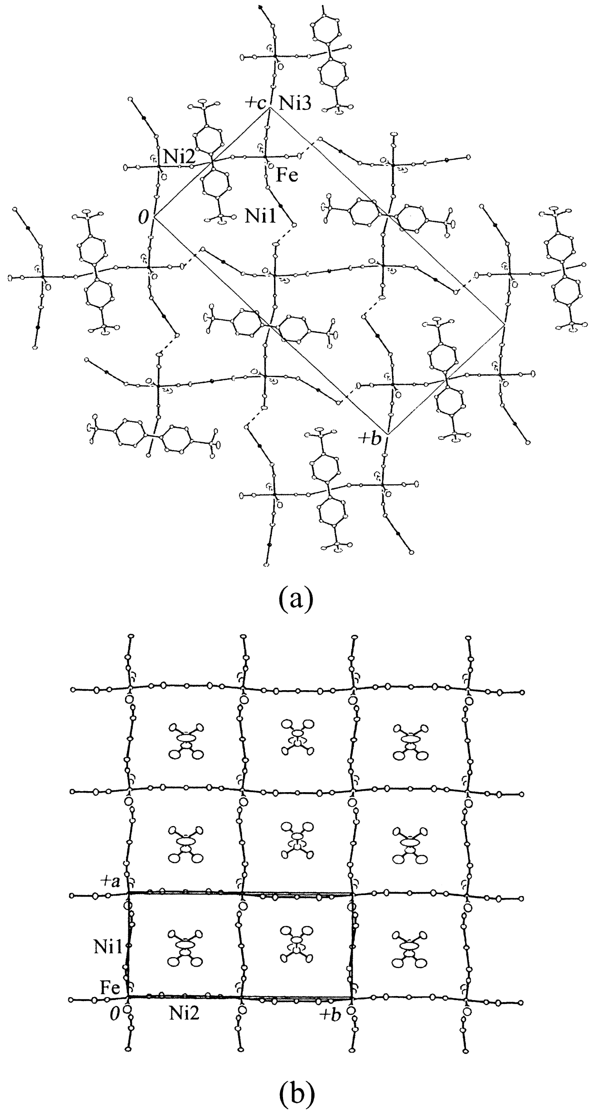
Fig. 1. An ORTEP drawing of the asymmetric unit of **1** with the atom numbering scheme.

Table 2. Selected Bond Distances and Angles for **1**

Bond Distances/Å					
Fe(1)–C(1)	1.96(1)	Fe(1)–C(2)	1.937(10)	Fe(1)–C(3)	1.93(1)
Fe(1)–C(4)	1.92(1)	Fe(1)–C(5)	1.95(1)	Fe(1)–C(6)	1.95(2)
Ni(1)–O(1)	2.198(7)	Ni(1)–N(1)	2.122(9)	Ni(1)–N(7)	2.122(9)
Ni(1)–N(8)	2.095(10)	Ni(1)–N(9)	2.109(9)	Ni(1)–N(10)	2.066(9)
Ni(2)–N(2)	2.159(9)	Ni(2)–N(11)	2.116(8)	Ni(2)–N(12)	2.095(10)
Ni(3)–N(3)	2.059(9)	Ni(3)–N(13)	2.14(1)	Ni(3)–N(14)	2.090(9)

Bond Angle/°			
C(1)–Fe(1)–C(2)	96.1(4)	C(1)–Fe(1)–C(3)	175.5(5)
C(2)–Fe(1)–C(3)	88.3(4)	N(1)–Ni(1)–O(1)	178.7(3)
N(2)–Ni(2)–N(2)*	180.0	N(3)–Ni(3)–N(3)′	180.0
Fe(1)–C(1)–N(1)	172.9(9)	Ni(1)–N(1)–C(1)	154.8(8)
Fe(1)–C(2)–N(2)	173(1)	Ni(2)–N(2)–C(2)	164.3(9)
Fe(1)–C(3)–N(3)	176.8(10)	Ni(3)–N(3)–C(3)	176(1)

Symmetry operation: (*) $-x, -y, -z-1$; (′) −x, −y, −z.



(a)

(b)

Fig. 2. (a) The projection of the pseudo 2-D structure of **1** onto the *bc* plane and (b) 2-D network structure of $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6]X$ ($X = CF_3SO_3^-$). The 1,1-dmen ligands and lattice water molecules are omitted for clarity.

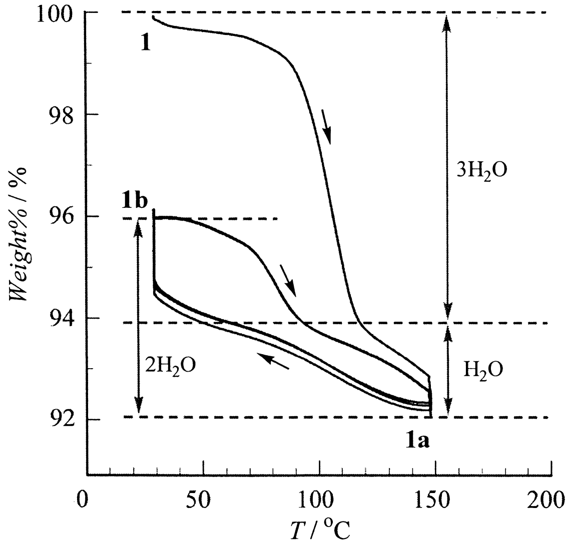


Fig. 3. Thermogravimetric analyses. The conversion of **1** into **1a** was achieved by heating a sample of **1** at 150 °C for 30 minutes and the conversion of **1a** into **1b** was achieved by allowing the sample at room temperature for 5 hours.

2-D sheets, with one sulfonate group on a hydrogen-bonded Fe_4Ni_4 unit and another sulfonate group on an adjacent Fe_4Ni_4 unit. The three lattice water molecules are captured in the crystal lattice.

The pseudo 2-D network structure of **1** (Fig. 2a) is related to the 2-D structure of $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6]X\cdot nH_2O$ (X^-: a uninegative anion) with a definite Fe_4Ni_4 square unit (Fig. 2b).[9] The S–S separation between the two sulfonate groups of $BPDS^{2-}$ is about 10.8 Å and this separation is considerably larger than the center–center separation of two adjacent square units of Fig. 2b (10.1–10.4 Å).[9] Because of the mismatch in the two-center electrostatic interaction between the $BPDS^{2-}$ and the definite 2-D network, the pseudo 2-D structure (Fig. 2a) must be preferred for **1**.

Thermogravimetric Studies. Thermogravimetric (TG) results for **1** are given in Fig. 3. The TG curve of **1** showed a weight loss corresponding to three water molecules at 100–120

Table 3. Selected IR Spectral Data of **1**, **1a** and **1b** (ν/cm^{-1})

	ν(OH)				ν(CN)			
1	3443	3355	3331	3271	2170	2139	2132	2122
1a						2139		2112
1b	3465		3331	3281	2154	2139	2123	2113

°C (weight loss 5.98%; calcd 5.94%) and another weight loss corresponding to one water molecule at 120–150 °C (weight loss 1.70%; calcd 1.98%). The former process is associated with the release of the lattice water molecules and the latter process is associated with the release of the water molecule that is coordinated to Ni(1) and hydrogen-bond to the adjacent chain. Resulting anhydrous $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}$ (**1a**) was very hygroscopic to adsorb atmospheric moisture in open air at room temperature affording $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot 2H_2O$ (**1b**) (weight increase 3.75%; calcd 3.96%). The TG curve of **1b** indicated the release of one water molecule (lattice water) at 40–80 °C and the release of another water molecule (coordinated water) at 100–150 °C. Thus, **1a** and **1b** can be reversibly interconverted by the dehydration at 150 °C and the hydration in open air at room temperature (see Fig. 3).

IR Spectra. Selected IR spectral data for **1**, **1a** and **1b** are summarized in Table 3. Compound **1** shows four ν(OH) bands of water and four ν(CN) bands of cyanide group in accord with its low dimensional network structure. The IR spectrum of **1a** is characterized by two ν(CN) bands at 2139 and 2112 cm^{-1}; no ν(OH) band was recognized for **1a**. The simple IR spectral feature of **1a** suggests an enhanced dimensionality of the network structure. It should be emphasized that the 2-D bimetallic compounds, $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6]X$ (Fig. 2b), have two ν(CN) bands at ~2140 and ~2110 cm^{-1} attributable to the bridging and the terminal cyanide groups, respectively.[9] It is most likely that the thermal elimination of water from the Fe–CN···H$_2$O–Ni–NC–Fe linkage of **1** forms the Fe–CN–Ni–NC–Fe linkage and provides a definite 2-D network structure like Fig. 2b. Such a conversion of a hydrogen-bonded pseudo 2-D network into a definite 2-D network by dehydration was reported by Miyasaka et al.[10,11] The dihydrate **1b** shows four ν(OH) bands and three ν(CN) bands. It is notable that **1** and **1b** have a marked similarity in the ν(OH) and ν(CN) modes except for the lack of one ν(CN) band in **1b**. Together with the thermogravimetric results discussed above, one of the two water molecules is hydrated at one Fe–CN–Ni–NC–Fe linkage of **1a**, reproducing a pseudo 2-D network structure with the Fe–CN···H$_2$O–Ni–NC–Fe linkage in **1b**. **1** and **1b**, however, must differ in the intersheet structure because **1** has three molecules of lattice water whereas **1b** has one molecule of lattice water. In fact we have confirmed that **1** and **1b** give different X-ray powder spectra.

Magnetic Properties. The cryomagnetic properties of **1**, **1a** and **1b** have been studied in connection with their network structures. The χ_M vs T plot for **1** is given in Fig. 4. The magnetic susceptibility per FeNi$_2$ at room temperature is 1.20×10^{-2} cm^3 mol^{-1} (4.96 μ_B) that is larger than the value expected for isolated one low-spin Fe^{III} and two Ni^{II} ions (7.93×10^{-3} cm^3 mol^{-1}, 4.36 μ_B). The χ_M value increased with decreasing temperature to a maximum value of 6.18 cm^3 mol^{-1} (12.8 μ_B) at 3.3 K and then decreased below this temperature. The magnetic moment at 3.3 K is much larger than the spin-only value for $S_T = 5/2$ (5.92 μ_B) resulting from the ferromagnetic coupling of two Ni^{II} ($S = 1$) and one Fe^{III} ($S = 1/2$) ions. It is evident that a ferromagnetic interaction operates between the adjacent Fe^{III} and Ni^{II} ions due to the strict orthogonality of magnetic orbitals[15–17] and a magnetic ordering occurs in the bulk. The overall magnetic behavior is metamagnetic, as judged from the drop in magnetic susceptibility below 3 K.

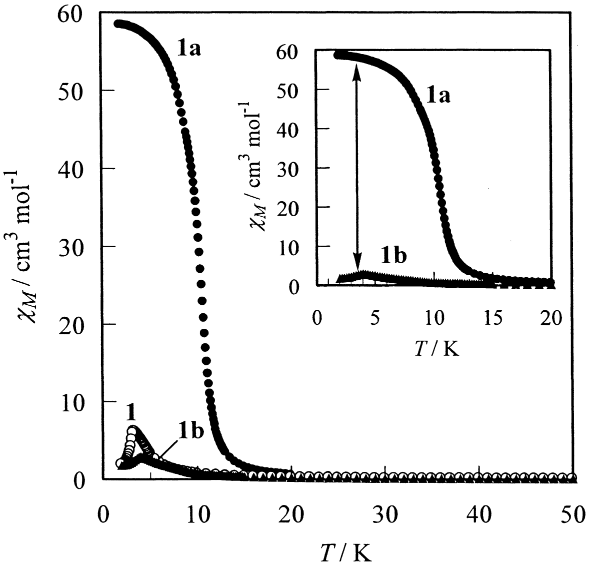


Fig. 4. χ_M vs T curves of **1**, **1a** and **1b** under 500 G.

The metamagnetic ordering in **1** has been confirmed by magnetization studies (Fig. 5). Each of the field-cooled magnetization (FCM), zero-field-cooled magnetization (ZFCM) and remnant magnetization (RM) curves under an applied field of 5 G has a maximum at ~3.3 K (= T_C) and shows a sharp decrease below this temperature. The ***M*** vs ***H*** curve (Fig. 5, insert) showed an initial slow increase in magnetization with applied field ($\boldsymbol{H} < 1$ kG) and then a sharp increase around 1.2 kG, followed by a gradual approach to the saturation value of 5 Nβ. The magnetization at 50 kG was 4.7 Nβ. The result indicates that the spin flip occurs from a metamagnetic ordering to a ferromagnetic ordering at ~1.2 kG. A ferromagnetic interaction between the adjacent Fe^{III} and Ni^{II} ions in the pseudo 2-D sheet and a significant antiferromagnetic interaction between two pseudo 2-D sheets explain the metamagnetic nature of **1**. For the cyanide-bridged 2-D bimetallic compounds, the intersheet magnetic interaction is weakly antiferromagnetic when the intersheet separation is smaller than 10 Å, whereas the magnetic interaction is negligibly weak when the intersheet separation is larger than 10 Å.[9,18]

Anhydrous **1a** differs from **1** in magnetic property. The magnetic susceptibility increased sharply below 13 K to reach

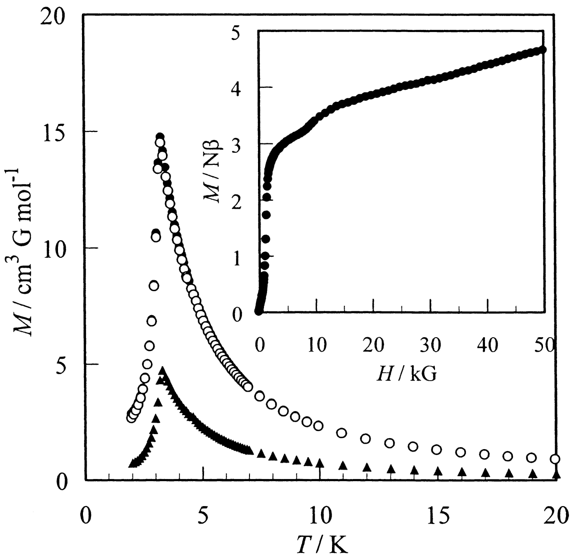


Fig. 5. FCM (●), ZFCM (○) and RM (▲) curves of **1** under an applied field of 5 G. The insert is the field-dependence of magnetization determined at 2 K.

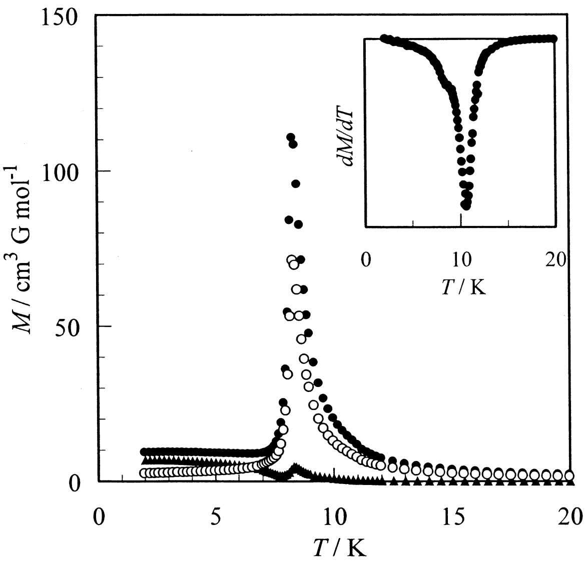


Fig. 6. FCM (●), ZFCM (○) and RM (▲) curves of **1a** under an applied field of 5 G. The insert shows the d*M*/d*T* plots.

a large saturation value of 58.4 cm^3 mol^{-1} (30.6 μ_B) near 2 K (see Fig. 4). This compound is also metamagnetic under a weak applied field of 5 G as evidenced by the decrease of the FCM, ZFCM and RM values below 6 K (Fig. 6). The T_C of this compound is determined to be 10.7 K based on d*M*/d*T* plots (see the insert of Fig. 6).

The field-dependence of magnetization of **1a** is shown in Fig. 7. The ***M*** vs ***H*** curve shows a sharp increase with applied field and the magnetization is larger than the Brillouin function curve for $S = 5/2$ ($g = 2.0$) in the field 1–35 kG. Thus, the apparent magnetic behavior of **1a** is ferromagnetic. However, the ***M*** vs ***H*** curve has an inflection near 200 G, indicating a spin flip from a metamagnetic ordering to a ferromagnetic ordering.

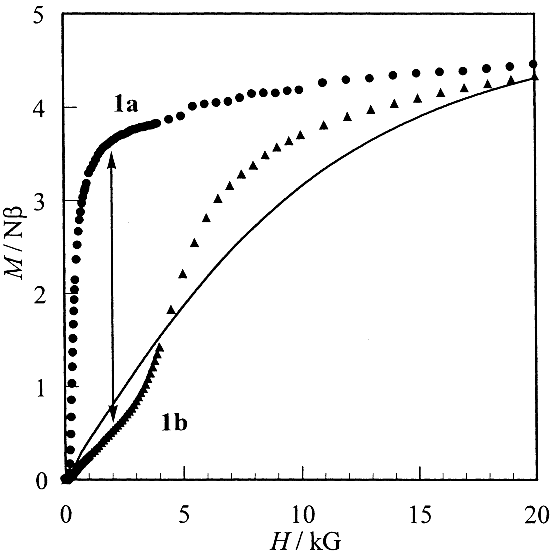


Fig. 7. The field-dependence of **1a** and **1b**. The solid line is the Brillouin function for $S = 5/2$ using $g = 2.0$.

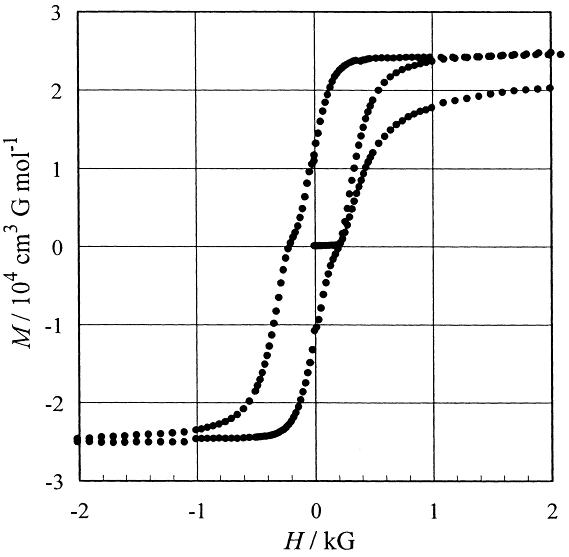


Fig. 8. Hysteresis loop of **1a** determined at 2 K.

The spin flip is also evident in the hysteresis loop (Fig. 8) that shows a small inflection around ±200 G. The metamagnetic nature of **1a** may arise from a weak antiferromagnetic interaction between two pseudo 2-D sheets. Nevertheless, **1a** can be regarded as a ferromagnetic compound, as judged from the magnetic behavior in Figs. 7 and 8.

The dihydrate **1b** resembles **1** in magnetic property, adding a support to its pseudo 2-D network structure similar to that in Fig. 2a. The χ_M vs T curve has a maximum magnetic susceptibility of 2.94 cm^3 mol^{-1} (9.70 μ_B) at 4.0 K (Fig. 4), and the ***M*** vs ***H*** curve shows an inflection near 4 kG due to the spin flip from a metamagnetic ordering to a ferromagnetic ordering. It must be noted that the spin flip of **1b** occurs at high magnetic field relative to that of **1**. This fact implies that the intersheet separation of **1b** (with one lattice water) is shorter than 9.880 Å of **1** (with three lattice water molecules) so that a strong intersheet antiferromagnetic interaction operates in **1b**.

Conclusion. $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot4H_2O$ (**1**) having a pseudo 2-D network structure is converted by dehydration into $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}$ (**1a**), which has a definite 2-D network structure and shows essentially a ferromagnetic ordering ($T_C = 10.7$ K) under a weak applied field (> 250 G). The 2-D network structure of **1a** is unstable because of the mismatch in the two-center electrostatic interaction between the $BPDS^{2-}$ and the 2-D network and adsorbs atmospheric moisture affording $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6](BPDS)_{0.5}\cdot2H_2O$ (**1b**). **1b** has a pseudo 2-D structure similar to that of **1** and shows a metamagnetic ordering ($T_C = 4.0$ K). Based on the reversible **1a** (2-D) $\rightleftarrows$ **1b** (pseudo 2-D) interconversion by hydration and dehydration treatments, a unique magnetic system exhibiting ferromagnetism/metamagnetism modulation has been produced in this work.

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