Magneto-optical Properties of Two-dimensional Cyanide-Bridged M^{III}Ni^{II} Bimetallic Assemblies (M=Fe, Co)

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Two-dimensional cyanide-bridged M^{III}Ni^{II} bimetallic assembies, [Ni(1,1-dmen)$_2$]$_2$[M(CN)$_6$]tfs·3.5H$_2$O (M=Fe (**1**), Co (**2**); 1,1-dmen = 1,1-dimethylethylenediamine, tfs$^-$ = trifluoromethanesulfonate ion), have been prepared. Each compound forms a 2-D grid structure extended by the M-CN-Ni linkages. Compound **1** shows a ferromagnetic ordering below T_c of 8.9 K based on a ferromagnetic interaction between low-spin Fe^{III} and high-spin Ni^{II}. MCD spectra for **1** show a strong Faraday ellipticity at ∼470 nm associated with the LMCT band of the Fe–CN bond. Its intensity increases with lowering temperature due to ferromagnetic ordering over the lattice. Compound **2** is paramagnetic and shows no remarkable Faraday effect.

The design of molecular magnetic material based on metal-assembled networks has been a fascinating research subject in past fifteen years.[1–4] It is known that a three-dimensional network of paramagnetic metal ions is advantageous for producing high T_c magnetic compounds as illustrated by [Mn(en)]$_3$[Cr(CN)$_6$]$_2$·4H$_2$O (T_c = 69 K)[5] and [Mn(glya)]$_3$[Cr(CN)$_6$]$_2$·2.5H$_2$O (glya = glycine amide) (T_c = 71 K)[6] of a defect cubane unit. Along with the production of high T_c magnetic compounds, a current attention is directed to the development of molecular magnetic systems exhibiting unique physical phenomena, i.e. magneto-optics.[7] Sato et al. have succeeded in photo-induced modulation of magnetic property of a Prussian blue analogue.[8] Ohkoshi et al. have been reported magneto-optical properties of film-type vanadium hexacyanochromate compounds.[9] Here, we report Faraday ellipticity spectra of the bimetallic magnetic compounds, [Ni(1,1-dmen)$_2$]$_2$[M(CN)$_6$]tfs·3.5H$_2$O (M=Fe (**1**), Co (**2**); 1,1-dmen = 1,1-dimethylethylenediamine, tfs$^-$ = trifluoromethanesulfonate ion) which have a two-dimensional grid structure.

The reaction of K$_3$[M(CN)$_6$] (110 mg, 0.33 mmol), [Ni(1,1-dmen)$_3$]Cl$_2$ (276 mg, 0.7 mmol) and a small excess of Natfc (85 mg, 0.5 mmol) in H$_2$O (20 mL) gave well-grown black crystals for **1** and purple crystals for **2**.[10] Both the compounds were efflorescent and gave dihydrate **1′** and **2′** after allowing stand in open air. The dihydrate compounds were used for magnetic and magneto-optical measurements.

In the previous work,[11] the structure of **1** could not be refined because of the efflorescent nature of the crystal. In this work, the structures of **1** and **2** have been determined by X-ray crystallographic studies.[12] They are isomorphous and form a two-dimensional grid structure extended by M-CN-Ni linkages in the lattice (Figure 1). Each tfs ion occupies the square cavity in the grid and the oxygen atoms of sulfonyl group form hydrogen bonds with amino protons of 1,1-dmen. The lattice water molecules locate between the layers. The nearest interlayer metal···metal separation is Fe···Ni2* = 10.030(6) Å for **1** and Co···Ni2* =
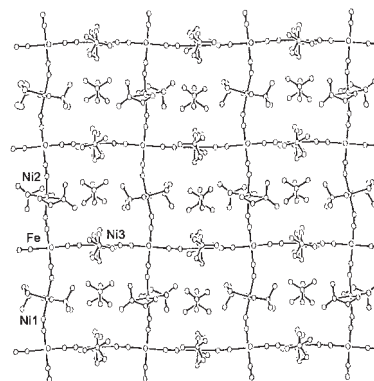

Figure 1. Two-dimensional grid structure of **1**.

10.272(5) Å for **2** (* indicates a symmetry operation $x - 1$, y, z), respectively.

χ_M vs T plots of **1′** showed an abrupt increase below 10 K, suggesting a ferromagnetic ordering over the lattice (Figure 2). The phase transition temperature (T_c = 8.9 K) was confirmed by weak field magnetic studies, dM/dT plots, and AC magnetic measurements. The saturation magnetization value of 4.96 μ_B (at 5 kG) agrees with the expected value arising from ferromagnetic coupling of one low-spin Fe^{III} (S = 1/2) and two Ni^{II} (S = 1) ions. The ferromagnetic interaction between the metal ions is explained by strict orthogonality of the magnetic orbitals of the adjacent Fe^{III} and Ni^{II} ions. Compound **1′** shows a magnetic hysteresis with coersive field of 90 G. On the other hand, **2′** is paramagnet because of the diamagnetic nature of [Co(CN)$_6$]$^{3-}$.

The Faraday spectra of **1′** were measured on a JASCO J-820 circular dichroism spectrometer using KBr disks in the range of
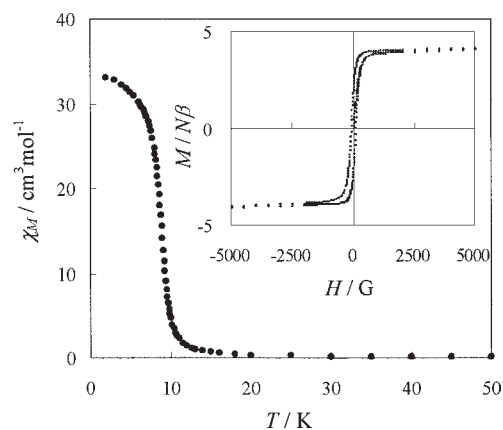

Figure 2. Temperature-dependence of magnetic susceptibility χ_M and a magnetic hysteresis loop (inside) of **1′**.

200–800 nm under an applied field of 200 G. A KBr disk containing ca. 1% of sample was prepared by applying a pressure of 8000 kg/cm^2. The temperature-dependence of molar Faraday ellipticity θ_M of $\mathbf{1'}$ under 200 G is given in Fig. 3. At room temperature a weak ellipticity (5.2×10^2 deg cm^{2}mol^{-1}) was observed at 450 nm. With decreasing temperature the θ_M value is enhanced with a shift of the peak position to 470 nm at 6 K. The maximum θ_M value reaches 2.4×10^5 deg cm^{2}mol^{-1} at 6 K. Furthermore, two bands of opposite sign are observed at 320 and 410 nm. The Faraday ellipticity spectrum was inverted in sign when the direction of applied magnetic field was inverted. The θ_M vs T plots show a sharp increase at 9 K ($\approx T_c$), and this behavior is in harmony with χ_M vs T plots of Figure 2. On the other hand, paramagnetic $\mathbf{2'}$ shows no remarkable ellipticity from the UV to visible region. K$_3$[Fe(CN)$_6$] shows a weak ellipticity (θ_M max = 38 deg cm^{2}mol^{-1}) around 420, 318, 292 and 254 nm at room temperature.[13] These results indicate that the MCD observed for $\mathbf{1'}$ around 470 nm is associated with the LMCT ($^2T_{1u}(\sigma t_{1u}) \rightarrow \, ^2T_{2g}$(Fe t_{2g})) band of Fe-CN[14] and the large enhancement in the Faraday ellipticity evidently arises from the ferromagnetic ordering over the lattice.
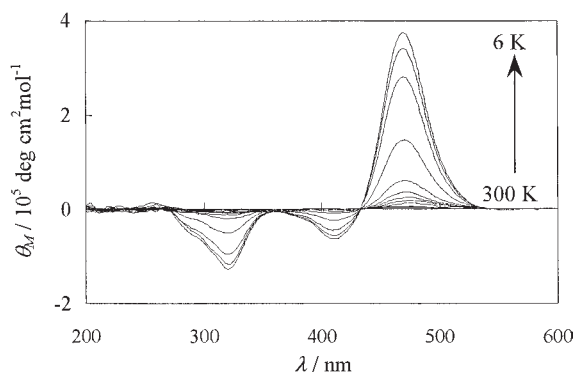

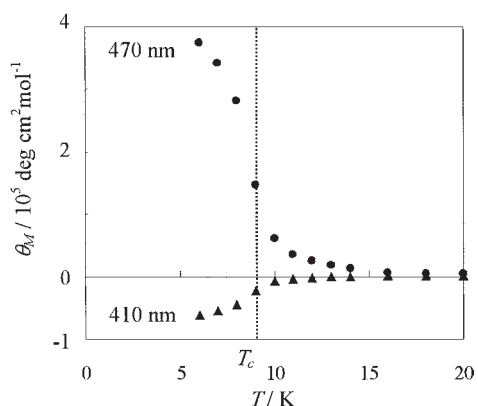**Figure 3.** Faraday ellipticity spectra of $\mathbf{1'}$ under the external magnetic field of 200 G.

Figure 4. Temperature-dependence of θ_M for $\mathbf{1'}$ at 470 nm (●) and at 410 nm (▲).

The magnetic nature of $\mathbf{1'}$ is variable by the replacement of the counter ion,[15] on dehydration[16] or by applying an external pressure.[15] Studies on magneto-optical properties of the resulting new magnetic systems are under way together with magneto-optical properties of related two-dimensional and three-dimensional magnetic compounds.

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10 Elemental Analyses: Anal. Calcd for [Ni(1,1-dmen)$_2$]$_2$[Fe(CN)$_6$]tfs·2H$_2$O ($\mathbf{1'}$), C$_{23}$H$_{52}$F$_3$FeN$_{14}$Ni$_2$O$_5$S: C, 31.86; H, 6.05; N, 22.62; S, 3.70; Fe, 6.44; Ni, 13.54%. Found: C, 31.81; H, 6.02; N, 22.59; S, 3.70, Fe, 6.58; Ni, 13.71%.; Calcd for [Ni(1,1-dmen)$_2$]$_2$[Co(CN)$_6$]tfs·2H$_2$O ($\mathbf{2'}$): C, 31.75; H, 6.02; N, 22.54; S, 3.69; Co, 6.77; Ni, 13.49%. Found: C, 31.83; H, 5.91; N, 22.64; S, 3.62; Co, 6.76; Ni, 13.50%. Metal and S analyses were made on Rigaku ZSX-100s X-ray fluorescence spectrometer.
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12 Crystal data for [Ni(1,1-dmen)$_2$]$_2$[Fe(CN)$_6$]tfs·3.5H$_2$O ($\mathbf{1}$) at $-30\,^\circ$C: C$_{23}$H$_{55}$F$_3$FeN$_{14}$Ni$_2$O$_{6.5}$S, fw = 894.08; brown block, monoclinic, space group P2$_1$/n, $a = 12.104(7)$, $b = 20.624(9)$, $c = 16.903(7)$ Å, $\beta = 91.017(5)^\circ$, $V = 4218(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.408$ gcm^{-3}, μ(Mo Kα) = 13.37 cm^{-1}. The final $R1$ factor was 0.069 for 6906 reflections $I > 2\sigma$(I) and $R = 0.099$, $R_w = 0.167$ for 9374 all reflections. [Ni(1,1-dmen)$_2$]$_2$[Co(CN)$_6$]tfs·3.5H$_2$O ($\mathbf{2}$) at $-30\,^\circ$C: C$_{23}$H$_{55}$CoF$_3$N$_{14}$Ni$_2$O$_{6.5}$S, fw = 906.17; purple block, monoclinic, space group P2$_1$/n, $a = 12.281(7)$, $b = 20.46(1)$, $c = 16.688(10)$ Å, $\beta = 91.160(8)^\circ$, $V = 4191(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.421$ gcm$^-$, μ(Mo Kα) = 13.95 cm^{-1}. The final $R = 0.0999$, $R_w = 0.143$ for 5335 reflections $I > 3\sigma$(I). One 1,1-dmen coordinated Ni3 shows a positional disorder in $\mathbf{1}$ and $\mathbf{2}$. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre (CCDC-189360 for $\mathbf{1}$ and 189361 for $\mathbf{2}$).
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