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Synthesis and Characterization of Novel Grid Coordination Polymer Networks Generated from Unsymmetrically Bridging Ligands

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Self-assembly between simple unsymmetrical ligands, such as 1-(3-pyridyl)-2-(4-pyridyl)ethene (**L**^{1}) and 1-methyl-1′-(3-pyridyl)-2-(4-pyrimidyl)ethene (**L**^{2}), and Co(NCS)$_2$ affords the unprecedented two-dimensional grid coordination polymers $[Co(\mathbf{L}^1)_2(NCS)_2]_\infty$ (**1**) and $[Co(\mathbf{L}^2)_2(NCS)_2]_\infty$ (**2**), respectively, with novel topological features which cannot be achieved using symmetrically bridging ligands.

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, which include magnetism, catalysis, nonlinear optics, and molecular sensing.[1] During the past few decades, a number of structures have been successfully designed and synthesized through judicious combination of a metal "node" and a ligand "spacer".[2] In particular, a large number of grid networks containing cavities with diverse sizes and shapes have been engineered by the assembly of ditopic ligands and square planar or octahedral metal centers.[3] So far, the synthetic focus in this area of research has been centered on the exploitation of the rodlike and symmetrically bridging ligands such as 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethene.[4] Very recently, a few unsymmetrical analogues of 4,4′-bipyridine such as 2,4′-bipyridine and 3,4′-bipyridine were exploited for coordination polymer synthesis, and their novel structures were published.[5] However, the use of unsymmetrical ligands is still rare. In this respect, our research has been focused on designing new unsymmetrically bridging ligands and investigating their self-assemblies with metal centers. The adoption of unsymmetrically bridging ligands is expected to lead to a broader palette of coordination polymers than can be achieved with symmetric ligands. In particular, owing to the possession of two or more coordination sites with differing donor ability, unsymmetrical ligands can be assembled around metal centers in diverse arrangements, consequently resulting in unprecedented structures with novel topological features.

We herein report on the exploitation of unsymmetrical ligands 1-(3-pyridyl)-2-(4-pyridyl)ethene (**L**^{1}) and 1-methyl-1′-(3-pyridyl)-2-(4-pyrimidyl)ethene (**L**^{2}).[6] Both of these have distinct coordination sites and a rigid spacer unit connecting them with a 120° angle between N-donor lone pairs (Chart 1). Their assemblies with Co(NCS)$_2$ afford novel two-dimensional grid coordination polymers $[Co(\mathbf{L}^1)_2(NCS)_2]_\infty$ (**1**) and $[Co(\mathbf{L}^2)_2(NCS)_2]_\infty$ (**2**), respectively. Especially, the structure of **2** is so intriguing that **L**^{2} generates two kinds of cobalt centers and connects them leading to an open framework structure having one-dimensional channels functionalized by a potential hydrogen-accepting group.

The orange crystals of **1** were obtained by slow diffusion of a solution of **L**^{1} in MeOH into a H$_2$O solution of Co(NCS)$_2$.[7] Formulation of $[Co(\mathbf{L}^1)_2(NCS)_2]_\infty$ was confirmed

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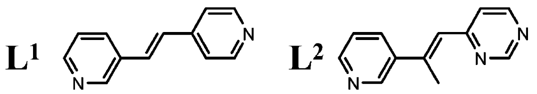
Chart 1. Line Drawing of L^1 and L^2



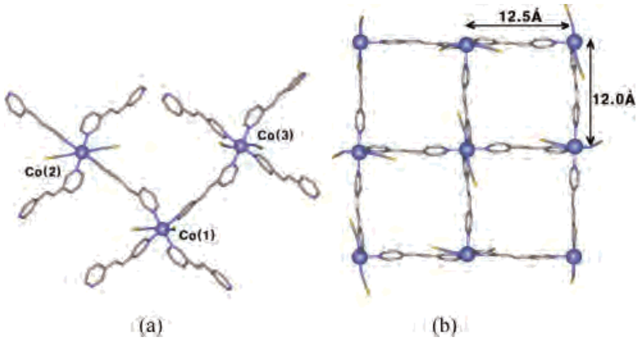


Figure 1. (a) Coordination environment around each Co center of **1**. (b) A 2-D grid layer of **1** with 12.5 × 12.0 Å^2 dimension.

by elemental analysis and use of the single-crystal X-ray diffraction method.[8] An X-ray diffraction study revealed the formation of interpenetrated two-dimensional grid layers. The asymmetry unit consists of four L^1 ligands and three Co(II) centers, two of which are imposed on the crystallographic inversion centers. Each cobalt center is in a compressed octahedral environment surrounded by two 3-pyridines and two 4-pyridines occupying equatorial sites and two SCN ligands occupying axial sites (Figure 1).

There are no significant differences between the three crystallographic independent cobalt centers. L^1 molecules link cobalt nodes in a "head to head" arrangement manner, such that two 3-pyridines and two 4-pyridines coordinate to a cobalt center in a *trans* configuration. Thus, in this manner, a two-dimensional sheet containing puckered square grids with about 12.5 × 12.0 Å^2 dimension is formed (Figure 1). Two sets of parallel layers give perpendicular interpenetration, and consequently, its voids are effectively filled. A closely packed architecture results (Figure 2).

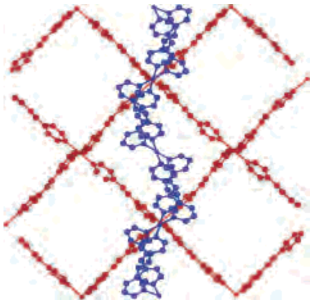


Figure 2. View of interpenetration of two sheets found in **1**.

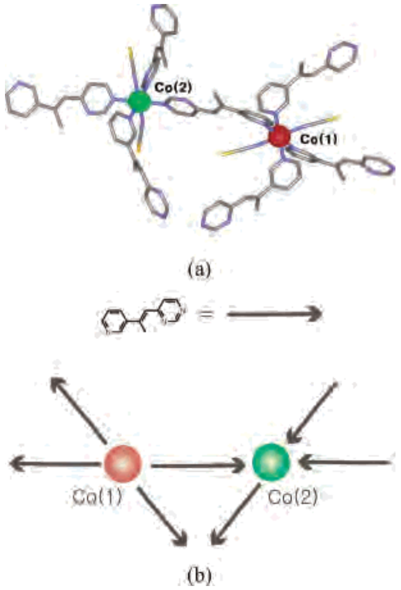


Figure 3. (a) Coordination environment around each Co center of **2**. (b) A schematic representation of the ligands coordinated to Co(1) (red) and Co(2) (green).

Self-assembly between 1-(3-pyridyl)-2-(4-pyrimidyl)-ethene and Co(NCS)$_2$ was attempted under the same reaction conditions as those applied to **1**. It was expected that if only one out of two pyrimidyl N atoms participated in coordination to generate a grid coordination-polymer network, the resulting cavities would be functionalized by the uncoordinated one. Unfortunately, X-ray diffraction analysis of this assembly could not be carried out because of its poor crystallinity. Instead, when a CH_3NO_2 solution containing L^2 was layered onto a MeOH solution of Co(NCS)$_2$ and stood for several days, crystals of **2** suitable for X-ray analysis were isolated.[7] Crystallographic analysis confirmed the formation of an unprecedented open framework architecture.[8] Each asymmetry unit of **2** consists of three molecules of L^2 and two distinct cobalt centers of Co(1) and Co(2). While both Co(1) and Co(2) adopt a compressed octahedral geometry, the arrangements of L^2 ligands around each center differ from each other (Figure 3).

In the equatorial plane, Co(1) is coordinated by four 3-pyridines and Co(2) by three 4-pyrimidines and one 3-pyridine. Co(1) resides on a crystallographic inversion center; therefore, there exists twice as many Co(2) as Co(1). Of the two pyrimidyl N atoms of L^2, only 4-N participates in the

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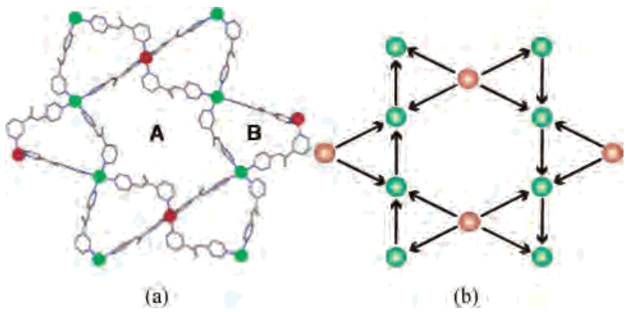
(7) Preparation of **1**: 0.020 g (0.11 mmol) of L^1 in 5 mL of MeOH was layered onto a solution of 0.010 g (0.057 mmol) of Co(NCS)$_2$ in 5 mL of H_2O. The resulting solution was stood for several days to give 0.023 g (0.046 mmol) of **1** (75%). IR (KBr): ν_{CN} 2059.6 (s) cm^{-1}. Anal. Calcd for **1**: C, 57.88; H, 3.74; N, 15.58; S, 11.99. Found: C, 57.68; H, 3.68; N, 15.23; S, 11.65. Preparation of **2**: 0.009 g (0.05 mmol) of Co(NCS)$_2$ in 5 mL of MeOH was layered onto a solution of 0.020 g (0.10 mmol) of L^2 in 5 mL of nitromethane. The resulting solution stood for several days to give 0.026 g (0.045 mmol) of **2** (90%). IR (KBr): ν_{CN} 2060.8 (s) cm^{-1}. Anal. Calcd for **2**·0.5-(CH_3OH): C, 54.35; H, 4.13; N, 19.14; S, 10.95. Found: C, 54.05; H, 4.00; N, 19.41; S, 11.06.

(8) Single-crystal X-ray data of **1** were collected on a SMART CCD diffractometer at 173 K, and those of **2** were collected on an Enraf-Nonius CCD diffractometer at room temperature using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXL-97) and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were treated as idealized contributions. Crystal data for **1**: $C_{52}H_{40}Co_2N_{12}S_4$ (173 K). M = 1079.06, monoclinic, space group $P2_1/n$, a = 10.7798(10) Å, b = 14.1407(13) Å, c = 34.336(3) Å, β = 90.014(2)°, V = 5288.97-(14) Å^3, Z = 4, ρ_{calcd} = 1.369 g/cm^3, absorption coefficient = 0.841 mm^{-1}, total reflections collected 31135, unique 12356 (R_{int} = 0.0364), GOF = 0.994, R_1 = 0.0421, R_w = 0.0925 ($I > 2\sigma(I)$). Crystal data for **2**: $C_{39}H_{33}Co_{1.50}N_{12}S_3\cdot(CH_3NO_2)\cdot5(CH_3OH)$ (293 K). M = 1075.60, monoclinic, space group $P2_1/n$, a = 11.4146(2) Å, b = 22.1549(3) Å, c = 26.9979(5) Å, β = 100.8008(7)°, V = 6706.53(19) Å^3, Z = 4, ρ_{calcd} = 1.065 g/cm^3, absorption coefficient = 0.516 mm^{-1}, total reflections collected 21999, unique 14431 (R_{int} = 0.0331), GOF = 0.983, R_1 = 0.0834, R_w = 0.2628 ($I > 2\sigma(I)$).



(a) (b)

Figure 4. (a) Two-dimensional open framework network in **2**. Each kind of Co center is represented by red (Co(1)) and green (Co(2)) color. SCN ligands are omitted for clarity. (b) A schematic representation of two-dimensional network of **2**. Ligands are expressed by arrows.

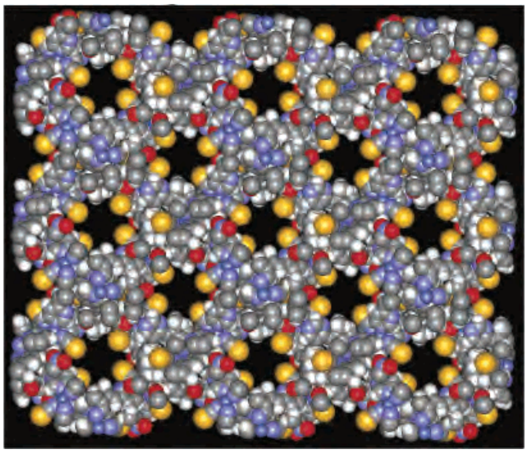


Figure 5. Packing of grid layers showing the formation of one-dimensional channels in **2**.

coordination and 2-N remains uncoordinated. Each $\mathbf{L^2}$ ligand coordinates to two cobalt centers and bridges them to lead into two kinds of cavities **A** and **B** (Figure 4). The cavity **A** is a little corrugated hexagonal shape, such that two Co(1) and four Co(2) are occupying each of the corners and six $\mathbf{L^2}$ are bridging them. Its cavity size is unusually large such that the metal−metal distances through the diagonal are 24.7, 22.2, and 21.0 Å, and the shortest diagonal distance of the cavity is 10.0 Å. Cavity **B** consists of one Co(1), two Co(2), and three $\mathbf{L^2}$ species to afford a triangular structure with a base of 11.6 Å and a height of 10.6 Å. The edges of the cavities of **A** and **B** are shared with each other, and in this way, two-dimensional layers with an open framework structure are extended (Figure 5).

Despite its huge cavity size, the layers are noninterpenetrated and piled up against each other through the aromatic $\pi-\pi$ interaction (Figure S2).[9] In such a way, cavities of **A** are stacked along the crystallographic *a* axis to form 1-D channels with an effective size of 7.7×7.2 Å^2 (Figure 5). The 1-D channels are occupied by solvent molecules. It is noteworthy that some uncoordinated 2-N atoms are situated at the channel wall and may functionalize the channel. The uncoordinated 2-N atoms are anticipated to act as a potential hydrogen acceptor or coordination site for guest inclusion. This is a rare example which is relevant to the rational modification of channel cavities in coordination polymers.[5c,10] Crystals of **2** rapidly lose solvent molecules and turn opaque within minutes under ambient atmosphere.[11]

In conclusion, we have demonstrated the ability of simple unsymmetrical ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ to assemble with square planar $Co(NCS)_2$ nodes and form novel coordination polymers **1** and **2** which have not been obtained using symmetrically bridging ligands. Their novelty originates from the angular bite angle and the unique arrangement manner of unsymmetrical ligands. Furthermore, the structure of **2** has also demonstrated a rational synthetic approach for the functionalization of cavities by modifying bridging ligands. Further research will be directed toward exploiting the potential of **2** for guiding the inclusion behaviors of guest molecules via potential hydrogen bonding with uncoordinated nitrogen atoms.

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Supporting Information Available: Synthesis of $\mathbf{L^2}$, additional figure (S2), and details from TGA, DSC, and powder XRD. X-ray crystallographic information files (CIF) for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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