Novel Supramolecular Isomerism in Coordination Polymer Synthesis from Unsymmetrical Bridging Ligands: Solvent Influence on the Ligand Placement Orientation and Final Network Structure

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Abstract: The assembly of $Co(NCS)_2$ with 1-methyl-1′-(3-pyridyl)-2-(4-pyridyl)ethene ($\mathbf{L}^1$) exhibits a novel supramolecular isomerism of $[Co(\mathbf{L}^1)_2(NCS)_2]_\infty$ caused by different placement orientation of $\mathbf{L}^1$ around metal centers. The reaction in MeOH/H_2O and EtOH/H_2O resulted in a double chain structure of **1,** and that in EtOH/CH_3NO_2 led to an open framework structure of **2**. The reaction in MeOH/CH_3NO_2 solvent system concomitantly afforded **1** and **2**. The assemblies of 1-(3-pyridyl)-2-(4-pyrimidyl)ethene ($\mathbf{L}^2$) with $Co(NCS)_2$ created the water-coordinated complexes of $Co(\mathbf{L}^2)_2(H_2O)_2(NCS)_2$ (**3** and **4**), an MeOH coordinated complex of $Co(\mathbf{L}^2)_2(H_2O)_2(NCS)_2$ (**5**), and an open framework coordination polymer of $[Co(\mathbf{L}^1)_2(NCS)_2]_\infty$ (**6**) depending on the reaction solvent system. From these observations, it is suggested that in the formation of **1**, the solvent-coordinated intermediate species would be generated first and its *trans* coordination configuration should define the placement orientation of $\mathbf{L}^1$ in the resulting polymer of **1**. On the other hand, it is presumed that the solvent-coordinated intermediate would not be produced during the formation of **2** due to the weaker coordination ability of EtOH and CH_3NO_2 molecules. The open framework coordination polymers of **2** and **6** are converted in the solid state into the isomeric coordination polymer of **1** and hydrogen bonded network structure of **3**, respectively.

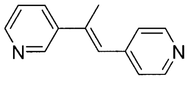
Keywords: crystal engineering • hydrogen bonds • isomers • self-assembly • solvent effects

Introduction

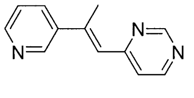
The rational design of new coordination polymers is of current interest in the field of supramolecular chemistry and crystal engineering, because of their exploitable properties; these include magnetism,[1] catalysis and separation,[2] nonlinear optics,[3] and molecular sensing.[4] During the last few decades, a large number of structures have been successfully designed and synthesized through the rational combination of organic ligand 'spacers' and metal 'nodes'.[5] In particular, much research has been concentrated on the exploitation of rodlike ligands such as 4,4′-dipyridine and 1,2-bis(4-pyridyl)ethene in the construction of versatile coordination polymer architectures.[6] However, relatively little use has been made of unsymmetrical bridging ligands.[7]

In this respect, our research has been focused on the exploitation of unsymmetrical bridging ligands in the hope of synthesizing novel coordination polymers.[8] This approach is attractive, because bridging ligands can potentially be arranged around metal centers in diverse ways, and therefore, can result in a variety of coordination polymer structures. Moreover, if the arrangement of a ligand in the coordination could be changed by the variation of synthesis conditions such as the solvent system, different coordination polymer species could be selectively afforded from the same components. In many previous examples, solvent molecules were found to produce a dramatic effect on the extended structure of the network by acting as a coordination ligand or a template for the assembly.[9] However, the influence of the solvent in the formation of coordination polymers is still relatively poorly understood and systematic studies on this subject are rare.[10]

In our efforts to exploit 1-methyl-1′-(3-pyridyl)-2-(4-pyridyl)ethene ($\mathbf{L}^1$) in coordination polymer synthesis, we found a very interesting solvent-dependent topological isomerism caused by the different placement orientation of $\mathbf{L}^1$ around metal centers. To the best of our knowledge, this kind of iso-



$\mathbf{L}^1$



$\mathbf{L}^2$

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merism has not been previously described in this context.[11] In order to understand the isomerism, we also investigated the self-assemblies of 1-(3-pyridyl)-2-(4-pyrimidyl)ethene (**L**^{2}) with Co(NCS)$_2$, and compared their adducts with those of **L**^{1}. Moreover, we discovered that the coordination ability of solvent molecules is a decisive factor in determining the isomerism. We herein report on the isomerism, which illustrates the influence of the solvent system on their assemblies. One of the structures in this contribution has been reported in a preliminary communication.[8a]

Results and Discussion

Assembly of L^1 with Co(NCS)$_2$: 1-Methyl-1′-(3-pyridyl)-2-(4-pyridyl)ethene, **L**^{1} and Co(NCS)$_2$ were assembled by a slow diffusion of two solutions containing each component. The assembly in MeOH/H$_2$O and EtOH/H$_2$O afforded block-shaped crystals of **1**. When the reaction was carried out in MeOH/CH$_3$NO$_2$, plate-shaped crystals of **2** were concomitantly raised together with those of **1**. Moreover, from the reaction in EtOH/CH$_3$NO$_2$, the crystals of **2** were exclusively obtained.

Single crystallography analyses revealed the formation of two isomeric coordination polymer network structures with the formulation of [Co(**L**^{1})$_2$(NCS)$_2$]$_\infty$, and the occurrence of concomitant polymorphism in the MeOH/CH$_3$NO$_2$ system.[11] In the crystal of **1**, a metallacyclic motif is formed by the coordination of two **L**^{1} ligands with two cobalt centers. All the pyridine rings in an **L**^{1} ligand are almost vertically rotated with respect to each other, and consequently, N donor lone pairs make a 104° bending angle. The metallacycles are enchained by the square planar cobalt nodes into a double chain structure (Figure 1 top). In the case of **2**, two kinds of cavities, hexagonal- and triangular-shaped, with a Kagomé net structure are created by the assembly of an angular spacer of **L**^{1} and a square planar Co(NCS)$_2$ node. The size of the hexagonal cavity is unusually large, such that the metal–metal distances through the diagonal ranged from 21.0 Å to 24.7 Å, and the shortest diagonal distance of the cavity is 10.0 Å. The cavities share their edges with each other, and in this way, a peculiar grid layer structure is ex-

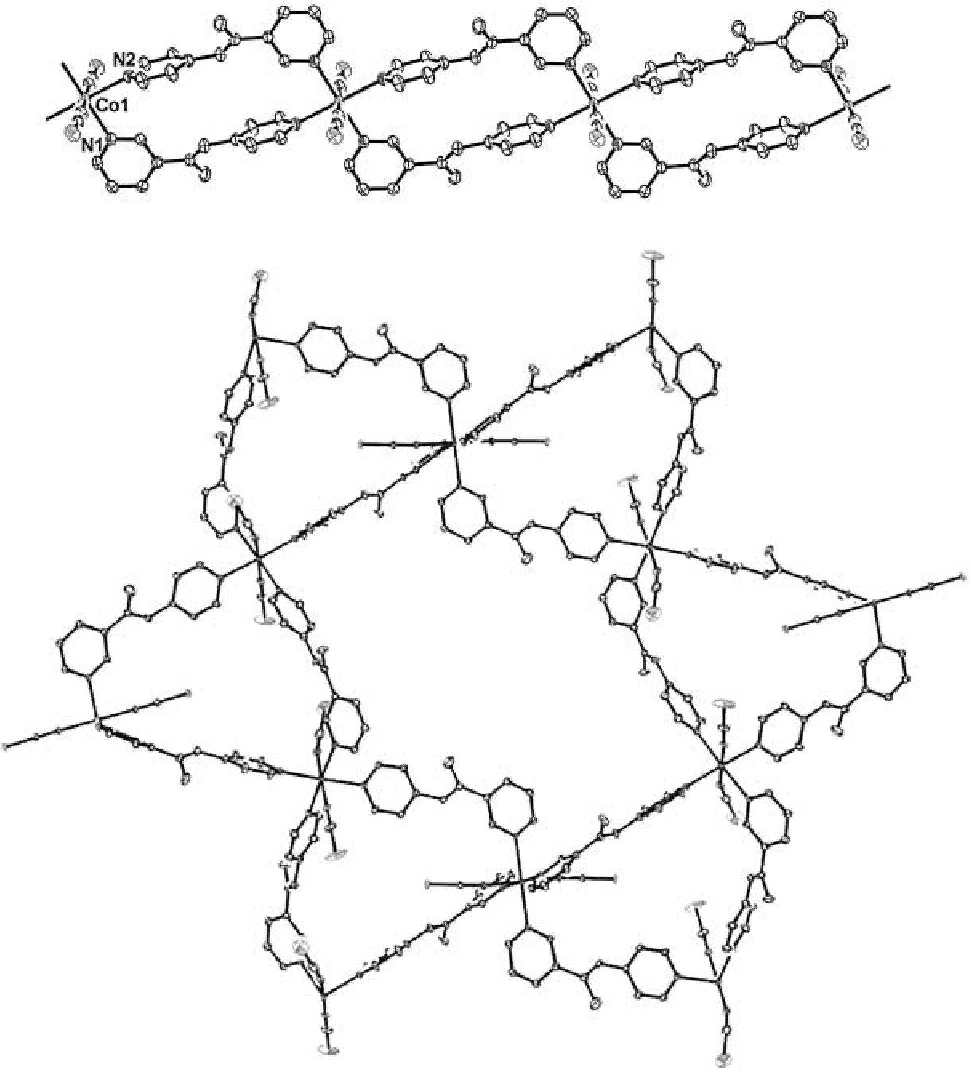

Figure 1. Top: double chain coordination polymer structure of **1** and bottom: two-dimensional coordination polymer network structure of **2**.

tended (Figure 1 bottom). In spite of the huge cavity size, the layers are noninterpenetrated and piled up against each other to create large one-dimensional channel structures with an effective area of 7.7×7.2 Å (Figure 2).[12] These channels are occupied by disordered solvent molecules. The volume fraction occupied by solvent molecules is estimated to be 32% out of the total space.[13]

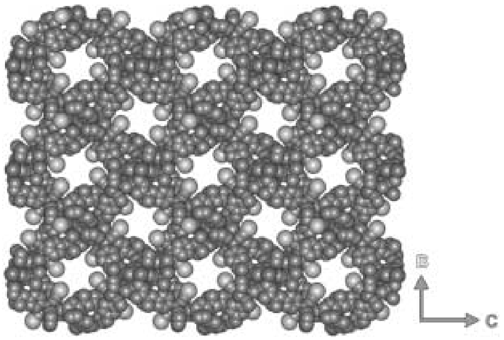

Figure 2. Packing diagram of the layers of **2** showing the formation of one-dimensional channel structures along the *a* axis.

The networks in **1** and **2** have an identical chemical composition and differ in dimension and topology. The fundamental differences between the two isomers are triggered by the change in the arrangement of $\mathbf{L}^1$ ligands around the cobalt center. In a chain of **1**, all of the $Co(NCS)_2$ centers are identically surrounded by two 4-pyridines and two 3-pyridines in *trans* configuration (Figure 3 top). On the other hand, in the network of **2**, two distinct $Co(NCS)_2$ centers exist coordinated by four 3-pyridines, three 4-pyridines, and one 3-pyridine, respectively (Figure 3 bottom). This supramolecular isomerism represents quite a novel example, which cannot be observed in the symmetrical bridging ligands.

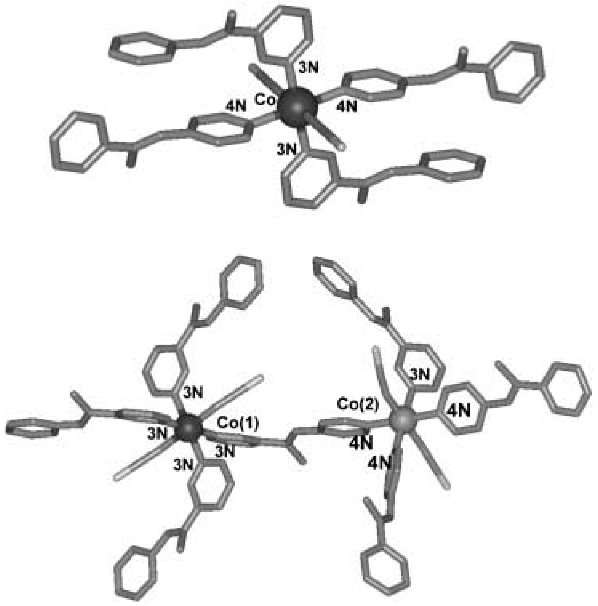

Figure 3. Ligand arrangements around cobalt centers found in **1** (top) and **2** (bottom).

Owing to its highly porous nature, the crystal of **2** loses the solvent and immediately turns opaque upon its removal from the mother liquor. The XRPD (X-ray powder diffraction) measurement shows that the framework of **2** cannot retain its structure upon the loss of guest molecules, which results in an amorphous structure, **2a**. Very interestingly, when solids of **2a** were immersed in water for a minute or exposed to water vapor, the occurrence of the crystalline phase of **1** was revealed by XRPD measurement (Figure 4). This phenomenon can be understood by reference to the transformation process from porous crystal structure into the energetically most favorable packing structure through an amorphous phase.[7c,11] This solid-to-solid transformation between the isomeric network structures has been little explored in the context of coordination polymers.[14]

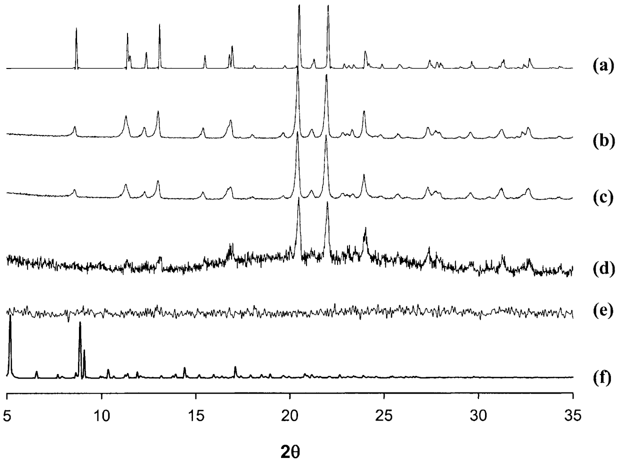

Figure 4. XRPD results; a) simulated for **1**; b) measured for **1**; c) measured after immersing **2a** in water for a minute; indicating the transformation to **1**; d) measured after exposing **2a** to water vapor for a minute; indicating the transformation to **1**; e) measured for **2a** and f) simulated for **2**.

Assembly of $\mathbf{L}^2$ with $Co(NCS)_2$: In order to obtain an understanding of the solvent influence on this isomerism, the assembly of $Co(NCS)_2$ with 1-metyl-1′-(3-pyridyl)-2-(4-pyrimidyl)ethene ($\mathbf{L}^2$) was thoroughly investigated under the same crystallization conditions as those applied for **1** and **2**. The structure of $\mathbf{L}^2$ is identical to that of $\mathbf{L}^1$, except for the presence of 4-pyrimidine instead of 4-pyridine. The complexation of $\mathbf{L}^2$ and $Co(NCS)_2$ in either $MeOH/H_2O$ or $EtOH/H_2O$ concomitantly afforded two kinds of crystals, **3** and **4**.

X-ray structure determination reveals that each of these crystals consists of a water-coordinated complex of $Co(\mathbf{L}^2)_2(H_2O)_2(NCS)_2$ with a distinct hydrogen bonding pattern, which denotes another kind of polymorphism. In both complexes, each cobalt center is octahedrally coordinated by two pyridines of $\mathbf{L}^2$, two water molecules, and two SCN ligands in a *trans* fashion. The uncoordinated pyrimidine of $\mathbf{L}^2$ forms hydrogen bonds with the coordinated water molecules. The polymorphism between **3** and **4** originates from the difference in the hydrogen bonding pattern between them. The pyrimidine of **3** creates hydrogen bonds with the coordinated water through both of its N-4 and N-2 atoms, which results in a two-dimensional hydrogen-bonding network (Figure 5 top). On the other hand, in the structure of **4**, only the N-4 atom of the pyrimidine participates in the hydrogen bonding, and thus a one-dimensional network is created (Figure 5 middle). Extended networks assembled by both coordination and hydrogen bonds are now well established.[15] During the reaction under the MeOH/CH_3NO_2 solvent system, four kinds of crystals, which include water-coordinated **3**, **4**, MeOH-coordinated **5**, and a two-dimensional coordination polymer of **6**, were formed from the same mother liquor. The growth of **3** and **4** is presumed to be due to the inclusion of water from the air during crystallization. The complex structure and hydrogen bonding of **5** is quite analogous to those found in **4**, except for the coordination of the MeOH instead of the water (Figure 5 bottom). It is worthwhile noting that the ligand conformations, the coordination configuration of the metal center, the network structures sustained by the combination of the coordination, and hydrogen bonds found in **3**, **4**, and **5** are quite analogous to the coordination network of **1**. The coordination polymer structure of **6** has quite a strong resemblance to that of **2**, which includes the formation of two-dimensional layers with two kinds of cavity, and the creation of huge channels by their stacking. One of the important features of **6** is the presence of channels functionalized by uncoordinated N-2 atoms (Figure 6). The N-2 atoms located on the channel wall are anticipated to act as a potential hydrogen acceptor or coordination site for guest inclusion. Moreover, the channel structure of **6** can be regarded as relevant for the selective incorporation and separation of specific guest molecules.[7c],[16] The reaction of $Co(NCS)_2$ with $\mathbf{L^2}$ in EtOH/CH_3NO_2 led to crystals of coordination polymer **6** as the unique product.

In the same way as **2**, the crystal of **6** loses its crystallinity and turns into an amorphous solid of **6a** just upon the removal from the mother liquor. Intriguingly, after the immersion of **6a** in water for a minute, or exposure to water vapor, it was found that solids of **6a** were converted into the crystalline phase of **3**, which suggests that the inclusion and coordination of water molecules converted the coordination polymer structure into a closely packed hydrogen-bonding network (Figure 7). This transformation of the covalent bonded framework into a hydrogen-bonding network is to our knowledge quite unique, and represents an important factor in the context of the control of solid materials.

Discussion

These observations suggest that the isomerism found between **1** and **2** is related to the differing coordination abilities of solvent molecules. In the assembly of $\mathbf{L^1}$ and $Co(NCS)_2$ under water-containing solvent systems, solvent-coordinated complexes would be formed first in the solu-

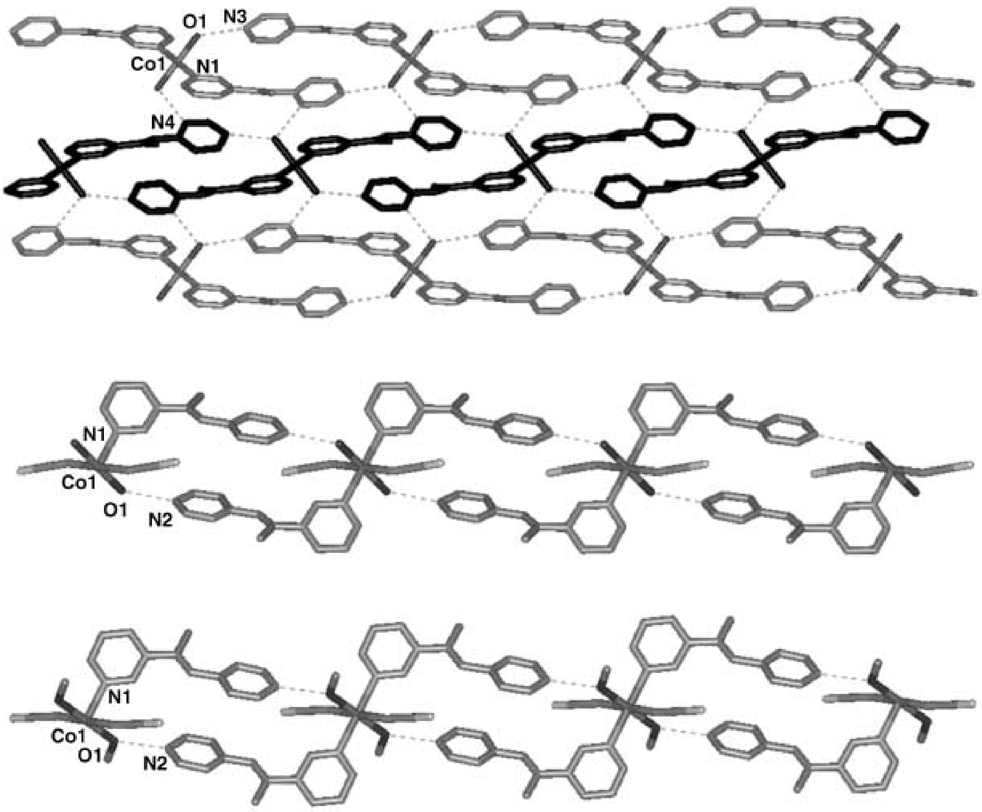

Figure 5. Network structures formed by the combination of the coordination and hydrogen bonds in **3** (top), **4** (middle), and **5** (bottom). Hydrogen bonds are represented as dot lines.

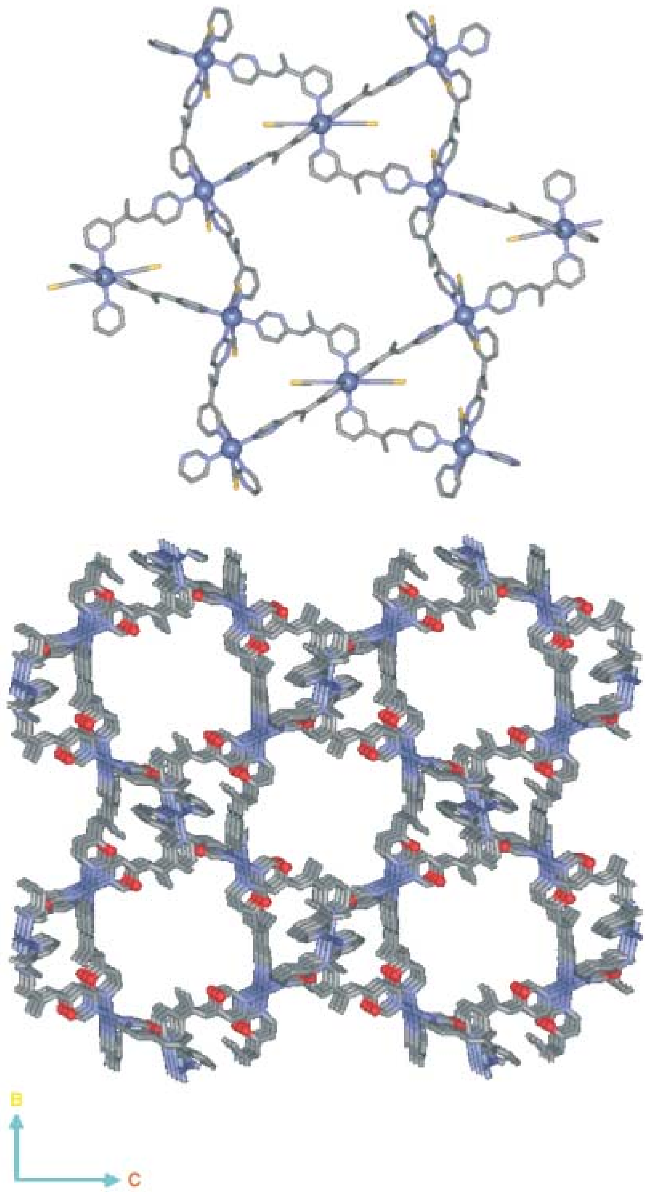

Figure 6. Top: two-dimensional coordination polymer network structure of **6**; bottom: packing diagram of the layers of **6** showing the one-dimensional channel structures along the *a* axis. Uncoordinated nitrogen atoms are represented as red balls, which face inside the channels. Hydrogen atoms and SCN ligands are omitted for clarity.

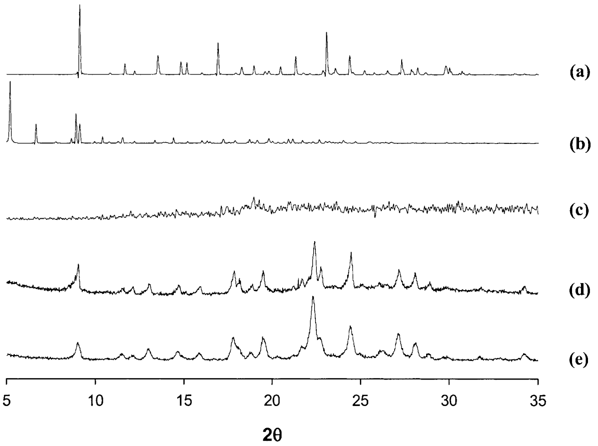

Figure 7. XRPD results; a) simulated for **3**; b) simulated for **6**. Specific peaks for **4** are represented as triangles; c) measured for **6a**; d) measured after immersing **6a** in water for a minute indicating the transformation to **3**, and e) measured after exposing **6a** to water vapor for a minute indicating the transformation to **3**.

tion, and then the polymeric structure of **1** would be crystallized by the replacement of the coordinated solvent molecule with 4-pyridine of $\mathbf{L^1}$. In the cases of **3** and **4**, the replacement of the coordinated solvent did not occur, presumably due to the weaker donor ability of pyrimidine, and the solvent-coordinated complexes are slowly crystallized out. On the other hand, it is presumed that the solvent-coordinated complexes analogous to **3** and **4** would not be formed during the formation of **2** and **6** due to the weaker coordination ability of EtOH and CH_3NO_2 molecules.[9c] The structure of solution-based intermediate complexes for the formation of **2** and **6** is hard to picture at this stage. However, it can be reasoned that the solvent molecules are very weakly bound around the metal center in that system and, thus, N donors of ligands, even of less basic pyrimidine, readily coordinate to the metal center; this results in the coordination polymers of **2** and **6**. The polymorphism in the MeOH/CH_3NO_2 system can be explained by the moderate coordination ability of MeOH molecules. During the reaction in the MeOH/CH_3NO_2 system, $\mathbf{L^1}$ molecules would be assembled around $Co(NCS)_2$ either via MeOH-coordinated intermediate or in a direct manner, which results in coordination polymer **1** or **2**, respectively. The simultaneous formation of the MeOH-coordinated complex of **5**, coordination polymer of **6** from the assembly of $\mathbf{L^2}$, and $Co(NCS)_2$ in MeOH/CH_3NO_2 conditions also supports the above explanation.

Experimental Section

General considerations: The reactions for the synthesis of $\mathbf{L^1}$ and $\mathbf{L^2}$ were carried out under nitrogen by using standard Schlenk techniques. Distilled, dry, and oxygen-free THF was used throughout. Routine ^{1}H NMR spectra and ^{13}C NMR were recorded with a Bruker 300 spectrometer. Elemental analyses were performed at National Center for Inter-University Research Facilities, Seoul National University. The EA measurements were carried out after samples were dried in vacuo for a day. High-resolution mass spectra were carried out at the Korea Basic Science Institute (Daegu). Infrared spectra were recorded on a JASCO FT/IR-660 spectrometer.

Preparation of 1-methyl-1′-(3-pyridyl)-2-(4-pyridyl)ethene ($\mathbf{L^1}$): 4-Picoline (1.9 mL, 19 mmol) at −78 °C was added to a solution of LDA (generated in situ by the reaction of diisopropylamine (3.0 mL, 21 mmol) in 30 mL of THF with *n*BuLi (9.0 mL, 23 mmol) at −78 °C). While the solution was stirred at room temperature for 30 min, the solution turned reddish. 3-Acetylpyridine (1.9 mL, 19 mmol) was addeed to the reddish solution at room temperature. The resulting reaction mixture was stirred at room temperature for 4 h before excess water (30 mL) was added. The residue was extracted with methylene dichloride, evaporated to dryness, and dissolved in 15 mL of pyridine. The pyridine solution was cooled to 0 °C. Excess $POCl_3$ (3 mL) was added to the pyridine solution, and it was then stirred at room temperature for 12 h. Ice was added to the solution to quench excess $POCl_3$. After evaporation of pyridine, the residue was dissolved in water (50 mL) and basified by aqueous NaOH (4 M). Extraction with methylene dichloride (100 mL) followed by chromatography on a silica gel column eluting with Et_2O/MeOH (v/v, 10:1) gave $\mathbf{L^1}$ (1.4 g, 38 % yield); ^{1}H NMR (300 MHz, $CDCl_3$):$\delta = 8.78$ (s, 1 H), 8.63 (d, 4.8 Hz, 2 H), 8.56 (d, 4.8 Hz, 1 H), 7.80 (d, 8.0 Hz, 1 H), 7.32 (dd, 8.0, 4.8 Hz, 1 H), 7.25 (d, 4.8 Hz, 2 H), 6.75 (s, 1 H), 2.32 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.09$, 149.23, 147.71, 147.69, 145.47, 133.72, 126.85, 124.09, 123.85, 123.62, 17.83 ppm; HRMS M^+ calcd 196.1000; found: 196.0998.

Preparation of 1-methyl-1′-(3-pyridyl)-2-(4-pyrimidyl)ethene ($\mathbf{L^2}$): The same procedure as the synthesis of $\mathbf{L^1}$ was applied, except 4-methylpyrimidine (1.9 mL, 21 mmol) was used instead of 4-picoline. $\mathbf{L^2}$ (1.1 g) was isolated (30 % yield); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.24$ (s 1 H), 8.82 (s 1 H), 8.71 (d, 5.2 Hz, 1 H), 8.59 (d, 4.0 Hz, 1 H), 7.82 (d, 8.0 Hz, 1 H), 7.32 (dd, 7.9, 5.2 Hz, 1 H), 7.27 (d, 5.2 Hz, 1 H), 6.71 (s, 1 H) 2.66 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.83$, 158.80, 157.34, 149.67, 147.84, 144.84, 133.76, 126.29, 126.06, 123.55, 121.82, 18.47 ppm; HRMS M^+ calc 197.0953; found: 197.0957.

Complexation of $\mathbf{L^1}$ with $\mathbf{Co(NCS)_2}$ in $\mathbf{MeOH/H_2O}$ or $\mathbf{EtOH/H_2O}$: Compound $\mathbf{L^1}$ (0.040 g, 0.20 mmol) in MeOH or EtOH (5 mL) was layered onto a solution of $Co(NCS)_2$ (0.020 g, 0.11 mmol) in H_2O (5 mL). The resulting solution was left to stand at room temperature for several days to give block-shaped crystals of **1** (85 % yield in MeOH/H_2O and 80 % yield in EtOH/H_2O); IR (KBr): $\tilde{\nu}_{CN} = 2059.6\ cm^{-1}$ (s); elemental analysis calcd for **1**: C 59.25, H 4.26, N 14.81, S 11.30; found: C 58.90, H 4.41, N 14.73, S 11.45.

Complexation of $\mathbf{L^1}$ with $\mathbf{Co(NCS)_2}$ in $\mathbf{EtOH/CH_3NO_2}$: $Co(NCS)_2$ (0.020 g, 0.11 mmol) in EtOH (5 mL) was layered onto a solution of $\mathbf{L^1}$ (0.040 g, 0.20 mmol) in CH_3NO_2 (5 mL). The resulting solution was stood for several days to give plate-shaped crystals of **2** (73 % yield); IR (KBr): $\tilde{\nu}_{CN} = 2067.3\ cm^{-1}$ (s) ; elemental analysis calcd for **2**: C 59.25, H 4.26, N 14.81, S 11.30; found: C 58.87, H 4.32, N 14.60, S 10.85.

Complexation of $\mathbf{L^1}$ with $\mathbf{Co(NCS)_2}$ in $\mathbf{MeOH/CH_3NO_2}$: $Co(NCS)_2$ (0.030 g, 0.16 mmol) in MeOH (5 mL) was layered onto a solution of $\mathbf{L^1}$ (0.060 g, 0.30 mmol) in CH_3NO_2 (5 mL). The resulting solution was left to stand for several days to give a mixture of **1** and **2**.

Complexation of $\mathbf{L^2}$ with $\mathbf{Co(NCS)_2}$ in $\mathbf{MeOH/H_2O}$ or $\mathbf{EtOH/H_2O}$: Compound $\mathbf{L^2}$ (0.040 g, 0.20 mmol) in MeOH or EtOH (5 mL) was layered onto a solution of $Co(NCS)_2$ (0.020 g, 0.11 mmol) in H_2O (5 mL). The resulting solution was left to stand for several days to give crystals of **3** and **4** simultaneously (0.052 g in total, 85 % yield); IR (KBr) for **3**: $\tilde{\nu}_{CN} = 2090.5\ cm^{-1}$ (s); elemental analysis calcd for **3**: C 51.57, H 4.33, N 18.50, S 10.59; found: C 51.64, H 4.34, N 18.27, S 10.65; IR (KBr) for **4**: $\tilde{\nu}_{CN} = 2077.0\ cm^{-1}$ (s); elemental analysis calcd for **4**: C 51.57, H 4.33, N 18.50, S 10.59; found: C 51.45, H 4.38, N 18.11, S 10.59.

Complexation of $\mathbf{L^2}$ with $\mathbf{Co(NCS)_2}$ in $\mathbf{EtOH/CH_3NO_2}$: $Co(NCS)_2$ (0.020 g, 0.11 mmol) in EtOH (5 mL) was layered onto a solution of $\mathbf{L^2}$ (0.040 g, 0.20 mmol) in CH_3NO_2 (5 mL). The resulting solution was left to stand for several days to give **6** (0.031 g, 51 % yield); IR (KBr): $\tilde{\nu}_{CN} = 2068.8\ cm^{-1}$ (s); elemental analysis calcd for **6**: C 53.07, H 4.77, N 17.68, S 10.02; found: C 53.43, H 4.52, N 17.60, S 9.85.

Complexation of $\mathbf{L^2}$ with $\mathbf{Co(NCS)_2}$ in $\mathbf{MeOH/CH_3NO_2}$: $Co(NCS)_2$ (0.020 g, 0.11 mmol) in MeOH (5 mL, 95 %) was layered onto a solution $\mathbf{L^2}$ (0.040 g, 0.20 mmol) in CH_3NO_2 (5 mL). The resulting solution was left to stand for several days to give **5** together with **3**, **4**, and **6**; IR (KBr) for **5**: $\tilde{\nu}_{CN} = 2065.4\ cm^{-1}$ (s); elemental analysis calcd for **5**: C 53.07, H 4.77, N 17.68, S 10.02; found: C 53.43, H 4.52, N 17.60, S 9.85.

Experience for the transformation of 2 to 1 and 6 to 3 in the solid state: Freshly prepared crystals of **2** (0.1 g) or **6** (0.1 g) were immersed in H_2O (10 ml) and then filtered immediately. The filtration and XRPD measurement of the powders revealed that the crystalline phase of **2** or **6** were transformed to that of **1** or **3**, respectively. When the resulting powers were immersed in CH_3OH and stirred for 2 days, no change was observed in the XRPD experiment.

Crystal structure determination: All diffraction data for single crystallography were measured by an Enraf-Nonius CCD single-crystal X-ray diffractometer at room temperature by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames and then refined by using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects by using DENZO.[17] The structure was solved by direct methods by using SHELXS-97, and refined by full-matrix least-squares with SHELXL-97.[18] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms not involving the hydrogen bonding were treated as idealized contributions. Crystal data and refinement results are summarized in Table 1. Selected bond length and angles are listed in Table 2. Crystallographic data (excluding structure factors) for **1**, **2**, **3**, **4**, **5**, and **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers from CCDC 219187 to 219192, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road,

Table 1. Crystal data and structure refinements for **1**, **2**, **3**, **4**, **5**, and **6**.

	1	**2**·(CH_3OH) **3**(CH_3NO_2)	**3**	**4**	**5**	**6**·5(CH_3OH)·(CH_3NO_2)
formula	$C_{28}H_{24}CoN_6S_2$	$C_{42}H_{36}Co_{1.50}N_9S_3\cdot(CH_4O)\cdot3(CH_3NO_2)$	$C_{26}H_{26}CoN_8O_2S_2$	$C_{26}H_{26}CoN_8O_2S_2$	$C_{28}H_{30}CoN_8O_2S_2$	$C_{39}H_{33}Co_{1.50}N_{12}S_3\cdot5(CH_4O)\cdot(CH_3NO_2)$
M_r	567.58	1066.55	605.60	605.60	633.65	1075.60
crystal system	triclinic	monoclinic	orthorhombic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1$/n	*Pbcn*	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	7.7313(4)	11.4426(2)	13.0527(4)	7.3340(10)	8.5090(10)	11.4146(2)
b [Å]	8.6962(4)	22.0767(4)	14.4977(5)	8.2690(10)	9.6470(10)	22.1549(3)
c [Å]	11.1696(4)	27.4792(5)	15.1746(4)	12.7310(10)	10.6910(10)	26.9979(5)
α [°]	109.211(3)	90	90	106.096(4)	81.895(3)	90
β [°]	98.562(3)	101.2330(10)	90	93.897(4)	66.579(2)	100.8008(7)
γ [°]	106.403(2)	90	90	101.240(4)	70.991(2)	90
V [Å^3]	8459.4(7)	6808.7(2)	2871.55(15)	721.45(14)	761.30(14)	6706.53(19)
Z	1	4	4	1	1	4
ρ_{calcd} [Mg m^{-3}]	1.438	1.040	1.401	1.394	1.382	1.065
θ range [°]	3.85–27.46	1.82–27.47	1.00–27.49	1.68–27.50	2.08–27.46	1.84–27.50
reflections collected	4149	26 690	6135	5080	5485	21 999
unique reflections	2942	15 521	3279	3294	3447	14 431
parameters	170	573	187	188	194	561
$R1$	0.0284	0.0984	0.0418	0.0444	0.0521	0.0834
$wR2$	0.0700	0.2961	0.1200	0.1218	0.1773	0.2628
goodness of fit	1.035	1.184	0.962	1.203	1.161	0.983

Table 2. Selected bond lengths [Å] and angles [°] for **1**, **2**, **3**, **4**, **5**, and **6**.

1					
Co(1)–N(1)	2.2457(12)	Co(1)–N(2)	2.2585(11)	Co(1)-N(3)	2.0555(14)
N(3)-Co(1)-N(1)	88.49(5)			N(1)-Co(1)-N(2)	91.05(4)
C(3)-N(1)-Co(1)	174.5			C(9)-N(2)-Co(1)	166.8
2					
Co(1)–N(1)	2.199(4)	Co(1)–N(3)	2.227(4)	Co(1)-N(4)	2.088(4)
Co(2)–N(8)	2.091(5)	Co(2)–N(2)	2.170(4)	Co(2)–N(9)	2.097(5)
Co(2)–N(6)	2.181(4)	Co(2)–N(5)	2.193(4)	Co(2)–N(7)	2.200(4)
N(4)-Co(1)-N(1)	91.27(15)			N(4)-Co(1)-N(3)	88.83(14)
N(1)-Co(1)-N(3)	91.04(15)			N(8)-Co(2)-N(2)	90.77(17)
N(9)-Co(2)-N(2)	91.08(17)			N(8)-Co(2)-N(6)	91.46(19)
N(9)-Co(2)-N(6)	87.58(18)			N(2)-Co(2)-N(6)	91.24(16)
N(2)-Co(2)-N(5)	89.98(15)			N(9)-Co(2)-N(5)	90.63(17)
N(8)-Co(2)-N(7)	88.18(18)			N(9)-Co(2)-N(7)	90.00(18)
C(3)-N(1)-Co(1)	178.3			C(9)-N(2)-Co(2)	177.6
C(35)-N(7)-Co(2)	177.8			C(29)-N(3)-Co(1)	177.0
C(16)-N(5)-Co(2)	176.8			C(22)-N(6)-Co(2)	173.1
3					
Co(1)–O(1)	2.0748(19)	Co(1)–N(2)	2.164(2)	Co(1)–N(1)	2.1772(18)
O(1)–N(3) [a]	3.15	O(1)–N(4)[b]	2.82		
O(1)-H(01)-N(3)[a]	173.6			O(1)-H(02)-N(4) [b]	174.1
O(1)-Co(1)-N(2)	83.45(8)			O(1)-Co(1)-N(1)	84.17(7)
N(2)-Co(1)-N(1)	86.61(7)			C(3)-N(1)-Co(1)	178.2
4					
Co(1)–O(1)	2.1056(18)	Co(1)–N(3)	2.109(2)	Co(1)–N(1)	2.1527(19)
O(1)–N(2) [c]	2.78			C(3)-N(1)-Co(1)	178.8
O(1)-H(01)-N(2)	171.0			O(1)-Co(1)-N(3)	90.43(8)
O(1)-Co(1)-N(1)	89.83(7)			N(3)-Co(1)-N(1)	89.93(8)
5					
Co(1)–N(1)	2.166(3)	Co(1)–N(4)	2.099(3)	Co(1)–O(1)	2.101(2)
O(1)–N(2) [d]	2.73				
O(1)-H(01)-N(2) [d]	174.9			N(4)-Co(1)-O(1)	92.30(12)
N(4)-Co(1)-N(1)	87.93(12)			O(1)-Co(1)-N(1)	89.80(11)
C(3)-N(1)-Co(1)	177.6			C(3)-N(1)-Co(1)	177.6
6					
Co(1)–N(1)	2.225(4)	Co(1)–N(2)	2.206(3)	Co(1)–N(3)	2.095(4)
Co(2)–N(4)	2.194(4)	Co(2)–N(5)	2.182(4)	Co(2)–N(6)	2.198(4)
Co(2)–N(7)	2.052(5)	Co(2)–N(8)	2.062(5)	Co(2)–N(10)	2.181(4)
N(3)-Co(1)-N(2)	91.05(14)			N(3)-Co(1)-N(1)	88.72(14)
N(2)-Co(1)-N(1)	89.37(13)			N(7)-Co(2)-N(8)	177.04(16)
N(7)-Co(2)-N(10)	92.26(17)			N(7)-Co(2)-N(5)	91.48(16)
N(7)-Co(2)-N(4)	89.15(16)			N(5)-Co(2)-N(4)	88.30(15)
N(10)-Co(2)-N(6)	91.48(16)			N(4)-Co(2)-N(6)	88.90(16)
C(8)-N(4)-Co(2)	176.4			C(28)-N(5)-Co(2)	175.45
C(15)-N(2)-Co(1)	176.5			C(20)-N(10)-Co(2)	177.1
C(3)-N(1)-Co(1)	175.2			C(33)-N(6)-Co(2)	173.3

[a] $2-x, 1-y, 1-z$. [b] $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$. [c] $-1+x, -1+y, -1+z$. [d] $x, 1+y, -1+z$.

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XRPD measurements: The simulated XRPD patterns were produced by using CERIUS2 or PowderCell 2.4 with single crystal reflection data. X-ray powder diffraction data (XRPD) were recorded on a Mac Science Co. M18XHF22-SRA diffractometer at 20 kV, 400 mA for $Cu_{K\alpha}$ (λ = 1.5406 Å) with a scan speed of 10 $deg\,min^{-1}$. Rietveld refinement plots for the samples prepared with $Co(NCS)_2$ and $\mathbf{L}^2$ in various conditions are shown in the Supporting Information.

Conclusion

We have demonstrated an unprecedented solvent-selective supramolecular isomerism in the coordination polymers, which originates from the diverse placement orientation of the unsymmetrical ligands around the metal center, and the solid-to-solid transformation between them. Moreover, we have illustrated the significant influence of solvents on this isomerism based on the differences in their coordination ability. This result suggests that the structure and properties of coordination polymers could be regulated by the rational selection of the reaction solvent and the consequent control of the solvent-based intermediate species. For example, we anticipate that a homochiral framework could be engineered by the usage of optically pure solvents. We will continue to undertake further research directed towards this goal.

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