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Cyano-Bridged Homometallic 1-D and Bimetallic 2-D Assemblies: Synthesis, Structures, and Magnetic Properties of $[Ni(baepn)(CN)]_n(ClO_4)_n$ and $[Ni(baepn)]_{2n}[Fe(CN)_6]_n(H_2O)_{8n}$

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Cyano-bridged homometallic complex $[Ni(baepn)(CN)]_n(ClO_4)_n$ (**1**) and bimetallic complex $[Ni(baepn)]_{2n}[Fe(CN)_6]_n(H_2O)_{8n}$ (**2**) [baepn = *N,N′*-bis(2-aminoethyl)-1,3-propanediamine] were synthesized and characterized. **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.560(3)$ Å, $b = 10.700(3)$ Å, $c = 14.138(9)$ Å, $\beta = 90.18(6)°$, and $Z = 4$; **2** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.951(2)$ Å, $b = 13.672(3)$ Å, $c = 14.392(3)$ Å, $\beta = 98.906(4)°$, and $Z = 4$. The complex **1** has one-dimensional structure whose chain vector runs along the *b* axis with baepn ligands and perchlorate anions alternately arranged up and down in the *c* direction. The antiferromagnetic nature of **1** was explained in terms of the infinite chain model and Haldane gap, giving $g = 2.33$, $J = -29.4$ cm^{-1}, and the magnitude of Haldane gap $E_g = 5.22$ K. The complex **2** that constitutes the first example of 2-D bimetallic assembly of Ni(II) ion and ferrocyanide anion is composed of the neutral layers based on the $[Ni_4Fe_4]$ square grid spanning in the *bc* plane. For **2**, the analysis with the Curie–Weiss law in 2–300 K range results in $\Theta = 0.200$ K and the magnetism was explained in terms of the ability of ferrocyanide in the –Ni–NC–Fe–CN–Ni unit to promote ferromagnetic Ni–Ni interaction.

Introduction

The synthesis of molecule-based magnets whose solid-state structures consist of arrays of molecular units has been actively pursued in recent years with the hope of finding their practical uses.[1] An applicable magnet must be magnetic well above room temperature, and a few examples were reported to have satisfactory ordering temperatures (T_c) to date.[2] All of them, except the tetracyanoethylene complex of vanadium,[2a] are Prussian blue analogues composed of cyanochromate anions and vanadium cations.[2b−d] These high-temperature molecular magnets, however, are air-unstable due to the V(II) moiety which is readily oxidized to V(III) or V(IV) and are insoluble.

In particular, efforts to study the magneto−structural relationship of cyanide-based assemblies which lack solubility due to the strong tendency of cyanides forming three-dimensional network have been made by introducing capping ligands into the coordination sphere of the cation, yielding many magnetic cyano-bridged complexes with oligonuclear,[3] one-dimensional,[4] two-dimensional,[5] or three-dimensional[6] structures. The capping ligands can control the topology of metal ions thereby enhancing the solubility of the resulting

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complexes, and so far chelating amines such as ethylenediamine, 1,3-propylenediamine, or 1,4,8,11-tetraazacyclotetradecane (abbreviated by cyclam) have been usually employed. For metal ions that form six-coordinated geometry, bis-bidentate- or tetradentate-capped metal centers can receive two additional ligands such as cyanides or cyanometalates to form new soluble cyanide-based supramolecular assemblies with reduced number of metal−cyano−metal linkages. Here, we introduce a different type of tetradentate capping ligand, baepn (=*N*,*N′*-bis(2-aminoethyl)-1,3-propanediamine), that has binding strength similar to cyclam but lacks high symmetry. With this ligand, one-dimensional homometallic cyano complex $[\mathrm{Ni(baepn)(CN)}]_n(\mathrm{ClO_4})_n$ (**1**) and two-dimensional heterometallic cyano complex $[\mathrm{Ni(baepn)}]_{2n}[\mathrm{Fe(CN)_6}]_n(\mathrm{H_2O})_{8n}$ (**2**) were synthesized and characterized by means of X-ray crystallography and magnetic measurements. Compound **2** constitutes the first example of 2-D bimetallic assembly composed of Ni(II) ion and ferrocyanide anion.

Experimental Section

Reagents and General Procedures. All reagents were purchased from Aldrich and Fluka and used without further purification.

Elemental analysis for C, H, and N were performed on a CE Instruments model Flash EA 1112 Series analyzer at the Elemental Analysis Service Center of the Korea Basic Science Institute. Infrared spectra were obtained from KBr pellets with a Bruker EQUINOX-55 spectrometer. Magnetic susceptibility measurements were carried out at the Korea Basic Science Institute using a Quantum Design MPMS-7 SQUID magnetometer. Corrections for the diamagnetism of the samples were estimated from Pascal's table.[7]

Synthesis. *Caution! Perchlorate complexes are potentially explosive. The use of small amount of materials is recommended.*

$[\mathrm{Ni(baepn)(CN)}]_n(\mathrm{ClO_4})_n$ (1). To an aqueous solution (20 mL) of nickel(II) perchlorate hexahydrate (180 mg, 0.50 mmol) was added neat baepn (80 μL, 0.50 mmol) with stirring. After 10 min of stirring, an aqueous solution (10 mL) of potassium cyanide (32 mg, 0.50 mmol) was added in dropwise manner. The resulting pink precipitate was dissolved by reflux for 1 h. The pink solution was filtered while hot, and the filtrate was slowly cooled to room temperature with the cooling rate of 2 °C/h. Pink crystals of **1** suitable for X-ray crystallography were obtained in 85% yield based on Ni. Anal. Calcd for $\mathrm{C_8H_{20}N_5ClO_4Ni}$: C, 27.90; H, 5.85; N, 20.33. Found: C, 28.05; H, 6.01; N, 20.10. Selected IR data (cm^{-1}, KBr pellet): 3375 (s), 3318 (s), 3285 (s), 2956 (s), 2921 (m), 2857 (m), 2128 (m), 1598 (s), 1456(w), 1427 (m), 1287 (w), 1103 (vs, broad), 1006 (m), 978 (m), 951 (s), 897 (w), 800 (w), 623 (s), 510 (m).

$[\mathrm{Ni(baepn)}]_{2n}[\mathrm{Fe(CN)_6}]_n(\mathrm{H_2O})_{8n}$ (2). The aqueous reaction of any nickel(II) salt, baepn, and potassium ferricyanide in molar ratio of 2:2:1 results in immediate formation of **2** as powder form. Single crystals of **2** suitable for X-ray diffraction study were obtained as following. To an aqueous solution (30 mL) of nickel(II) nitrate haxahydrate (150 mg, 0.50 mmol) was added neat baepn (80 μL, 0.50 mmol) by syringe with stirring. The pink reaction mixture was heated to 90 °C, and an aqueous solution (20 mL) of potassium ferricyanide (82 mg, 0.25 mmol) was added dropwise to the hot mixture. The resulting red brown solution was filtered while hot, and the filtrate was left undisturbed with continuous heating to keep the temperature at 90 °C. After 4 days, well-shaped red brown crystals of **2** were obtained in 78% yield based on Ni. Anal. Calcd for $\mathrm{C_{20}H_{56}N_{14}O_8FeNi_2}$: C, 30.25; H, 7.11; N, 24.70. Found: C, 30.40; H, 6.96; N, 24.85. Selected IR peaks (cm^{-1}, KBr pellet): 3434 (vs, broad), 3269 (shoulder), 2923 (m), 2863 (m), 2042 (s), 1637 (m), 1601 (m), 1453 (w), 1426 (w), 1324 (w), 1286 (w), 1107 (m), 1058 (m), 1032 (m), 972 (m), 885 (w), 583 (m), 509 (w), 435 (w).

Crystallographic Data Collection and Structure Determination. A suitable single crystal of each compound was carefully selected under a polarizing microscope and mounted on a glass fiber. Crystallographic data for **1** were collected on an Enraf-Nonius CAD4TSB diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 293 K in $\omega/2\theta$ scan mode. Cell parameters were calculated by least-squares refinement of 25 well-centered reflections in the range of $22.614° < 2\theta < 34.707°$. Lorentz−polarization and absorption corrections were applied to the data. A total of 1902 reflections with the maximum θ value of 23.97° were measured, and 1451 reflections were assumed to be observed by applying the condition $F_o > 2\sigma(F_o)$. The structure was solved by direct methods with the SIR92 program,[8] and all non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic parameters by the SHELXL-93 program.[9]

The data collection for **2** was performed on a Bruker 1K SMART CCD-equipped diffractometer with graphite-monochromated Mo

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Table 1. Crystallographic Data for **1** and **2**

	1	**2**
empirical formula	$C_8H_{20}N_5O_4ClNi$	$C_{20}H_{56}N_{14}O_8FeNi_2$
fw	344.45	794.06
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	9.560(3)	8.951(2)
b (Å)	10.700(3)	13.672(3)
c (Å)	14.138(9)	14.392(3)
β (deg)	90.18(6)	98.906(4)
V (Å^3)	1445.9(10)	1740.0(7)
Z	4	4
F(000)	720	840
d_{calcd} (g cm^{-3})	1.582	1.516
μ (mm^{-1})	1.544	1.544
λ (Å)	0.710 73	0.710 73
θ range (deg)	2.39−23.97	2.07−28.05
no. of tot. reflcns	1902	3960
no. of obsd reflcns[a]	1451	3599
no. of params	172	205
R1[b]	0.0608	0.0409
wR2[c]	0.1534	0.1200
GOF	1.137	1.081
weighting scheme:[c] x, y	0.0977, 1.7214	0.0852, 0.5009

[a] Criterion: $F_o > 2\sigma(F_o)$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_c|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$. $P = (F_o^2 + 2F_c^2)/3$.

Kα radiation (λ = 0.710 73 Å) at 293 K.[10] The hemisphere of reflection data was collected as ω scan frames with a width of 0.3° and exposure time of 10 s/frame. Cell parameters were determined and refined by SMART program.[10] Data reduction and Lorentz polarization correction were performed using SAINT software.[10] An empirical absorption correction was applied with the SADABS program.[10] The structure solving by direct methods with the command line of "TREF −1"[11] and the refinement of all non-hydrogen atoms by full-matrix least-squares techniques with anisotropic parameters were carried out with the SHELXTL software package.[10] For both compounds, hydrogen atoms were calculated at idealized positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Crystallographic data and details of data collection for both compounds are listed in Table 1.

Results and Discussion

Synthesis. The equimolar reaction of nickel(II) perchlorate hexahydrate with baepn and potassium cyanide in aqueous solution gives pink precipitate **1**. The chain complex **1** is only slightly soluble in water at room temperature but dissolves well in boiling water. Reflux for 1 h is sufficient to make the precipitate disappear into the solution. The addition of potassium cyanide solution into the reaction mixture of Ni^{II} and baepn must be done in dropwise manner to prevent the precipitation of other insoluble pink side product, presumably $[Ni(baepn)(CN)_2]$ as judged by the absence of a ν(Cl−O) peak at the 1000 cm^{-1} region in IR spectrum. Fast addition or the use of overdose of cyanide causes the formation of this precipitate.

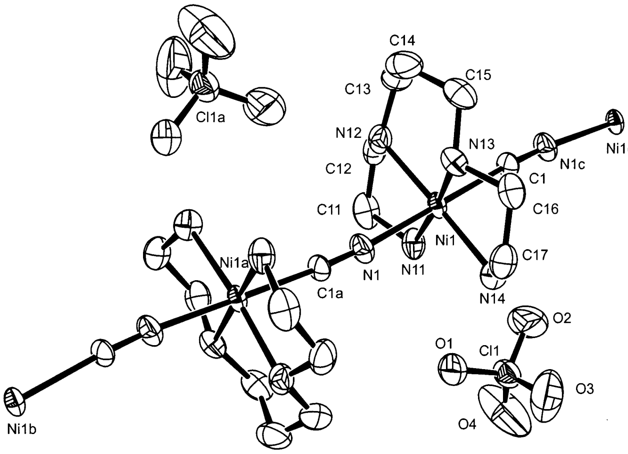

Figure 1. Repeating unit of **1**. Symmetry code: (a) 0.5 − x, 0.5 + y, 1.5 − z; (b) x, 1 + y, z; (c) 0.5 − x, −0.5 + y, 1.5 − z.

The reaction of Ni(II) salts, baepn, and ferricyanide, which gives dark brown precipitate **2**, is accompanied by the reduction of ferricyanide to ferrocyanide. The occurrence of a ν(CN$^-$) peak of **2** at 2042 cm^{-1} is a clear indication of the reduction. The nature of the reduction is not understood, and the additional use of a strong oxidizing reagent such as hydrogen peroxide or potassium persulfate with the reaction mixture of Ni(II) salts, baepn, and ferricyanide failed to retain the oxidation state of Fe center. The reduction of Fe(III) was not observed in previously reported Ni(II)−NC−Fe(III) bridged systems[12] although it was seen for Cu(II)−NC−Fe(III) bridged systems.[13] The use of potassium ferrocyanide instead of potassium ferricyanide also gave the product **2** as confirmed by IR spectroscopy. To prepare single crystals of **2**, the reaction must be carried out at high temperature to suppress the strong tendency of nucleation caused by the poor solubility of the product. The extended standing of the hot reaction mixture afforded single crystals of **2**.

Crystal Structures. $[Ni(baepn)(CN)]_n(ClO_4)_n$ (1). The molecular view of the asymmetric unit and part of the symmetry-generated unit is displayed in Figure 1. Selected bond distances and bond angles are listed in Table 2. The coordination sphere of Ni1 is approximately octahedral with four nitrogen atoms from the baepn capping ligand in equatorial plane and atoms from cyanides in axial positions. Metal−ligands bond distances are 2.099(7)−2.145(7) Å for amine nitrogen atoms, 2.133(7) Å for cyanide nitrogen atom, and 2.096(8) Å for cyanide carbon atom.

Unlike other homometallic cyanide complexes with two different metal centers of [NC−M−CN] and [CN−M−NC],[4h,14] the bridging cyanide ligands in the compound **1** link the nickel centers to form one-dimensional chains with one kind of [NC−Ni−NC] bridging structure.

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[10] *SMART, SAINT, SADABS and SHELXTL softwares*; Bruker AXS, Inc.: Madison, WI, 1998.

[11] When the default value of 256 for the "TREF" command line was employed, the structure solving followed by the refinement gave the residual value of >20%. The same unsatisfactory results were always observed for more than 20 single crystalline samples that were prepared from various synthetic batches.

[12] The references for the Ni(II)−NC−Fe(III) bridged systems are listed in refs 3a, 4a, 5h, 5e, 6b, and 6f.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

	Bond Distances (Å)		
Ni1−C1	2.096(8)	Ni1−N1	2.133(7)
Ni1−N11	2.117(7)	Ni1−N12	2.109(7)
Ni1−N13	2.099(6)	Ni1−N14	2.145(7)
C1−N1	1.135(10)	Cl1−O1	1.435(6)
Cl1−O2	1.389(7)	Cl1−O3	1.412(9)
Cl1−O4	1.383(8)		
	Bond Angles (deg)		
C1−Ni1−N1	179.2(3)	C1−Ni1−N11	90.6(3)
C1−Ni1−N12	92.0(3)	C1−Ni1−N13	92.8(3)
C1−Ni1−N14	91.4(3)	N1−Ni1−N11	88.6(3)
N1−Ni1−N12	87.9(3)	N1−Ni1−N13	87.9(3)
N1−Ni1−N14	88.7(3)	N11−Ni1−N12	83.6(3)
N11−Ni1−N13	175.0(3)	N11−Ni1−N14	100.1(3)
N12−Ni1−N13	92.6(3)	N12−Ni1−N14	175.0(3)
N13−Ni1−N14	83.5(3)	O1−Cl1−O2	111.9(4)
O1−Cl1−O3	107.0(5)	O1−Cl1−O4	111.1(5)
O2−Cl1−O3	105.9(6)	O2−Cl1−O4	112.5(6)
O3−Cl1−O4	108.0(8)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**

	Bond Distances (Å)		
Fe1−C1	1.916(2)	Fe1−C2	1.912(2)
Fe1−C3	1.925(2)	Ni−N1	2.1107(19)
Ni−N2	2.096(2)	Ni−N4	2.1145(19)
Ni−N7	2.1056(19)	Ni−N11	2.1111(19)
Ni−N14	2.109(2)		
	Bond Angles (deg)		
N1−C1−Fe1	177.23(19)	N2b−C2−Fe1	177.05(19)
N3−C3−Fe1	178.8(2)	N1−Ni−N2	178.29(9)
N1−Ni−N4	92.21(8)	N1−Ni−N7	89.83(8)
N1−Ni−N11	86.63(8)	N1−Ni−N14	88.63(9)
N2−Ni−N4	87.45(8)	N2−Ni−N7	91.79(9)
N2−Ni−N11	93.84(8)	N2−Ni−N14	89.80(9)
N4−Ni−N7	83.09(8)	N4−Ni−N11	175.36(7)
N4−Ni−N14	101.54(8)	N7−Ni−N11	92.42(8)
N7−Ni−N14	175.18(7)	N11−Ni−N14	82.93(8)
C1−N1−Ni	147.28(18)	C2c−N2−Ni	150.27(18)

The N1c−C1−Ni1, C1−Ni1− N1, and Ni1−N1−C1a angles of 175.5(3), 179.2(3), and 174.8(3)°, respectively, reflect the extent of linearity of the chain. The chain direction coincides with the *b* axis. The extended view of molecular structure of **1** along the *b* axis is deposited to the Supporting Information. The baepn ligands are lined up along the *b* direction such that the dihedral angle between two adjacent NiN_4 best planes is 0.0°, and the propylene groups of the baepn ligands are alternately positioned in opposite direction in the *c* direction. The shortest intra- and interchain Ni−Ni distances are 5.350(4) and 8.683(6) Å, respectively.

$[Ni(baepn)]_{2n}[Fe(CN)_6]_n(H_2O)_{8n}$ (2). The structure of the secondary building unit and selected bond distances and angles for **2** are presented in Figure 2 and Table 3, respectively. Packing water molecules are omitted for clarity.

The ferrocyanide anion coordinates to four adjacent square planar Ni(baepn) units with its four cyanide nitrogen atoms (N1, N2, N3, and N4) in the *bc* plane to form a two-dimensional structure based on $[Ni_4Fe_4]$ square grid units. Compound **2** constitutes the first example of 2-D bimetallic assembly of Ni(II) ion and ferrocyanide anion since only 1-D[15] and 3-D[6(b)] systems are reported to date. The remaining two trans cyanide groups are hanging uncoordinated and tilted by ca. 30° from the vector perpendicular to the layer plane. All packing water molecules are disposed between neighboring layers and do not participate in forming any hydrogen bonding. It is interesting to note that the interlayer separation of ca. 3.4 Å is as short as that of graphite. The extended layer molecular view showing the packing water molecules and short separation is also deposited to the Supporting Information. The shortest intra- and interlayer Ni−Ni distances are 6.838(2) and 8.951(2) Å, respectively. The bond distances and angles associated with **2** are not unusual. The bridging C−N−Ni angles are in the range of 147.28(18)−150.27(18)°, and this kind of bending feature of cyanide bridge is usually observed in other cyanide-bridged bimetallic complexes.

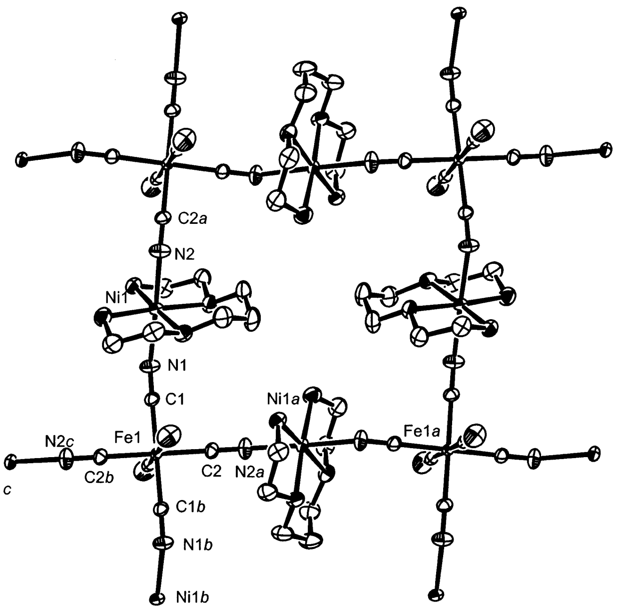

Figure 2. Secondary building unit of **2**. Packing water molecules are omitted for clarity. Symmetry code: (a) −*x* + 1, *y* − 0.5, −*z* + 0.5; (b) −*x* + 1, −*y*, −*z*; (c) *x*, −*y* + 0.5, *z* − 0.5.

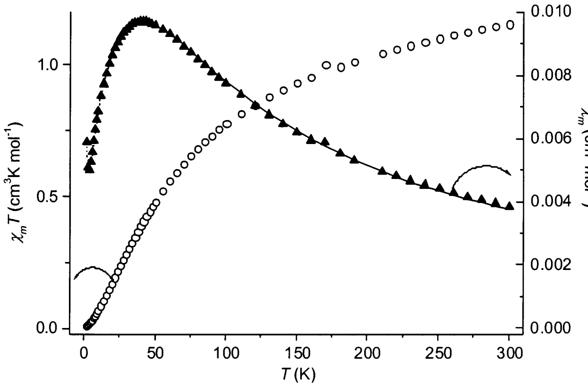

Figure 3. Temperature dependence of $\chi_m T$ (○) and χ_m (▲) for **1**. The solid and dotted lines denote the theoretical fits.

Magnetic Properties. $[Ni(baepn)(CN)]_n(ClO_4)_n$ (1). The temperature dependence of magnetic susceptibility measured in 2−300 K under the external magnetic field of 1000 Oe is illustrated in Figure 3. The value of $\chi_m T$ is 1.15 cm^3 K mol^{-1} at room temperature and decreases continuously with lowering temperature to reach 0.0118 cm^3 K mol^{-1} at 2 K. This is a typical phenomenon for antiferromagnetically coupled

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system. On the other hand, the χ_m value shows a broad maximum around 40 K and decreases sharply below 40 K, which is characteristic of a one-dimensional Haldane-gap system.[16] The magnetic data in high-temperature region (T > 40 K) were fitted with infinite chain model derived by Fisher:[17]

$$\chi_m = \frac{N^2 g^2 \beta^2 S(S+1)}{kT}\cdot\frac{1+u}{1-u}$$

$$u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right] \qquad (1)$$

The best fit gives $g = 2.33$ and $J = -29.4$ cm^{-1} with agreement factor $R = 5.69 \times 10^{-5}$, which is defined as $R = [\Phi/(n - k)]^{1/2}$, where n is the number of data points, k is the number of parameters, and $\Phi = \Sigma[(\chi_m T)_i^{obs} - (\chi_m T)_i^{calc}]^2$. This result implies the existence of strong antiferromagnetic couplings between neighboring Ni^{II} ions in each chain, being in good agreement with the expectation from the $\chi_m T$ vs T plot. In the temperature region lower than 40 K, the magnetic data were fitted with Haldane gap, given by eq 2,[16] where E_g denotes the magnitude of Haldane gap. The data were best fit with $E_g = 5.22$ K and $R = 1.37 \times 10^{-5}$.

$$\chi(T) = \chi(0) + C\exp(-E_g/kT) \qquad (2)$$

[Ni(baepn)]$_{2n}$[Fe(CN)$_6$]$_n$(H$_2$O)$_{8n}$ (2). Figure 4 shows the temperature dependence of magnetic susceptibility for **2** measured in 2−300 K range under the applied magnetic field of 1000 Oe. Upon cooling, the $\chi_m T$ value of 2.57 cm^3 K mol^{-1} at room temperature remains relatively constant down to 40 K and starts to increase to the maximum value of 2.80 cm^3 K mol^{-1} at 6 K. Analysis of the magnetic data by Curie−Weiss law[18] reveals the ferromagnetic coupling with the Weiss constant of $\Theta = 0.200$ K.

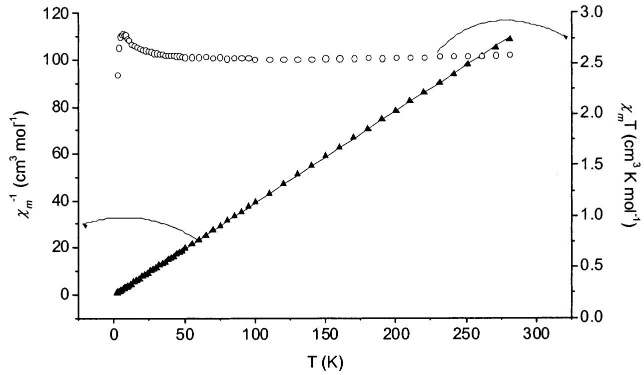

Figure 4. $\chi_m T$ (○) and χ_m^{-1} (▲) vs T plots for **2**. The solid line denotes the theoretical fit.

The ferromagnetic behavior of **2** can be explained in terms of the ability of ferrocyanide in −Ni−NC−Fe−CN−Ni unit to promote ferromagnetic Ni−Ni interaction. Similar type of ferromagnetic behavior has been reported for bimetallic assemblies of Ni(II) ion and ferrocyanide anion such as the three-dimensional compound [NiL$_2$]$_3$[Fe(CN)$_6$](PF$_6$)$_2$ (L = en, tn)[6(b)] and the branched chain system [Ni(en)$_2$]$_4$[Fe(CN)$_5$NO][Fe(CN)$_6$]·5H$_2$O.[14]

Conclusions

Two cyano-bridged assemblies of formula [Ni(baepn)(CN)]$_n$(ClO$_4$)$_n$ (**1**) and [Ni(baepn)]$_{2n}$[Fe(CN)$_6$]$_n$(H$_2$O)$_{8n}$ (**2**) were prepared by the aqueous reaction between [Ni(baepn)]$^{2+}$ and CN$^-$ or [Fe(CN)$_6$]$^{3-}$. The one-dimensional homometallic chain complex **1** has a Ni−Ni vector running along the *b* crystallographic axis with uniquely arranged baepn ligands. The compound **1** comprises an antiferromagnetic system with $g = 2.33$, $J = -29.4$ cm^{-1}, and the magnitude of Haldane gap $E_g = 5.22$ K. The extended structure of **2** is two-dimensional layer based on [Ni$_4$Fe$_4$] square grids spanning in the *bc* plane. The compound **2** constitutes the first example of a 2-D bimetallic ferromagnetic assembly of Ni(II) and ferrocyanide ions with the Weiss constant of $\Theta = 0.200$ K.

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Supporting Information Available: Crystallographic data in CIF format and the extended views for the structures of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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