

1D Zigzag Coordination Polymers of Copper(II) and Nickel(II) with Mixed Ligands – Syntheses and Structures

Han Woong Park,^[a] Soo Mi Sung,^[a] Kil Sik Min,^[a] Hyochoon Bang,^[b] and Myunghyun Paik Suh*^[a]

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The one-dimensional coordination polymers $[\text{Cu}(\text{NO}_3)_2(2,2'\text{-bipy})(4,4'\text{-bipy})]_n \cdot 2n\text{CH}_3\text{OH}$ (**1**) and $[\text{Ni}(\text{tren})(4,4'\text{-bipy})]_n(\text{ClO}_4)_{2n}$ (**2**), have been synthesized by the self-assembly of a copper(II) complex of 2,2'-bipy and a nickel(II) complex of tren with 4,4'-bipy (2,2'-bipy = 2,2'-bipyridine, 4,4'-bipy = 4,4'-bipyridine, and tren = tris-(2-aminoethyl)amine). Their X-ray crystal structures show that the metal ions in **1** and **2** display a distorted octahedral coordination geometry to bind two 4,4'-bipy ligands at the *cis* positions. Each 4,4'-bipy links

two $[\text{Cu}(\text{NO}_3)_2(2,2'\text{-bipy})]$ units in **1** and two $[\text{Ni}(\text{tren})]^{2+}$ units in **2** to form 1D zigzag chains. In the structure of **1**, these chains are linked by offset π - π interactions through 2,2'-bipy ligands, giving rise to a 2D network. The pyridine rings in the 4,4'-bipy ligand are coplanar in **1** but twisted in **2**. The coordination polymer **1** shows a weak antiferromagnetic interaction between copper(II) ions with $J = -0.53 \text{ cm}^{-1}$ ($H = -J \sum_{i=1}^{n-1} S_{A_i} S_{A_{i+1}}$).

Introduction

The construction of coordination polymers based on metal and organic building blocks is a rapidly developing area of research.^[1] Coordination polymers with diverse architectures, such as linear or zigzag chains, helices, honeycombs, square grids, ladders, brick walls, and interwoven diamondoids have been extensively developed.^[2] These coordination polymers attract a great deal of attention because of their interesting structural properties and potential applications to magnetism,^[1f,3] electrical conductivity,^[4] ion exchange,^[5] separation,^[1h,6] and catalysis.^[7] Many important properties of coordination polymers arise from their structures and topology, and thus the rational design and construction of specific architectures are particularly important. To construct the desired framework, rigid organic building blocks are most often used.^[8]

Here we report the synthesis and crystal structures of two 1D zigzag coordination polymers $[\text{Cu}(\text{NO}_3)_2(2,2'\text{-bipy})(4,4'\text{-bipy})]_n \cdot 2n\text{CH}_3\text{OH}$ (**1**) and $[\text{Ni}(\text{tren})(4,4'\text{-bipy})]_n(\text{ClO}_4)_{2n}$ (**2**), where the $[\text{Cu}(\text{NO}_3)_2(2,2'\text{-bipy})]$ units and $[\text{Ni}(\text{tren})]^{2+}$ units are linked by a 4,4'-bipy ligand. The bidentate ligand 4,4'-bipy was chosen as the rigid organic building block that connects the metal ions because of its rod-like shape.^[9] The coordination polymer **1** shows an antiferromagnetic interaction between the copper(II) ions.

Results and Discussion

Synthesis and Properties

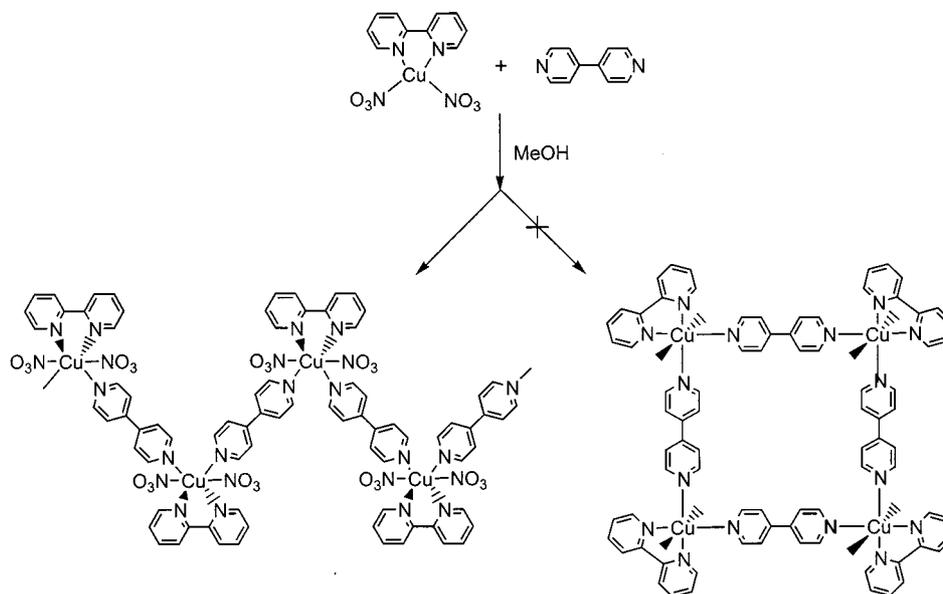
The 1D zigzag coordination polymer $[\text{Cu}(\text{NO}_3)_2(2,2'\text{-bipy})(4,4'\text{-bipy})]_n \cdot 2n\text{CH}_3\text{OH}$ (**1**) was synthesized in high yield by the self-assembly of $[\text{Cu}(\text{NO}_3)_2(2,2'\text{-bipy})]$ and 4,4'-bipy in MeOH. Similarly, the 1D zigzag polymer $[\text{Ni}(\text{tren})(4,4'\text{-bipy})]_n(\text{ClO}_4)_{2n}$ (**2**) was obtained by the self-assembly of $[\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}]$, 4,4'-bipy, and tren in MeOH. Although the assemblies could have resulted in compounds with a square architecture (Schemes 1 and 2),^[10] we were only able to isolate the zigzag polymers. The IR and UV/Vis spectroscopic data of **1** and **2** are summarized in Table 1.

The coordination polymer **1** is purple in the solid state, and forms a blue solution upon addition of H₂O, DMF, or DMSO as it dissociates into the building blocks. It is insoluble in most other organic solvents. The UV/Vis spectrum of **1** in the solid state shows a band at 597 nm; an aqueous solution of **1** shows λ_{max} at 678 nm ($\epsilon = 39.9 \text{ M}^{-1}\text{cm}^{-1}$), which is similar to the absorption of $[\text{Cu}(\text{NO}_3)_2(2,2'\text{-bipy})]$.^[11] Compound **1** shows an OH stretching band at 3468 cm^{-1} and C=C stretching bands for the bipy rings at 1612, 1569, and 1535 cm^{-1} . By comparison with the IR spectrum of $[\text{Cu}(\text{NO}_3)_2(2,2'\text{-bipy})]$,^[11] the peaks at 1612 and 1569 cm^{-1} can be assigned to those of 2,2'-bipy and the peak at 1535 cm^{-1} to that of 4,4'-bipy.

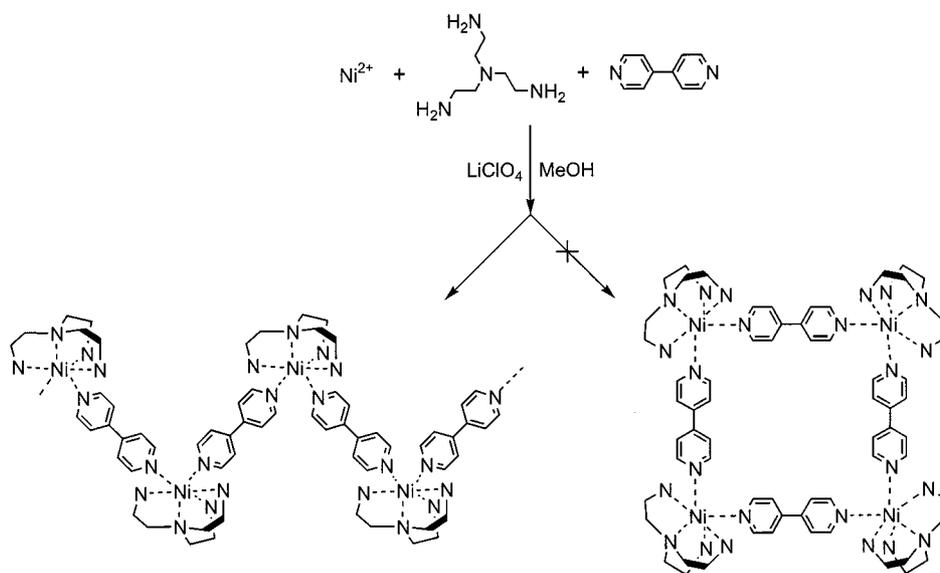
The coordination polymer **2** is pale violet in the solid state. It is soluble in H₂O, MeCN, MeNO₂, DMF, or DMSO, but insoluble in most other organic solvents. The diffuse reflectance spectrum of **2** shows a maximum absorption at 495 nm. When **2** is dissolved in MeCN/H₂O (1:1 v/v), however, the absorption band (λ_{max}) shifts to 552 nm ($\epsilon = 10.6 \text{ M}^{-1}\text{cm}^{-1}$), which is similar to that of $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]^{2+}$ in MeCN/H₂O ($\lambda_{\text{max}} = 555 \text{ nm}$, $\epsilon = 9.3$

^[a] School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-747, Republic of Korea
Fax: (internat.) +82-2/886-8516
E-mail: mpsuh@snu.ac.kr

^[b] Department of Chemistry, Duksung Women's University, Seoul 132-714, Republic of Korea



Scheme 1



Scheme 2

Table 1. Spectral properties of the complexes

	IR [cm ⁻¹] ^[a]	UV/Vis λ _{max} [nm] (ε [M ⁻¹ cm ⁻¹])
[Cu(NO ₃) ₂ (2,2'-bipy)] ^[b]	1610, 1570, 1490, 1275, 1035, 808	676 ^[c]
[Cu(NO ₃) ₂ (2,2'-bipy)(4,4'-bipy)] _n ·2nCH ₃ OH (1)	ν _{OH} 3600, 3468 ν _{py} 1612, 1569, 1535 ν _{NO₃} 1300–1400	678(39.9) ^[c] 597 ^[d]
[Ni(tren)(H ₂ O) ₂] ²⁺ [Ni(tren)(4,4'-bipy)] _n (ClO ₄) _{2n} (2)	ν _{tren} 3344, 3296, 1608 ν _{py} 1535 ν _{ClO₄} 1089	555(9.3) ^[e] 495 ^[d] 552(10.6) ^[f]

^[a] Measured as a Nujol mull. – ^[b] Ref.^[9] – ^[c] Measured in water. – ^[d] Diffuse reflectance spectrum. – ^[e] Measured with an MeCN/water solution containing 1 equiv. of [Ni(OAc)₂·4H₂O] and 1 equiv. of tren. – ^[f] Measured in MeCN/water.

$\text{m}^{-1}\text{cm}^{-1}$). We assume that the $[\text{Ni}(\text{tren})]^{2+}$ moiety coordinates two water molecules in water according to the X-ray crystal structure of $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]\text{SO}_4$ previously reported.^[12] It is obvious that the polymeric structure decomposes into discrete units of $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]^{2+}$ and 4,4'-bipy in MeCN/ H_2O . The infrared spectrum of **2** shows strong absorption bands at 3344 cm^{-1} and 3296 cm^{-1} , which are attributed to the N–H stretching modes of the tren ligand. The NH_2 bending mode of tren appears at 1608 cm^{-1} and the C=C stretching of 4,4'-bipy at 1535 cm^{-1} .

X-ray Crystal Structure of **1**

An ORTEP view of **1** is shown in Figure 1a. Table 2 shows the selected bond lengths and angles. In the structure, the copper(II) ion shows a distorted octahedral coordination geometry by binding a 2,2'-bipy and two 4,4'-bipy ligands in the equatorial positions and two nitrate anions at the axial sites. The average Cu–N_{2,2'-bipy} and Cu–N_{4,4'-bipy} bond lengths are 2.013(1) and 2.034(1) Å, respectively. The average Cu–O bond length involving nitrate li-

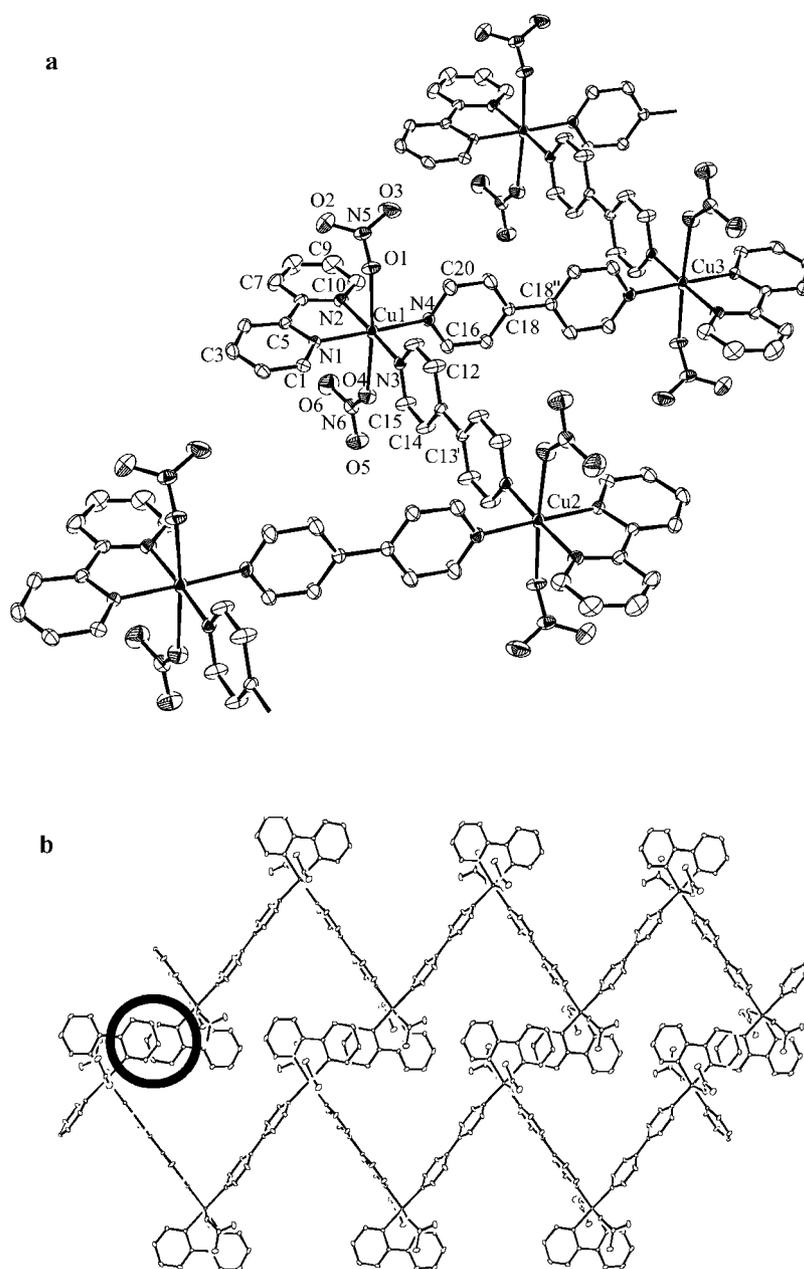


Figure 1. (a) ORTEP drawing of **1** with atomic numbering scheme ($' = 1 - x, -y, 1 - z$; $'' = 1 - x, -y, -z$); thermal ellipsoids are shown at the 30% probability level; (b) extended 2D structure of **1**; the interchain offset π - π interactions are indicated by a solid circle

Table 2. Selected bond lengths [Å] and angles [°] for 1

Cu1–N1	2.021(2)	C2–C3	1.376(5)
Cu1–N2	2.005(2)	C3–C4	1.389(5)
Cu1–N3	2.022(2)	C4–C5	1.380(4)
Cu1–N4	2.045(2)	C5–C6	1.488(4)
Cu1–O1	2.532(1)	C6–C7	1.391(5)
Cu1–O4	2.479(1)	C7–C8	1.384(6)
N1–C1	1.346(4)	C8–C9	1.359(7)
N1–C5	1.351(4)	C9–C10	1.388(6)
N2–C6	1.342(4)	C11–C12	1.381(5)
N2–C10	1.343(4)	C12–C13	1.378(4)
N3–C11	1.324(4)	C13–C13 ^[a]	1.484(6)
N3–C15	1.341(4)	C13–C14	1.376(4)
N4–C16	1.338(4)	C14–C15	1.372(5)
N4–C20	1.330(4)	C16–C17	1.381(5)
N5–O1	1.250(3)	C17–C18	1.384(4)
N5–O2	1.246(3)	C18–C18 ^[b]	1.489(6)
N5–O3	1.225(3)	C18–C19	1.383(5)
N6–O4	1.243(3)	C19–C20	1.386(5)
N6–O5	1.237(3)	C21–O7	1.412(5)
N6–O6	1.232(3)	C22–O8	1.263(7)
C1–C2	1.376(4)		
N1–Cu1–N2	81.20(10)	O4–N6–O5	119.2(2)
N1–Cu1–N3	94.18(10)	O4–N6–O6	120.4(2)
N1–Cu1–N4	178.35(9)	O5–N6–O6	120.3(2)
N2–Cu1–N3	174.88(10)	N1–C1–C2	122.9(3)
N2–Cu1–N4	97.23(10)	N1–C5–C4	121.4(3)
N3–Cu1–N4	87.37(10)	N1–C5–C6	114.4(3)
O1–Cu1–N1	85.64(7)	N2–C6–C5	115.3(2)
O1–Cu1–N2	89.03(8)	N2–C6–C7	121.8(3)
O1–Cu1–N3	88.42(8)	N2–C10–C9	122.0(4)
O1–Cu1–N4	93.81(8)	N3–C11–C12	123.0(3)
O4–Cu1–N1	88.13(7)	N3–C15–C14	123.2(3)
O4–Cu1–N2	93.56(8)	N4–C16–C17	122.8(3)
O4–Cu1–N3	88.46(8)	C1–C2–C3	118.7(3)
O4–Cu1–N4	92.51(8)	C2–C3–C4	119.1(3)
C1–N1–C5	118.4(3)	C3–C4–C5	119.5(3)
C1–N1–Cu1	127.3(2)	C4–C5–C6	124.1(3)
C5–N1–Cu1	114.3(2)	C5–C6–C7	122.9(3)
C6–N2–C10	118.8(3)	C6–C7–C8	118.4(4)
C6–N2–Cu1	114.7(2)	C7–C8–C9	120.0(4)
C10–N2–Cu1	126.4(2)	C8–C9–C10	119.0(4)
C11–N3–C15	116.6(3)	C11–C12–C13	120.8(3)
C11–N3–Cu1	122.6(2)	C12–C13–C14	115.8(3)
C15–N3–Cu1	120.8(2)	C12–C13–C13 ^[a]	122.4(3)
C16–N4–Cu1	120.8(2)	C13–C14–C15	120.7(3)
C20–N4–C16	117.3(3)	C14–C13–C13 ^[a]	121.9(3)
C20–N4–Cu1	121.6(2)	C16–C17–C18	120.5(3)
O1–N5–O2	118.7(2)	C17–C18–C18 ^[b]	121.8(3)
O1–N5–O3	120.8(3)	C19–C18–C17	116.2(3)
O2–N5–O3	120.6(2)	C19–C18–C18 ^[b]	122.0(3)

^[a] Marked atoms are generated by the symmetry operation $1 - x, -y, 1 - z$. ^[b] Marked atoms are generated by the symmetry operation $1 - x, -y, -z$.

gands is 2.505(1) Å, which is significantly longer than the equatorial Cu–N bond lengths because of a Jahn–Teller distortion. The angles N1–Cu1–N3 and N2–Cu1–N4 between 2,2'-bipy and 4,4'-bipy are greater than 90° because the chelate angle of 2,2'-bipy and the angle between two 4,4'-bipy ligands are less than 90°. The copper(II) ion lies 0.025(1) Å out of the square-coordination plane toward O4. Each 4,4'-bipy ligand links two copper(II) ions to form a zigzag chain which extends parallel to the *c* axis. The 4,4'-bipy unit is perfectly coplanar, with a dihedral angle of 0.0°

Table 3. Selected bond lengths [Å] and angles [°] for 2

Ni1–N1	2.112(3)	N6–C16	1.332(5)
Ni1–N2	2.148(4)	C1–C2	1.503(7)
Ni1–N3	2.097(4)	C3–C4	1.479(7)
Ni1–N4	2.143(4)	C5–C6	1.519(7)
Ni1–N5	2.217(3)	C7–C8	1.362(6)
Ni1–N6	2.111(3)	C8–C9	1.387(6)
N1–C1	1.477(6)	C9–C10	1.377(6)
N1–C3	1.499(6)	C9–C12	1.473(6)
N1–C5	1.485(6)	C10–C11	1.364(6)
N2–C2	1.481(6)	C12–C13	1.367(6)
N3–C4	1.464(6)	C12–C14	1.401(6)
N4–C6	1.469(6)	C13–C16 ^[a]	1.390(6)
N5–C7	1.353(5)	C14–C15 ^[a]	1.378(6)
N5–C11	1.353(5)	C15–C14 ^[b]	1.378(6)
N6–C15	1.324(5)	C16–C13 ^[b]	1.390(6)
N1–Ni1–N2	81.33(14)	C1–N1–Ni1	105.8(3)
N1–Ni1–N3	81.58(14)	C1–N1–C3	111.3(3)
N1–Ni1–N4	82.70(14)	C1–N1–C5	113.0(4)
N1–Ni1–N5	103.53(13)	C2–N2–Ni1	120.4(3)
N1–Ni1–N6	169.10(13)	C3–N1–Ni1	110.8(3)
N2–Ni1–N3	92.99(15)	C4–N3–Ni1	109.3(3)
N2–Ni1–N4	161.45(14)	C5–N1–Ni1	105.4(3)
N2–Ni1–N5	87.68(13)	C5–N1–C3	110.3(4)
N2–Ni1–N6	98.47(13)	C6–N4–Ni1	108.8(3)
N3–Ni1–N4	93.94(16)	C7–N5–C11	115.5(3)
N3–Ni1–N5	174.88(13)	C7–N5–Ni1	129.0(3)
N3–Ni1–N6	87.55(14)	C11–N5–Ni1	115.4(3)
N4–Ni1–N5	86.95(14)	C15–N6–C16	117.6(4)
N4–Ni1–N6	98.99(14)	C15–N6–Ni1	120.9(3)
N5–Ni1–N6	87.33(13)	C16–N6–Ni1	121.4(3)
N1–C1–C2	110.8(3)	C7–C8–C9	119.6(4)
N1–C3–C4	112.4(4)	C8–C9–C10	117.2(4)
N1–C5–C6	109.8(4)	C8–C9–C12	122.3(4)
N2–C2–C1	110.8(4)	C9–C10–C11	120.3(4)
N3–C4–C3	111.5(4)	C9–C12–C13	121.7(4)
N4–C6–C5	108.8(4)	C9–C12–C14	120.7(4)
N5–C7–C8	124.0(4)	C10–C9–C12	120.5(4)
N5–C11–C10	123.4(4)	C12–C14–C15 ^[a]	118.5(4)
N6–C15–C14 ^[b]	123.9(4)	C12–C13–C16 ^[a]	119.8(4)
N6–C16–C13 ^[b]	122.5(4)	C13–C12–C14	117.6(4)

^[a] Marked atoms are generated by the symmetry operation $2.5 - x, -0.5 + y, 1.5 - z$. ^[b] Marked atoms are generated by the symmetry operation $2.5 - x, 0.5 + y, 1.5 - z$.

between the two pyridyl ring planes. The dihedral angles between a 2,2'-bipy plane and the pyridine ring planes of 4,4'-bipy involving N3 and N4 are 87.4(1)° and 87.0(1)°, respectively. These perpendicular orientations must be attributed to the steric hindrance between the α -hydrogen atoms of the two different bipyridine ligands located at the *cis* positions. The dihedral angle between the two coordinating pyridyl ring planes involving different 4,4'-bipy ligands is 79.2(1)°. The distances Cu1...Cu2 and Cu1...Cu3 within a chain are 11.144(1) and 11.172(1) Å, respectively. The shortest interchain Cu...Cu distance is 6.980(1) Å. There are offset π - π interactions involving 2,2'-bipy groups between the zigzag chains. The centroid separation and the dihedral angle between the interacting 2,2'-bipy groups are 3.911 Å and 0.0°. The interactions propagate along the *b*-*a* direction, which leads to a 2D network structure (Figure 1b). The methanol guest molecule is involved in a hy-

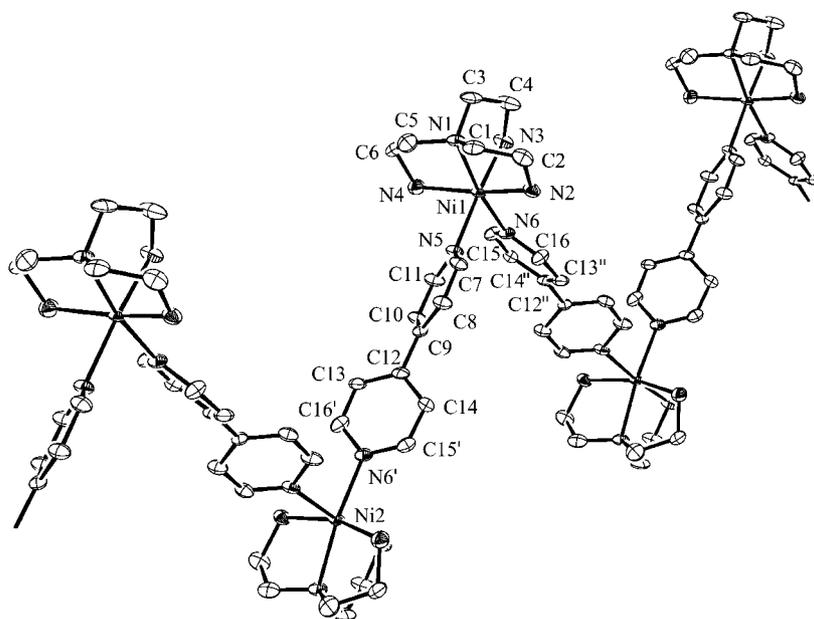


Figure 2. ORTEP drawing of **2** with atomic numbering scheme ($' = 2.5 - x, -0.5 + y, 1.5 - z$; $'' = 2.5 - x, 0.5 + y, 1.5 - z$); thermal ellipsoids are shown at the 40% probability level

drogen-bonding interaction with the oxygen atom of the coordinated nitrate anion [$O5 \cdots O7(-1+x, y, z)$: 2.796 Å; $O5 \cdots H7A-O7$: 165.5°].

X-ray Crystal Structure of 2

An ORTEP view of **2** is shown in Figure 2. Table 3 shows the selected bond lengths and angles. In the structure, the nickel(II) ion is coordinated to one tertiary and three secondary nitrogen atoms of a tren and two 4,4'-bipy ligands to form a distorted octahedral geometry. The average Ni–N_{tren} and Ni–N_{4,4'-bipy} bond lengths are 2.123(2) and 2.164(2) Å, respectively. The bite angles of tren are in the range 81–83°. Two 4,4'-bipy ligands coordinate a nickel(II) ion at the *cis* positions and each 4,4'-bipy ligand links adjacent $[Ni(tren)]^{2+}$ units, which gives rise to a 1D zigzag chain extending parallel to the *b* axis. In contrast to the structure of **1**, the 4,4'-bipy ligand is not planar. The dihedral angle between the two pyridyl ring planes in a 4,4'-bipy ligand is 37.9(3)°. This distortion is not unusual and has been observed with other complexes bridged by 4,4'-bipy ligands.^[13] The dihedral angle between two pyridyl ring planes involving N5 and N6 is 76.8(3)°. This angle is lower than that in the structure of **1**, which must be attributed to steric hindrance with the tren ligand. The shortest Ni \cdots Ni distance within a chain is 11.371(2) Å, and the shortest interchain Ni \cdots Ni distance is 7.936(1) Å.

Magnetic Properties of 1

The effective magnetic moment of **1** measured at 300 K is 1.75 μ_B , in good agreement with the spin-only value of copper(II) (1.78 μ_B). The temperature dependence of the

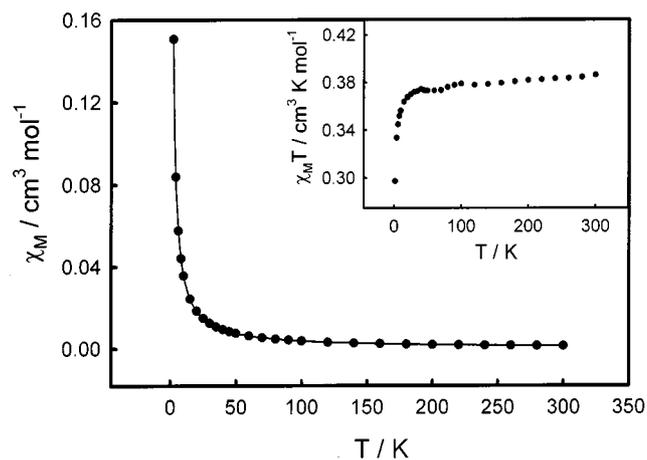


Figure 3. Plots of χ_M vs. T and $\chi_M T$ vs. T (inset) for **1**; the solid line represents the best-fit curve to Equation (1)

magnetic susceptibility of **1** is shown in Figure 3. The susceptibility data in the temperature range 20–300 K follow the Curie–Weiss law, where $\chi_M = C/(T - \theta)$ and $\theta = -1.8$ K. The value of $\chi_M T$ decreases as the temperature is lowered, indicating that an antiferromagnetic interaction exists between the copper(II) ions. To obtain the magnetic parameters, the magnetic susceptibility data were fitted to Equation (1), where N , β , and k are the Avogadro number, the Bohr magneton, and the Boltzmann constant, respectively.^[14–15] For the simple chain made by an array of equally spaced copper(II) ions with $S = 1/2$ local spins, the spin Hamiltonian in zero-field describing the isotropic interaction between the nearest neighbor ions is expressed as Equation (2) and the magnetic susceptibility is expressed as Equation (1).^[14]

Table 4. Magnetic properties of various compounds bridged by 4,4'-bipy

Compounds ^[a]	θ [K]	J [cm ⁻¹]	g	ref.
[Cu(NO ₃) ₂ (2,2'-bipy)(4,4'-bipy)] _n ·2 <i>n</i> CH ₃ OH	-1.8	-0.53	2.01	This work
[Cu ₂ (ClO ₄) ₂ (dien) ₂ (4,4'-bipy)](ClO ₄) ₂	-0.4	-0.3	2.03	16
[Cu ₂ (tren) ₂ (4,4'-bipy)](BPh ₄) ₄		< 1.0		17
[Ni(Bu-dtp) ₂ (4,4'-bipy)] _n	-32			20

^[a] Abbreviations used: dien = diethylenetriamine; Bu-dtp = dibutyldithiophosphate.

$$\chi = \frac{Ng^2\beta^2}{kT} \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3}, \text{ where } x = \frac{|J|}{kT} \quad (1)$$

$$H = -J \sum_{i=1}^{n-1} S_{Ai} S_{Ai+1} \quad (2)$$

The solid line in Figure 3 represents the best fit of the data to Equation (1), which provides $g = 2.01$ and $J = -0.53 \text{ cm}^{-1}$ with $R = 4.0 \times 10^{-6}$. The data are compared with those of other complexes bridged by a 4,4'-bipy ligand in Table 4. It is known that compounds bridged by 4,4'-bipy show almost no, or very weak, magnetic interactions because of the long distance of 4,4'-bipy (almost 11 Å)^[16] and the weak Cu–N bond with the weak base 4,4'-bipy.^[17] In addition, the C–C bond connecting two pyridine rings in 4,4'-bipy has a single bond character [the bond length of C13–C13' is 1.484(6) Å], which breaks the conjugation of the 4,4'-bipy molecules. This also interrupts the magnetic interactions. The weak antiferromagnetic interaction in **1** must be attributed to the unfavorable π -type exchange pathway as well as the long σ -type exchange pathway for the 4,4'-bipy bridging ligand.

Experimental Section

General: All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. Infrared spectra were recorded with a Perkin–Elmer 2000 FT-IR spectrophotometer. Electronic spectra were measured with a CARY 300 Bio UV/Vis spectrophotometer. Magnetic susceptibility was measured on a Quantum Design MPMS superconducting quantum interference device (SQUID). Elemental analyses were performed by the analytical laboratory of the Seoul National University.

Safety Note: Although we have experienced no problem with the compounds reported in this work, perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with great caution.

[Cu(NO₃)₂(2,2'-bipy)]: An EtOH solution (10 mL) of [Cu(NO₃)₂·3H₂O] (4.82 g, 0.02 mol) was mixed with an EtOH solution (10 mL) of 2,2'-bipy (3.2 g, 0.02 mol). The blue precipitate formed was filtered, washed with EtOH, and dried in air. Yield: 6.19 g, 90%. – C₁₀H₈CuN₄O₆ (343.74): calcd. C 34.94, H 2.346, N 16.30; found C 34.78, H 2.055, N 16.35.

[Cu(NO₃)₂(2,2'-bipy)(4,4'-bipy)]_n·2*n*CH₃OH (1**):** [Cu(NO₃)₂·(2,2'-bipy)] (0.068 g, 0.20 mmol) was dissolved in MeOH (1 mL) in

a test tube. A MeOH solution (1 mL) of 4,4'-bipy (0.031 g, 0.20 mmol) was then carefully added to the top of this blue solution, without disturbing it. A violet solid precipitated immediately at the interface of the two solutions, and violet crystals were formed over 10 days as the diffusion proceeded. These crystals were filtered, washed with MeOH, and dried in air. Yield: 0.089 g, 80%. – C₂₂H₂₄CuN₆O₈ (564.01): calcd. C 46.85, H 4.289, N 14.90; found C 45.28, H 3.30, N 15.93.

[Ni(tren)(4,4'-bipy)]_n(ClO₄)_{2n} (2**):** A methanol solution (10 mL) of tris-(2-aminoethyl)amine (0.63 g, 4.3 mmol) and a methanol solution (1 mL) of 4,4'-bipy (0.64 g, 4.3 mmol) were added dropwise to a methanol solution (10 mL) of [Ni(CH₃CO₂)₂·4H₂O] (1.04 g, 4.2 mmol). The solution was stirred for about 30 min. at room temperature and then a methanol solution (5 mL) of LiClO₄ (1.81 g, 17 mmol) was added. A pale violet precipitate formed immediately, which was filtered off, washed with methanol, and dried in vacuo. Yield: 2.07 g, 86%. The single crystals used for the X-ray diffraction study were obtained by the recrystallization of the product from a 1:1 mixture of water and MeCN. – C₁₆H₂₆Cl₂N₆NiO₈ (560.01): calcd. C 34.32, H 4.68, N 15.01; found C 34.34, H 4.42, N 15.36.

X-ray Diffraction Measurements: Single crystals of **1** and **2** were sealed in glass capillaries containing their mother liquor. X-ray

Table 5. Crystallographic data for **1** and **2**

	1	2
Formula	C ₂₂ H ₂₄ CuN ₆ O ₈	C ₁₆ H ₂₆ Cl ₂ N ₆ NiO ₈
Formula mass	564.01	560.01
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	9.3422(2)	9.449(2)
<i>b</i> [Å]	9.4593(2)	15.649(3)
<i>c</i> [Å]	14.6960(1)	15.071(3)
α [°]	80.739(1)	90
β [°]	76.790(1)	91.03(2)
γ [°]	89.212(1)	90
<i>V</i> [Å ³]	1247.49(4)	2228.3(7)
<i>Z</i>	2	4
<i>D</i> _{calc} [g cm ⁻³]	1.502	1.669
<i>T</i> [K]	293(2)	293(2)
λ [Å]	0.71073	0.71073
μ [mm ⁻¹]	0.934	1.168
<i>F</i> (000)	582	1160
Collected	6135	3966
Unique	4182	3644
Observed	3699	2996
Parameters	316	298
GOF	1.064	0.974
<i>R</i> ₁ (4 σ data) ^[a]	0.0449	0.0708
<i>wR</i> ₂ (4 σ data) ^[b]	0.1279	0.1747

^[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. – ^[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

data were collected at room temperature using graphite monochromated Mo- K_{α} radiation on a Siemens CCD diffractometer for **1** and on an Enraf–Nonius CAD4 diffractometer for **2**. The orientation matrix and unit cell parameters were determined from 25 machine-centered reflections with $22.76^{\circ} < 2\theta < 25.18^{\circ}$. Axial photographs were used to verify the unit cell choice. Data were corrected for Lorentz and polarization effects. An absorption correction was made for **1**, but not for **2**. The crystal structures were solved by a Patterson synthesis^[18] and refined by full-matrix least-squares refinement using the SHELXL-97 computer program.^[19] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model. The detailed crystallographic data of **1** and **2** are summarized in Table 5.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-160921 (**1**) and -160922 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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