Perpendicular Interpenetration of Independent Square Grid Sheets. Synthesis and Structural Properties of $[Co(NCS)_2(Py_2L)_2]_n$ (Py_2L=*trans*-1,2-Bis(4-pyridyl)ethylene, 1,2-Bis(4-pyridyl)ethane)

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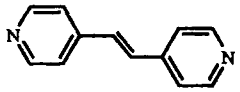
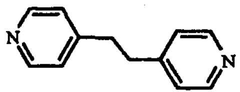
Novel coordination polymers of general form $[Co(NCS)_2(Py_2L)_2]_n$ (Py_2L=*trans*-1,2-bis(4-pyridyl)ethylene (bpee), **1**; 1,2-bis(4-pyridyl)ethane (bpea), **2**) have been synthesized by slow diffusion of aqueous solution of $Co(NCS)_2$ with ethanolic solution of appropriate spacer ligand, Py_2L, in a mole ratio of 1 : 2. X-ray analyses on both **1** and **2** have provided similar unit and infinite structures with space group Ibam. The local geometry around the cobalt(II) atoms is an octahedral arrangement with two NCS groups in trans position (N-Co-N, 180.0° (**1**); 180.0° (**2**)) and four pyridine units in propeller fashion. Each spacer ligand connects two cobalt(II) ions defining the edges of a $[Co(II)]_4$ rhombus. The most fascinating feature is the occurrence of perpendicular interwoven of independent square grid sheets: this is, one molecular network is perpendicularly interpenetrated through the centers of the $[Co(II)]_4$ rhombuses of another independent network with all of the cobalt(II) atoms in a coplanar sheet. The physicochemical properties of the present unique structures were studied.

Introduction

The infinite structures of metal based coordination complexes have emerged as new motif of molecular architecture due to both aesthetic facet and potential applicability such as electrical conductivity, molecular magnet, host-guest chemistry, crystal bending effect, and catalysis.[1~5] Of the known infinite 2D and 3D structures, in particular, mutual interpenetration of independent frameworks has attracted considerable attention.[6] An essential aspect of these structures is that rings belonging to one framework are intimately interlocked with rings from the other(s) in the same sort of topological relationship as that between adjacent links in a chain. Such a research is particularly relevant in the context of solid-state chemistry since rational design of solids has important ramifications for the development of new materials with unusual properties. The structural topology can be designed by selecting the coordination geometry of metals, the structure of spacer ligands, counter ions, and reaction conditions.[6~8] Among diverse elegant efforts to find key factors in the development of the works, the use of unique spacer ligands is worthy of close attention as a rational design strategy. The appropriate angle and flexible components of a bridging ligand play an important role in the self-assembly via coordination.[9~13] Among various ligands that can serve as molecular bridges between metal centers, exploitation of *trans*-1,2-bis(4-pyridyl)ethylene (bpee) and 1,2-bis(4-pyridyl)ethane (bpea) as spacer ligands has been explored for a remarkable class of materials containing diverse architectures and functions.[2c,6c,9b,12] In particular, $[Fe(bpee)(NCS)_2]\cdot CH_3OH$ was found to exhibit spin crossover in a catenane system.[2c] Though the spacers have been used for a wide range of molecular building blocks, the factors that control the complex system including interpenetration structures remain largely unproven. We report results on structural properties that the skeletal ligands can impart to $Co(NCS)_2$ compound.



bpee



bpea

Experimental

Materials and instrumentation. $Co(NCS)_2$, *trans*-1,2-bis(4-pyridyl)ethylene (bpee), and 1,2-bis(4-pyridyl)ethane (bpea) were purchased from Aldrich and used without purification. Elemental analysis (C, H, N) was carried out at the Chemical Analysis Center in KIST. Infrared spectra were obtained in 4000-400 cm^{-1} range on a Perkin Elmer 16F PC FTIR spectrometer with sample prepared as KBr pellet. Temperature-dependent magnetic measurements were recorded on a Quantum Design MPMS-5 SQUID magnetometer at a field of strength 10 kG. Thermal analysis was performed on a Stanton Red Croft TG 100 with a scanning rate of 10 °C/min when heating.

Preparation of $[Co(NCS)_2(bpee)_2]_n$ (1). An ethanolic solution (15 mL) of bpee (183 mg, 1.0 mmol) was slowly diffused into an aqueous solution (5 mL) of $Co(NCS)_2$ (87 mg, 0.5 mmol). Pink crystals were formed in a week. Yield, 216 mg (80%). IR(KBr, cm^{-1}): 2104 (s, C-N), 1606(s), 1552(w), 1502(w), 1426(m), 1298(w), 1256(w), 1218(w), 1204(w), 1066(m), 1016(s), 972(s), 954(m), 844(m), 828(s), 554(s), 468(w).

Preparation of $[Co(NCS)_2(bpea)_2]_n$ (2). An ethanolic solution (15 mL) of bpee (185 mg, 1.0 mmol) was slowly diffused into an aqueous solution (5 mL) of $Co(NCS)_2$ (87 mg, 0.5 mmol). Pink crystals were formed in a week. Yield, 208 mg (77%). IR(KBr, cm^{-1}): 2060 (s, C-N), 1612(s), 1560(w), 1500(w), 1422(m), 1222(m), 1068(w), 1016(w), 826(m), 548(m). Elemental analysis (C, H, N) of the two compounds gave satisfactory results.

X-ray crystal analysis. Each crystal was wedged in

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Table 1. Crystal data and structure refinement for **1** and **2**

Empirical formula	$C_{26}H_{20}N_6S_2Co$	$C_{26}H_{22}N_6S_2Co$
Formula weight	539.54	541.55
Temperature, K	293(2)	293(2)
Wavelength, Å	0.71073	0.71073
Space group	Ibam (No.72)	Ibam (No.72)
a, Å	15.688(4)	14.476(3)
b, Å	16.435(4)	15.872(5)
c, Å	15.066(3)	16.623(5)
V, Å^3	3885(2)	3819(2)
Z	8	8
D_{cal}, Mg/m^3	0.923	0.938
μ, mm^{-1}	0.567	0.576
F(000)	1108	1108
Crystal size, mm	0.32×0.20×0.20	0.30×0.24×0.20
θ, deg	2.60-24.99	2.81-24.84
Index ranges	h, k, l	h, k, l
Reflections collected	796	723
Parameters refined	126	128
Goodness-of-fit on F^2	1.447	1.046
Final R [I>2σ(I)]	R1=0.0783	0.0757
R indices (all data)	R1=0.0814	0.0875
Largest diff. eÅ^{3}	0.375 and −0.747	0.432 and −0.422

a Lindemann capillary with mother liquor. All X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo Kα (λ= 0.71073 Å) at ambient temperature. Each unit cell dimension was based on 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical psi-scan method. The structures were solved by Patterson method (SHELXS-86), and were refined by full-matrix least squares techniques (SHELXL-93).[14] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added at calculated positions. For **1**, the carbon atoms of pyridyl group (C(2), C(3), C(4), C(5), C(6), and C(7)) were disordered with two positions (see positional parameters of Supplementary Material). For **2**, the carbon atoms of pyridyl group (C(2), C(3), C(5), and C(6)) and S were disordered. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1. Final atomic coordinates and isotropic thermal parameters are given in Supporting Information.

Results and Discussion

Synthesis. The reaction of $Co(NCS)_2$ with the present bridging ligands afforded the title complexes. The title compounds were isolated as pink crystals (suitable for X-ray diffraction) by slow diffusion of aqueous solution of $Co(NCS)_2$ with ethanolic solution of appropriate linker in a mole ratio of 1 : 2. They are insoluble in water and common organic solvents, but are slightly soluble in Me_2SO. In particular, for the present spacer ligands, the reaction produces the unique perpendicular interwoven structure instead of the formation of simple network coordination polymers such as $[Co(bpy)_2(NCS)_2]_n$.[7b] Of course, since such a crystal engineering is delicately dependent on reaction conditions, the structures and properties of the title compounds may be changed by the solvent used. However, the reaction of Co $(NCS)_2$ with bpea affords two different shape crystals, implying two isomeric forms, presumably due to the presence of *gauche* or *anti* conformation of the bpea ligand.[9b] Up to now, the structure of *gauche* bpea analog could not elucidated. The ratio of the isomeric mixture seems to be dependent on the reaction conditions, and confirmed by the ν (C-N) stretching frequencies.

Crystal structures. The molecular structures of **1** and **2** are depicted in Figures 1 and 2, and the relevant bond distances and angles are listed in Table 2. X-ray analyses have provided very similar crystallographic unit structures: the local geometry of the cobalt atom is an octahedral arrangement with two NCS groups in *trans* position (N-Co-N, 180.0° (**1**); 180.0° (**2**)) and four pyridine units in propeller fashion building the basal plane (Figures 1(a) and 2(a)). Each linker ligand connects two cobalt(II) ions defining the edges of a $[Co(II)]_4$ rhombus, thus forming 44-membered ring. The network arrangement within an individual polymer network is shown in Figure 2(b). The most interesting feature is that the crystal structures show the occurrence of the perpendicular interpenetration of parallel lay-

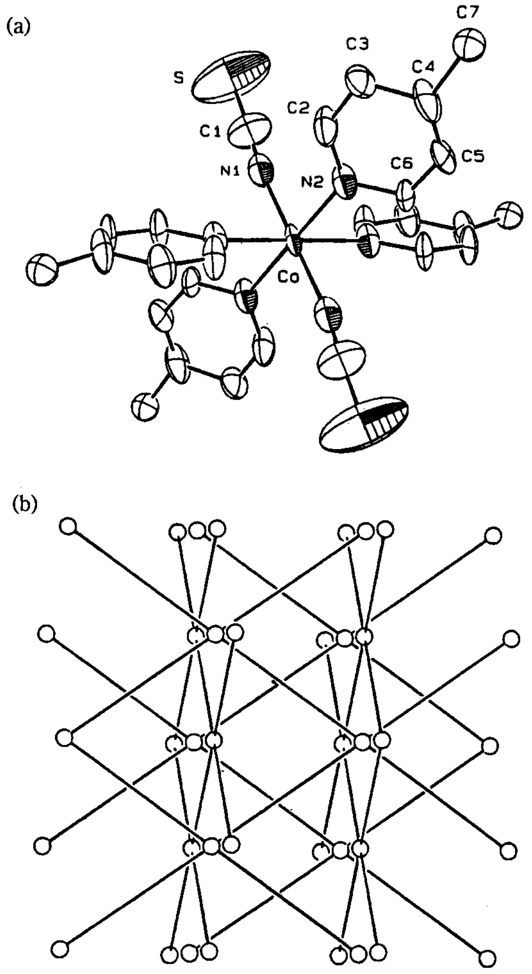

Figure 1. (a) ORTEP view of **1**. (b) Infinite perpendicular penetration structure of **1**. Co(II) centers only are shown.

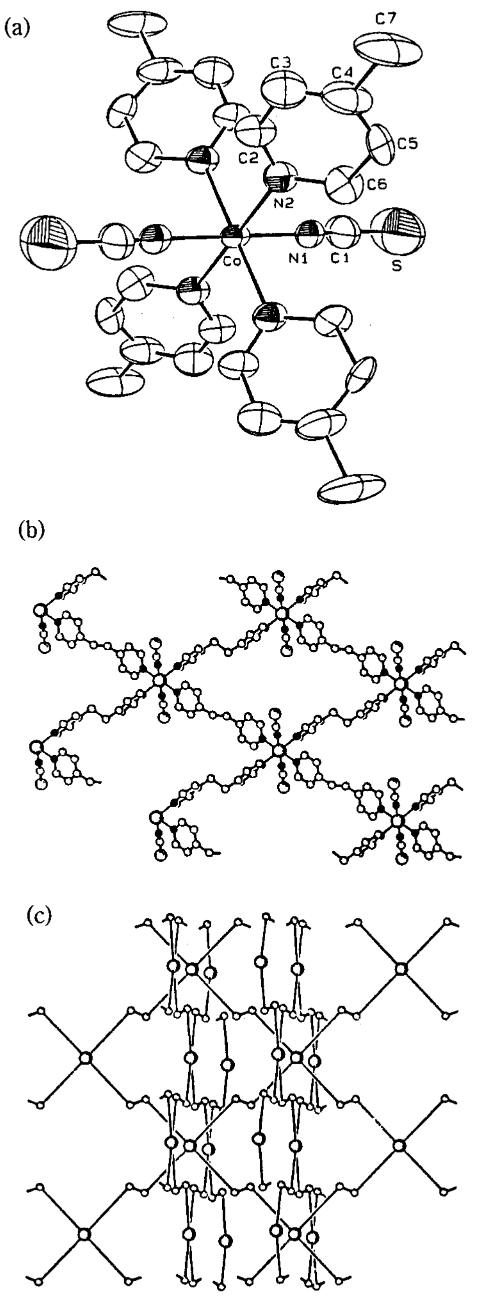

Figure 2. (a) ORTEP view of **2**. (b) View of a layer showing $[Co(II)]_4$ rhombuses of **2**. (c) Infinite perpendicular penetration structure of **2**. Pyridine and NCS groups are omitted for clarity. Co(II) centers and $-CH_2CH_2-$ groups only are shown. Large circles represent Co.

Table 2. Selected bond lengths (Å) and angles (deg) of **1** and **2**

	1	2
Co-N(1)	2.08(1)	2.13(2)
Co-N(1)#1	2.08(1)	2.13(2)
Co-N(2)	2.177(7)	2.181(8)
Co-N(2)#1	2.177(7)	2.181(8)
Co-N(2)#2	2.177(7)	2.181(8)
Co-N(2)#3	2.177(7)	2.181(8)
N(1)-C(1)	1.14(2)	1.08(2)
C(1)-S	1.59(2)	1.55(6)
N(1)-Co-N(1)#1	180.0	180.0
N(2)-Co-N(2)#1	180.0	180.0
N(2)#2-Co-N(2)#3	180.0	180.0
N(1)-Co-N(2)#2	90.1(3)	89.4(3)
N(1)#1-Co-N(2)#2	89.9(3)	90.6(3)
N(1)-Co-N(2)	89.9(3)	90.6(3)
Co-N(1)-C(1)	173(1)	173(1)
N(1)-C(1)-S	177(2)	168(3)

ers separated by 11.15 Å and 10. 74 Å for **1** and **2**, respectively (Figures 1(b) and 2(c)). For **1**, the two pyridine rings and the ethylene group of each bpee ligand are coplanar. The metal-metal separation through the spacer ligand (bpee or bpea) is 13.63 (**1**) and 13.58 Å (**2**), whereas the metal-metal distances through the diagonals of the rhombus are 21.48× 16.62 Å for **1** and 22.30× 15.69 Å for **2**. The edge-shared rhombuses define the grid-layered structures mentioned above, with all of the cobalt(II) atoms in a coplanar sheet. Parallel sheets are displaced so that the cobalt centers of the first sheet are vertically above those of the third, fifth, and the further odd-numbered sheets, while vertically above the midpoints of $[Co(II)]_4$ rhombuses of the even-numbered sheets. In particular, the structure of **2** discloses that the linker ligand is *trans* form. Among two possible linkage isomers of NCS group, an isothiocyanate mode (Co-NCS) was observed. The Co-N bond lengths involving NCS group (2.08(1) Å for **1**; 2.13(2) Å for **2**) is much shorter than the corresponding bond involving the bpym ligand (2.177(7) Å for **1**; 2.181(8) Å for **2**). The connection between Co atom and the isothiocyanate group is slightly bent with C(1)-N(1)-Co (173(1)° for **1**; 173(1)° for **2**).

Such a unique structure seems to be strongly dependent on the subtleties such as the angle, flexibility, and length of a bridging ligand. The *trans* CH=CH and CH_2CH_2 chains between the two pyridine groups may control the length as well as the angle of the ligands, and thus afford the perpendicular interwoven coordination polymers. For instance, simple bipyridine analog, $[Co(NCS)_2(4,4'\text{-bpy})_2]_n$,[7b] has network structure instead of such an interwoven structure. The length and angle of the two spacers are very similar, forming the same skeletal structure. Exploitation of spacers with conformational freedom such as bpea shows the possibility of the isomerism in the coordination polymers, which is in progress.

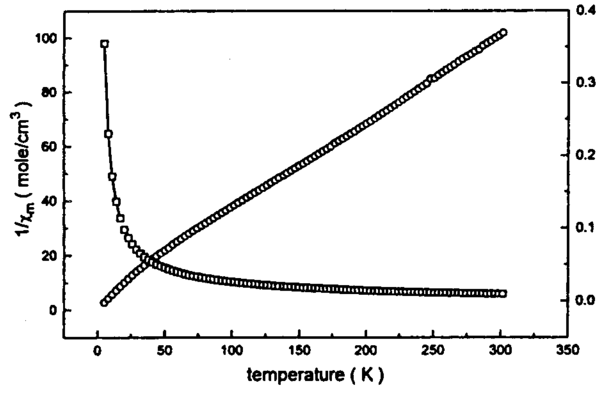

Figure 3. Temperature dependence of χ_m (□) and $1/\chi_m$ (○) for **2**.

Physicochemical properties. The relevant IR feature is those associated with the presence of linkage isomeric NCS ligand. Bonding mode of metal (iso)thiocyanate complexes have been well established for whether the NCS group is bonded to thiocyanate (M-SCN) or isothiocyanate (M-NCS).[15] The ν(C-N) band in the region of 2000-2200 cm^{-1} has been used to discern the bonding fashion of the NCS anion: thiocyanate complexes exhibit very sharp ν(C-N) above 2100 cm^{-1}, whereas isothiocyanate complexes do relatively broad and intensive band around or below 2100 cm^{-1}. Strong and broad bands at 2104 cm^{-1} (**1**) and 2060 cm^{-1} (**2**) of the present complexes are strongly indicative of isothiocyanate bonding mode, which is well consistent with the X-ray structure. The simple C-N stretching frequency seems to be indebted to the *trans* isomer.

The isomeric mixture of **2** is thermally stable up to approximately 220 °C. Its thermal decomposition starts with complicate endothermic steps in the temperature range above 220-290 °C, presumably corresponding to one bpea weight loss, followed by further weight loss continues at above 320 °C. Finally, it seems to be degradated to cobalt oxide. In particular, appearance of complicate endotherms may be an evidence for the presence of isomeric mixture.

The temperature-dependent magnetic susceptibility of **2** was measured in the temperature range 5-300 K. The magnetic susceptibility obeys the Curie law: χ_m=C/T-θ (C=2.27 and θ=0); the linear region in $1/\chi_m$ at the temperature range confirms this conclusion. This magnetic susceptibility is typical behavior of a compound in which cobalt(II) ion is in the high spin state. This data indicate that the present spacer ligand, bpea, is not a significant bridge for propagating an exchange interaction between the Co^{II} ions; Haddad *et al.* already considered that 4,4'-bipyridine analogs are too long to propagate magnetic interactions.[16] Thus, it is concluded that the interpenetration structure does not show a prominent featured temperature-dependent magnetic behavior.

In conclusion, the title complexes are rare examples of the perpendicular interpenetration of independent square grid sheets. The complexes may be devoted to the development of rational synthetic routes to obtain characteristic interwoven coordination polymers that have applications as molecular-based materials. Though the mechanism of the unique structural formation is manifestly unpredictable, understanding features that can be used to direct key factors may be clue to the development of self-assembly materials that exhibit desirable properties.

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Supporting Information Available. Details of X-ray analyses for **1** and **2** (pages) are available from OSJ.

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