

Self-Assemblies of New Rigid Angular Ligands and Metal Centers toward the Rational Construction and Modification of Novel Coordination Polymer Networks

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Self-assemblies of rigid angular ligands with 120° molecular angle and metal centers have been investigated with the aim of achieving the rational construction and modification of coordination polymer structures. The reactions of $\text{Co}(\text{NCS})_2$ with 1,3-bis(*trans*-4-styrylpyridyl)benzene (L^1), 2,6-bis(*trans*-4-styrylpyridyl)pyridine (L^2), 1,3-bis(*trans*-4-styrylpyrimidyl)benzene (L^3), and 1,3-bis(*trans*-4-styrylquinoly)benzene (L^4) afford complexes $[\text{Co}(\text{L}^1)_2(\text{NCS})_2]_\infty$ (**1**), $[\text{Co}(\text{L}^2)_2(\text{NCS})_2]_\infty$ (**2**), $\text{Co}(\text{L}^3)_2(\text{NCS})_2(\text{CH}_3\text{OH})_2$ (**3**), and $[\text{Co}(\text{L}^4)(\text{NCS})_2]_\infty$ (**4**), respectively. The resulting complexes exhibit open framework, stairlike hydrogen-bonded chain and single-stranded helical coil structures, which are controlled by the variation of the geometry around the coordination site in ligands. Moreover, the coordination of L^1 and L^2 to $\text{Mn}(\text{hfac})_2$ ($\text{hfac} = 1,1,1,5,5,5$ -hexafluoroacetylacetonate) yields single-stranded helical coordination polymers of $[\text{Mn}(\text{L}^1)(\text{hfac})_2]_\infty$ (**5**) and $[\text{Mn}(\text{L}^2)(\text{hfac})_2]_\infty$ (**6**), respectively.

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, which include magnetism,¹ catalysis and separation,² nonlinear optics,³ and molecular sensing.⁴ Judicious combination of a metal “node” and a ligand “spacer” has been the most

common synthetic approach for producing predictable network architectures. During the last few decades, a number of structures have been successfully designed and synthesized by the selection of the metal’s coordination preference and ligand geometry.

Topologies of coordination polymers are influenced by several factors such as the structure of ligands, coordination preference of metal ions, coordination behavior of counterions, and the solvent system.⁵ The chemical structure of organic ligands including the molecular angle, length, and relative orientation of the donor groups plays an extremely important role in dictating polymer topology. So far, much research effort has been concentrated on the exploitation of rodlike ligands such as pyrazine and 4,4'-dipyridine in the construction of versatile coordination polymer architectures including one-dimensional chains and ladders, two-dimensional grids, and three-dimensional diamondoid and helical staircase networks.⁶ However, there has been comparatively

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little effort directed toward angular ligands with a molecular angle other than 180°. The use of angular ligands should allow the discovery of coordination networks with unprecedented structures and unique properties.

In this respect, our research has been focused on designing new angular ligands and investigating the rational control of their self-assembly with metal centers. All four ligands, namely 1,3-bis(*trans*-4-styrylpyridyl)benzene (**L**¹), 2,6-bis(*trans*-4-styrylpyridyl)pyridine (**L**²), 1,3-bis(*trans*-4-styrylpyrimidyl)benzene (**L**³), and 1,3-bis(*trans*-4-styrylquinoly)benzene (**L**⁴), chosen in this study contain two N-donor sites and rigid spacer units connecting them with a roughly 120° angle. We herein report their assembly with Co(NCS)₂ and the resultant structures of [Co(**L**¹)₂(NCS)₂]_∞ (**1**), [Co(**L**²)₂(NCS)₂]_∞ (**2**), Co(**L**³)₂(NCS)₂(CH₃OH)₂ (**3**), and [Co(**L**⁴)(NCS)₂]_∞ (**4**), which serve to illustrate the formation of open framework structure containing huge channels, the intended modification and functionalization of the coordination polymer, and control over the coordination preference and the consequent generation of helical structure through the rational synthetic strategy with simple variation of ligand structures. We also wish to report the rational construction and functionalization of helical coordination polymers of [Mn(**L**¹)(hfac)₂]_∞ (**5**) and [Mn(**L**²)(hfac)₂]_∞ (**6**) by combining **L**¹ and **L**² with a right-angled node of Mn(hfac)₂ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate), respectively. The structure of **1** has been previously communicated by us.⁸

Experimental Section

General Considerations. All reactions for the synthesis of ligands were carried out under nitrogen using standard Schlenk techniques. Distilled, dry, and oxygen-free solvents were used throughout. Routine ¹H NMR spectra and ¹³C NMR were recorded with a Bruker 300 spectrometer. Elemental analyses were performed at National Center for Inter-University Research Facilities, Seoul National University. High-resolution mass spectra were carried out at the Korea Basic Science Institute (Daegu, Korea). Temperature-dependent magnetic measurements were recorded on a Quantum Design MPMS5 SQUID magnetometer at a field of strength 10 kG. 1,3-Bis(*trans*-4-styrylpyridyl)benzene (**L**¹) was previously reported and prepared according to the modified procedure.⁹

Preparation of 2,6-Bis(*trans*-4-styrylpyridyl)pyridine (L**²).** 2,6-Dibromopyridine (0.50 g, 2.1 mmol) and 4-vinylpyridine (0.49 g, 4.7 mmol) were dissolved in 3 mL of TEA, and Pd(OAc)₂ (17 mg, 0.076 mmol) and PPh₃ (40 mg, 0.15 mmol) were added. The resulting solution was refluxed for 3 days and then cooled to room temperature. The residue was extracted with 200 mL of dichloromethane and saturated ammonium chloride solution followed by chromatography on a silica gel column eluting with Et₂O/MeOH (v/v, 10:1) to give 0.25 g (0.88 mmol) of **L**² (47%). ¹H NMR (CDCl₃): δ 8.62 (d, *J* = 4.9 Hz, 4 H), 7.71 (t, *J* = 7.8 Hz, 2 H), 7.66 (d, *J* = 15.9 Hz, 2 H), 7.45 (d, *J* = 5.1 Hz, 4 H), 7.36 (d, *J* = 16.0 Hz, 2 H), 7.30 (d, *J* = 7.7 Hz, 2 H). ¹³C NMR (CDCl₃): δ 154.59, 150.46, 144.08, 137.52, 132.39, 130.67, 122.25, 121.50. IR (KBr pellet): 3379 (m, br), 3024 (m), 1587 (s), 1496 (w), 1444 (m), 1410 (m), 1277 (w), 1227 (w), 1155 (w), 1090 (w), 978 (s), 862 (w), 814 (s), 735 (m), 534 (m) cm⁻¹. HRMS: M⁺ calcd 285.1266, obsd 285.1265.

Preparation of 1,3-Bis(*trans*-4-styrylpyrimidyl)benzene (L**³).** To a solution of LDA (generated in situ by the reaction of diisopropylamine (3.4 mL, 25 mmol) in 50 mL of THF with *n*-BuLi (12 mL, 30 mmol) at -78 °C) was added 4-methylpyrimidine (2.4 mL, 25 mmol) at -78 °C. While the solution was stirred at room temperature for 30 min, the solution turned to yellowish. To the yellowish solution was added isophthalic dicarboxaldehyde (1.60 g, 12 mmol) at room temperature. The resulting solution was stirred for 4 h and quenched by addition of water (30 mL) and dichloromethane (200 mL). The dichloromethane layer was collected, evaporated to dryness, and dissolved in 20 mL of pyridine. The pyridine solution was cooled to 0 °C. Excess POCl₃ (5 mL) was added dropwise to the pyridine solution. The resulting solution was stirred at room temperature for 3 h and quenched by addition of ice. After evaporation of pyridine, the residue was dissolved in water (200 mL) and basified by addition of aqueous 4 M NaOH. Extraction with dichloromethane (200 mL) followed by chromatography on a silica gel column eluting with Et₂O/MeOH (v/v, 10:1) gave 1.10 g of **L**³ (31%). ¹H NMR (CDCl₃): δ 9.19 (d, *J* = 1.2 Hz, 2 H), 8.70 (d, *J* = 5.2 Hz, 2 H), 7.93 (d, *J* = 16.0 Hz, 2 H), 7.82 (s 1 H), 7.60 (dd, *J* = 7.6, 1.6 Hz, 2 H), 7.46 (t, *J* = 7.1 Hz, 1 H), 7.34 (dd, 5.2, 1.4 Hz, 2 H), 7.13 (d *J* = 16.0 Hz, 2 H). ¹³C NMR (CDCl₃): δ 162.28, 159.28, 157.91, 137.14, 136.59, 129.86, 128.92, 127.22, 126.66, 119.24. IR (KBr pellet): 3037 (w), 1633 (m), 1570 (s), 1456 (s), 1381 (s), 1165 (m), 980 (s), 872 (m), 831 (w), 796 (m), 683 (s), 536 (s) cm⁻¹. HRMS: M⁺ calcd 287.1218, obsd 287.1215.

Preparation of 1,3-Bis(*trans*-4-styrylquinoly)benzene (L**⁴).** The same procedure as the synthesis of **L**³ was applied except for lepidine (3.5 mL, 24 mmol) instead of 4-methylpyrimidine. Yield: 0.50 g (1.3 mmol, 11%). ¹H NMR (CDCl₃): δ 8.93 (d, *J* = 4.6 Hz, 2 H), 8.26 (dd, *J* = 8.6, 1.0 Hz, 2 H), 8.15 (dd, *J* = 8.3, 0.8 Hz, 2 H) 7.90 (d, *J* = 16.1 Hz, 2 H), 7.76 (ddd, *J* = 6.8, 6.8, 1.3 Hz, 2 H), 7.64 (d, *J* = 4.5 Hz, 2 H), 7.66–7.54 (m 4 H), 7.51 (dd, *J* = 8.3, 7.0 Hz, 2 H), 7.40 (d *J* = 16.1 Hz, 2 H). ¹³C NMR (CDCl₃): δ 150.64, 149.11, 143.11, 137.63, 135.02, 129.87, 129.83, 127.67, 127.04, 126.78, 126.47 124.06, 123.87, 117.57. IR (KBr pellet): 3400 (m, br), 3035 (m), 2949 (w), 1624 (w), 1570 (s), 1500 (m), 1469 (w), 1425 (w), 1383 (m), 1294 (m), 1246 (w), 966 (s), 864 (m), 825 (m), 758 (s), 687 (w), 557 (m) cm⁻¹. HRMS: M⁺ calcd 384.1626, obsd 384.1627.

Synthesis of [Co(L**¹)₂(NCS)₂]_∞ (**1**).** Co(NCS)₂ (50 mg, 0.29

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Table 1. Crystal Data and Structure Refinement for 1–3

	1	2	3	4	5	6
empirical formula	C ₆₃ H ₄₈ Co _{1.50} N ₉ S ₃	C ₆₀ H ₄₅ Co _{1.50} N ₁₂ S ₃	C ₄₀ H ₃₆ CoN ₁₀ O ₂ S ₂	C ₃₃ H ₂₉ CoN ₇ O ₆ S ₂	C ₃₀ H ₁₈ F ₁₂ MnN ₂ O ₄	C ₂₉ H ₁₇ F ₁₂ MnN ₃ O ₄
fw	1115.68	1118.66	811.84	742.68	753.40	754.40
cryst system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>C2/m</i>	<i>C2/m</i>	<i>P1</i>	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> , Å	19.8676(10)	20.702(3)	9.9613(3)	9.54000(10)	11.3643(7)	11.3690(10)
<i>b</i> , Å	32.6591(13)	31.164(4)	10.5477(3)	23.5649(5)	20.6764(7)	20.6240(10)
<i>c</i> , Å	15.0359(7)	15.5365(14)	11.0869(4)	16.6758(3)	14.2671(10)	14.2440(10)
α , deg	90	90	65.2000(16)	90	90	90
β , deg	119.879(3)	125.538(6)	71.9521(15)	104.4352(12)	90.962(3)	90.928(3)
γ , deg	90	90	74.359(2)	90	90	90
<i>V</i> , Å ³	8459.4(7)	8156.3(17)	992.18(5)	3630.52(11)	3351.9(3)	3339.4(4)
<i>Z</i>	4	4	1	4	4	4
<i>d</i> (calcd), Mg/m ³	0.876	0.911	1.359	1.359	1.493	1.501
θ range, deg	2.09–27.48	2.07–25.12	2.18–27.48	2.80–26.62	2.66–27.47	3.93–25.00
tot. no. data	15 999	11 889	6507	20 105	5733	18 146
no. unique data	9423	7229	6507	7432	4669	5838
no. params refined	362	348	506	419	442	442
R1	0.0948	0.1303	0.0373	0.0750	0.0792	0.0768
wR2	0.2240	0.3456	0.0879	0.2217	0.2175	0.1704
gof	1.056	1.184	1.086	0.943	1.037	1.012

mmol) in 5 mL of MeOH was layered onto a solution of **L**¹ (160 mg, 0.57 mmol) in 5 mL of nitromethane and stood for several days to give single crystals of **1** (150 mg, 0.20 mmol, 70%). IR (KBr pellet): 3396 (m, br), 3028 (w), ν_{CN} 2062 (vs), 1603 (s), 1495 (m), 1419 (m), 1327 (w), 1213 (m), 1007 (m), 964 (s), 862 (m), 814 (s), 681 (m), 534 (s) cm⁻¹. Anal. Calcd for C₄₂H₃₂CoN₆S₂·CH₃·OH: H, 4.68; C, 66.57; N, 10.83; S, 8.26. Found: H, 4.44; C, 66.20; N, 10.96; S, 8.08.

Synthesis of [Co(L²)₂(NCS)₂]_∞ (2). Co(NCS)₂ (8 mg, 0.046 mmol) in 4 mL of MeOH was layered onto a solution of **L**² (25 mg, 0.088 mmol) in 4 mL of nitromethane and stood for several days to give of single crystals of **2** (26 mg, 0.035 mmol, 80%). IR (KBr pellet): 3398 (m, br), 3041 (w), ν_{CN} 2063 (vs), 1603 (s), 1568 (m), 1496 (w), 1444 (m), 1419 (m), 1217 (m), 1157 (w), 1003 (m), 970 (m), 866 (w), 822 (s), 731 (w), 540 (m) cm⁻¹. Anal. Calcd for C₄₀H₃₀CoN₈S₂·H₂O: H, 4.38; C, 61.45; N, 14.33; S, 8.20. Found: H, 4.09; C, 61.64; N, 14.41; S, 8.24.

Synthesis of Co(L³)₂(NCS)₂(CH₃OH)₂ (3). **L**³ (20 mg, 0.07 mmol) in 4 mL of MeOH solution was layered onto an aqueous solution of Co(NCS)₂ (7 mg, 0.04 mmol) in 4 mL of water and stood for several days to give single crystals of **3** (25 mg, 0.031 mmol, 89%). IR (KBr pellet): 3039 (s, br), 2802 (w), ν_{CN} 2065 (vs), 1635 (m), 1583 (s), 1533 (m), 1469 (m), 1385 (m), 1302 (m), 1174 (m), 1007 (s), 974 (s), 874 (m), 831 (m), 795 (m), 681 (m), 544 (m) cm⁻¹. Anal. Calcd for C₄₀H₃₆CoN₁₀S₂O₂: H, 4.47; C, 59.18; N, 17.25; S, 7.90. Found: H, 4.49; C, 58.61; N, 17.32; S, 7.70.

Synthesis and Structure of [Co(L⁴)₂(NCS)₂]_∞ (4). Co(NCS)₂ (9 mg, 0.05 mmol) in 5 mL of MeOH was layered onto a solution of **L**⁴ (20 mg, 0.005 mmol) in 4 mL of nitromethane and stood for several days to give **4** (23 mg, 82%). IR (KBr pellet): 3438 (w, br), 3053 (w), ν_{CN} 2060 (vs), 1622 (w), 1577 (s), 1508 (m), 1387 (m), 1294 (m), 960 (m), 906 (m), 758 (m), 648 (w), 574 (w) cm⁻¹. Anal. Calcd for C₃₀H₂₀CoN₄S₂·CH₃NO₂: H, 3.74 C, 60.00 N, 11.28 S, 10.33. Found: C, 60.29; H, 4.01; N, 11.16; S, 10.01.

Synthesis of [Mn(L⁴)(hfac)₂]_∞ (5). Mn(hfac)₂ (33 mg, 0.07 mmol) in 4 mL of acetonitrile solution was layered onto a solution of **L**⁴ (20 mg, 0.07 mmol) in 4 mL of MeOH, and the mixed solvent was evaporated in several days to give **5** (42 mg, 79% yield). IR (KBr pellet): 3435 (m, br), 3059 (w), 1649 (s), 1612 (m), 1556 (m), 1529 (m), 1495 (s), 1429 (w), 1257 (s), 1200 (s), 1146 (s), 1093 (m), 1016 (w), 823 (w), 796 (m), 663 (s), 582 (m), 528 (w) cm⁻¹. Anal. Calcd for C₃₀H₁₈F₁₂MnN₂O₄: H, 2.41; C, 47.83; N, 3.72. Found: C, 47.78; H, 2.33; N, 4.09.

Synthesis of [Mn(L²)(hfac)₂]_∞ (6). A 33 mg (0.07 mmol) amount of Mn(hfac)₂ in 4 mL of acetonitrile solution was layered onto the solution of 20 mg (0.07 mmol) of **L**² in 4 mL of MeOH, and the mixed solvents were evaporated in several days to give 25 mg of **6** (47% yield). IR (KBr pellet): 3398 (w, br), 3043 (w), 1647 (s), 1610 (s), 1556 (m), 1529 (m), 1429 (m), 1344 (w), 1255 (s), 1196 (s), 1142 (s), 1095 (m), 958 (m), 866 (m), 816 (m), 796 (m), 685 (m), 663 (s), 582 (m), 528 (m) cm⁻¹. Anal. Calcd for C₂₉H₁₇F₁₂MnN₃O₄: H, 2.27; C, 46.17; N, 5.57. Found: C, 46.82; H, 2.44; N, 4.93.

Crystal Structure Determination of 1–6. All diffraction data for structure determination were measured by an Enraf-Nonius CCD single-crystal X-ray diffractometer at room temperature using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Preliminary orientation matrixes and unit cell parameters were obtained from the peaks of the first 10 frames and then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO.¹⁰ The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares fitting with SHELXL-97.¹¹ All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms not involving hydrogen bonding were treated as idealized contributions. Crystal data and refinement results are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

Results and Discussion

Synthesis of Ligands. The synthesis of ligands has been carried out through the modification of a previously reported procedure as in Scheme 1.⁹ Treatment of 1,3-benzenedicarbaldehyde with the lithium carbanion of 4-picoline, 4-methylpyrimidine, and 4-lepidine followed by protonation and dehydration gave bis-monodentate ligands of **L**¹, **L**², and **L**⁴, respectively. **L**³ was afforded by the Heck-type coupling reaction between 2,6-dibromopyridine and 4-vinylpyridine as in Scheme 2.

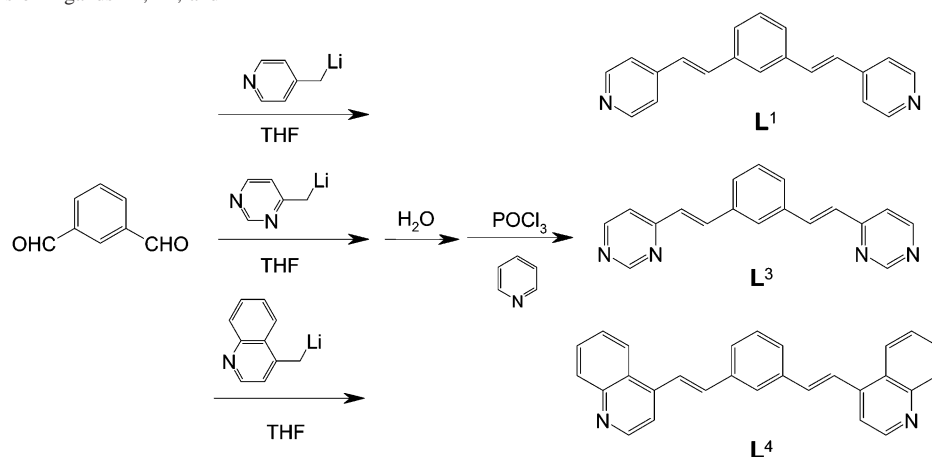
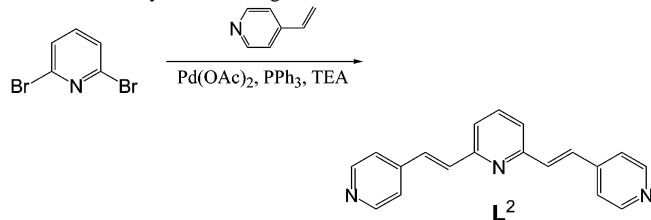
All the ligands have common structural features in that they contain two heterocyclic rings as coordination sites and

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Table 2. Selected Intra- and Intermolecular Bond Lengths (Å) and Angles (deg) for **1–6**

1					
Co(1)–N(1)	2.201(4)	Co(1)–N(3)	2.107(8)	Co(2)–N(2)	2.236(4)
Co(2)–N(4)	2.078(4)	Co(2)–N(5)	2.203(4)		
N(3)–Co(1)–N(1)	91.35(19)			N(4)–Co(2)–N(5)	91.06(14)
N(4)–Co(2)–N(2)	90.36(15)				
2					
Co(1)–N(1)	2.234(8)	Co(1)–N(2)	2.218(6)	Co(1)–N(3)	2.059(7)
Co(2)–N(5)	2.223(11)	Co(2)–N(6)	2.1696(3)		
N(3)–Co(1)–N(2)	89.5(3)			N(3)–Co(1)–N(1)	90.5(3)
N(2)–Co(1)–N(1)	86.7(3)			N(6)–Co(2)–N(5)	89.6(3)
3					
Co(1)–N(3)	2.102(8)	Co(1)–N(4)	2.104(7)	Co(1)–O(1)	2.127(6)
Co(1)–O(2)	2.129(6)	Co(1)–N(2)	2.228(6)	Co(1)–N(1)	2.268(6)
O(2)–NC10 ^a	2.83	O(1)–NC8	2.84		
N(3)–Co(1)–O(1)	89.8(3)			N(4)–Co(1)–O(2)	89.7(3)
N(3)–Co(1)–N(2)	86.2(2)			N(4)–Co(1)–N(2)	93.5(2)
4					
Co–N(3)	1.943(5)	Co–N(4)	1.957(6)	Co–N(1)	2.038(4)
Co–N(2)	2.037(4)				
N(3)–Co–N(4)	106.5(2)			N(3)–Co–N(1)	113.33(18)
N(4)–Co–N(1)	113.7(2)			N(3)–Co–N(2)	113.66(18)
N(4)–Co–N(2)	104.4(2)			N(1)–Co–N(2)	105.12(16)
5					
Mn(1)–O(2)	2.150(5)	Mn(1)–O(3)	2.185(5)	Mn(1)–O(4)	2.208(5)
Mn(1)–N(2)	2.222(5)	Mn(1)–O(1)	2.226(4)	Mn(1)–N(1)	2.227(5)
O(2)–Mn(1)–O(4)	91.9(2)			O(3)–Mn(1)–O(4)	79.31(19)
O(2)–Mn(1)–N(2)	85.52(19)			O(4)–Mn(1)–N(1)	162.9(2)
N(2)–Mn(1)–N(1)	89.0(2)			O(2)–Mn(1)–N(1)	102.9(2)
6					
Mn(1)–O(4)	2.149(5)	Mn(1)–O(2)	2.205(4)	Mn(1)–N(2)	2.234(5)
Mn(1)–O(1)	2.186(5)	Mn(1)–N(1)	2.229(5)	Mn(1)–O(3)	2.234(4)
O(4)–Mn(1)–O(3)	79.42(17)			O(4)–Mn(1)–O(2)	91.71(18)
O(4)–Mn(1)–N(1)	85.36(19)			O(1)–Mn(1)–N(1)	94.26(18)
N(1)–Mn(1)–N(2)	89.09(17)			O(4)–Mn(1)–N(2)	103.0(2)

^a $x + 1, y - 1, z + 1$.**Scheme 1.** Synthesis of Ligands **L¹**, **L³**, and **L⁴****Scheme 2.** Synthesis of Ligand **L²**

a rigid interconnecting spacer such as 1,3-diethynylbenzene and 1,3-diethynylpyridine. Thus, the two 4-N donors located on both sides in a molecular structure are about 12.5 Å apart and the angles between their lone pairs are rigidly fixed at

120°. The difference between **L¹** and **L²** lies in the bridging section linking two 4-pyridine rings, such that **L²** has a 2-pyridine moiety instead of benzene. **L³** contains 4-pyrimidines as coordinating groups instead of 4-pyridines in **L¹**. Therefore, **L²** and **L³** carry additional N donors potentially acting as hydrogen-bonding acceptors or coordination sites. **L⁴** has 4-quinoline groups instead of 4-pyridines, such that it bears sterically bulky aromatic rings near its coordination sites.

Synthesis and Structure of [Co(L¹)₂(NCS)₂]_∞ (1**).** In many previous examples, Co(NCS)₂ was found to act as a square planar node with a 90° coordination angle to generate

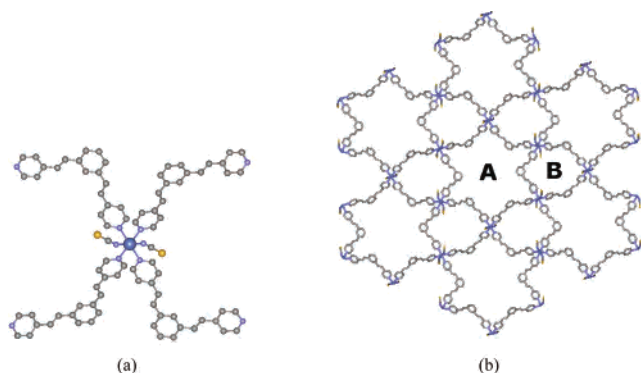


Figure 1. (a) Octahedral coordination geometry around a cobalt center in **1**. (b) Two-dimensional grid structure of **1** containing to kinds of cavities, A and B.

layered coordination-polymer networks.¹² It has recently been reported that a metallacalix [4, 6] arene-like structural motif resulted from the reaction of a pyrimidine spacer with an angle of 120° and a metal node with an angle of 90°.¹³ Thus, the reaction of **L**¹ with Co(NCS)₂ was anticipated to afford a layered coordination polymer network bearing metallacyclic structures analogous to calixarenes.

When a solution of Co(NCS)₂ in MeOH was layered onto a solution of **L**¹ in CH₃NO₂ and stood for several days, crystals of **1** were grown at the interface of the two solutions. The X-ray structural analysis reveals the formation of a 2-dimensional open framework structure with the formulation of [Co(**L**¹)₂(NCS)₂]_∞.

Two crystallographically independent Co(II) centers exist in the crystal, and there are no significant differences between coordination environments around them. Each cobalt center is in a compressed octahedral environment surrounded by four pyridines occupying equatorial sites and two SCN ligands occupying axial sites (Figure 1a). Each cobalt center is linked by four **L**¹ ligands and plays the role of a square planar node in a network. The ligand of **L**¹ adopts a nearly planar molecular structure and symmetrically bridges two cobalt centers with intermetal distances of 17.04 and 16.33 Å, respectively. Thus, in this manner, two different types of nanosized cavities (A and B) are formed. The cavity A exhibits a puckered David's star shape. It is isostructural with the anticipated metallacalix [6] arene motif, such that six cobalt centers occupy each corner of a hexagon and six **L**¹ ligands bridge them with a 1,3,5-alternative arrangement. Its cavity size is so huge that the metal–metal distances through the diagonal are 32.67 and 34.09 Å and the shortest diagonal distance of the cavity is 21.90 Å. The cavity of B consists of three cobalt nodes and three molecules of **L**¹ bridging them and has a bowl-like structure. The distances between the cobalt center and the nearest carbon of the phenyl rings

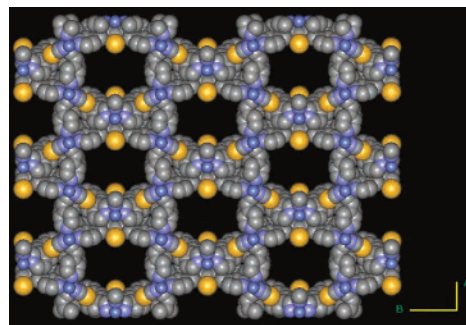


Figure 2. One-dimensional channel structures found in **1**.

at opposite sides are 17.32 and 19.02 Å, respectively. Cavities A and B share their edges with each other, and in this way, a grid layer structure is extended (Figure 1b). When relatively large cavities are generated in a network, interpenetration of independent networks usually occurs to mitigate against the stable open framework structure.¹⁴ Surprisingly, despite the existence of huge cavities, the 2D layers of **1** are noninterpenetrated and stacked with each other to form 1D channels with repeating units consisting of one A cavity and two B cavities (Figure 2). The effective dimension of the channel is 11.4 × 7.3 Å, and most of the channel region is occupied by disordered solvent molecules. Owing to its highly porous nature, the stability of the crystal **1** is insufficient to prevent it from losing its crystallinity and it turns opaque upon removal of solvate molecules. Therefore, further characterization of its physical properties could not be conducted.

Synthesis and Structure of [Co(L**²)₂(NCS)₂]_∞ (**2**).** Encouraged by the above study, we sought to establish functional channels with a potential chemical affinity relevant to the specific selective incorporation of guest molecules. To create channel walls modified by hydrogen-bonding accepting groups, we prepared the ligand **L**² by introduction of a pyridine moiety instead of benzene to **L**¹ and attempted a complexation with Co(NCS)₂. The 2-N atom in **L**² is regarded to be sterically unfavorable to coordinate to a cobalt center compared to 4-N atoms.¹⁵ Therefore, it was expected that only 4-N donors located at both edges of the molecular skeleton could participate in coordination to generate a framework structure like **1** and then the resulting channels would be functionalized by the uncoordinated 2-N atoms.

With this in mind, a reaction of **L**² with Co(NCS)₂ was carried out under the same conditions as applied to **1**. Orange crystals of **2**, [Co(**L**²)₂(NCS)₂]_∞, were isolated from the interface between a solution of **L**¹ in CH₃NO₂ and a MeOH solution of Co(NCS)₂. When they are taken out of the mother liquor, they immediately lose their crystallinity in the same way as **1**. An X-ray structural analysis reveals that, corresponding to our initial expectation, only 4-N atoms of **L**² take part in the coordination bonds and its 2-N atom remains

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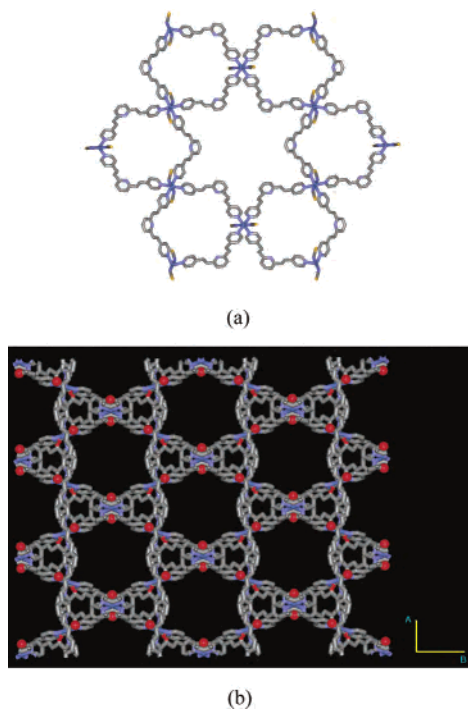


Figure 3. (a) Two-dimensional grid structure of **2**. (b) One-dimensional channel structures found in **2**. 2-N atoms on the channel wall are shown in red color. SCN ligands are omitted for clarity.

uncoordinated. The uncoordinated 2-N atom does not exert any significant influence on the construction of coordination polymer network structure, and thus, an open framework network with very close structural resemblance to **1** is generated. The crystal structure of **2** is almost isostructural with **1**, such that L^2 symmetrically bridges square planar cobalt nodes, resulting in a two-dimensional grid sheet including two kinds of cavities (Figure 3a). The only structural difference between **1** and **2** is in the orientation of the double bond in L^1 and L^2 . The sheets are stacked with respect to each other such that 1D channels create an effective dimension of $10.3 \times 7.4 \text{ \AA}$ (Figure 3b). This overall situation is quite similar to that found in **1**. It is noteworthy that uncoordinated 2-N atoms of L^2 are exposed on the resulting channel wall and functionalize the channel region. The uncoordinated 2-N atoms are anticipated to act as potential hydrogen-bonding acceptors for selective guest inclusion or coordination site for a catalytic reaction. This is a rare example of the rational modification of channel regions in coordination polymers.¹⁶

Synthesis and Structure of $\text{Co}(L^2)_2(\text{NCS})_2(\text{CH}_3\text{OH})_2$ (**3**).

In an attempt to incorporate more nitrogen atoms in the channel region, L^3 ligand with pyrimidine groups instead of pyridines in L^1 was employed for the self-assembly with $\text{Co}(\text{NCS})_2$. We expected that if L^2 was assembled into a framework structure like **1**, the resulting cavities would be functionalized by 2-N atoms of two pyrimidine groups.

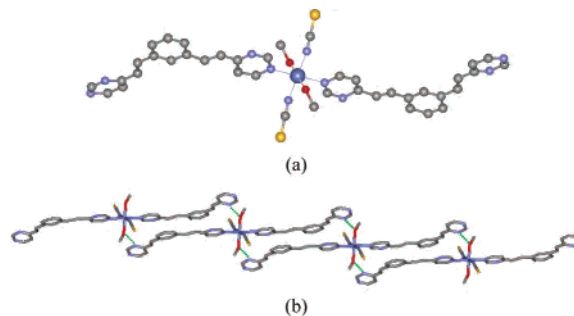


Figure 4. (a) Coordination geometry around a cobalt center in **3**. (b) Hydrogen bonding network found in **3**.

Self-assembled crystals were obtained by a slow diffusion of an MeOH solution of L^3 into an aqueous solution of $\text{Co}(\text{NCS})_2$. Unexpectedly, the X-ray structural analysis showed that the assembly did not produce a coordination polymer but a 2:1 complex $\text{Co}(L^3)_2(\text{NCS})_2(\text{CH}_3\text{OH})_2$ (**3**) being hydrogen-bonded into a one-dimensional network structure. The coordination mode around the Co(II) center is completely different from those found in **1** and **2**, such that each metal center is coordinated with two pyrimidines from L^2 , two SCN ligands, and two MeOH of solvent molecules (Figure 4a). The direct coordination of solvent molecules is frequently found in coordination structures.¹⁷ The coordination bond lengths and angles of **3** fall in the range of previously reported similar complexes.^{12d,17} Of the two pyrimidines of L^2 , one makes a coordination bond with Co(II) to afford the 2:1 coordination complex and the other acts as a hydrogen-bonding acceptor to the coordinated MeOH molecule to yield a one-dimensional hydrogen-bonded network. Adjacent complexes are connected via two pairs of hydrogen bonds as shown in Figure 4b, and consequently, a stairlike network results. The shortest distance between metal centers in the network is 15.718 \AA . In the structure of **3**, the hydrogen bonding presumably stabilizes the solvent coordination, which seems to restrict the generation of a coordination polymer like **1** by occupying available coordination sites at the metal center.

Synthesis and Structure of $[\text{Co}(L^4)(\text{NCS})_2]_\infty$ (4**).** The coordination geometry of a metal node is one of the primary factors that determine the topology of coordination polymers. In many previous examples, the variations of the metal coordination environment have led to diverse final architectures.⁵ So far, most of these variations have been contributed by the unintended coordination of counteranions and solvent molecules whereas the approach which includes the rational control of a metal coordination preference to achieve specific geometry has been hardly developed.¹⁸ It is well-known that the Co(II) center can adopt either an octahedral or a tetrahedral coordination geometry because of the small

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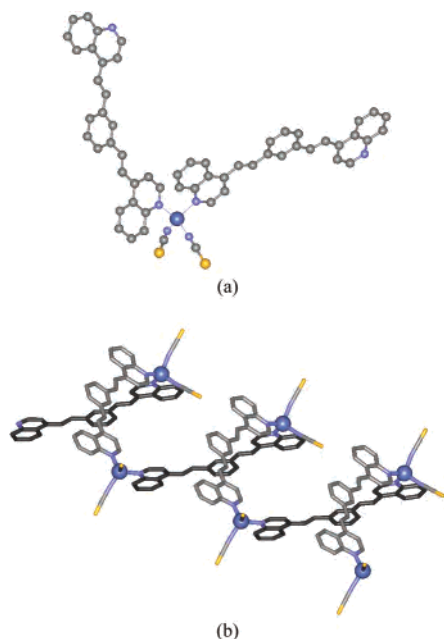


Figure 5. (a) Tetrahedral coordination geometry around a cobalt center in **4**. (b) Single-stranded helical chain structure found in **4**.

energy difference between them.¹⁹ While the octahedral Co(II) center has been widely incorporated in a coordination polymer network to afford large number of structures, the usage of tetrahedral Co(II) centers is quite rare.²⁰ We envisioned that if the ligands bearing bulky groups near the coordination site were complexed with Co(II), a tetrahedral coordination mode should be favored rather than a sterically crowded octahedral one. In this respect, an L^4 ligand with bulk aromatic rings near 4-N atoms was prepared and its self-assembly with $\text{Co}(\text{NCS})_2$ was carried out. We expected that if a tetrahedral Co(II) center was generated as anticipated, the divergent combination of L^4 with an angle of 120° and a tetrahedral Co(II) center with an angle of 105° would afford a zigzag or helical chain structure. Zigzag polymers have been widely encountered, whereas helices remain rare in the context of coordination polymers.²¹

By the slow diffusion of a solution of L^4 in CH_3NO_2 into an MeOH solution of $\text{Co}(\text{NCS})_2$, a green crystalline complex **4** was obtained. Its formulation $[\text{Co}(L^4)(\text{NCS})_2]_\infty$ was confirmed by elemental analysis and the use of the single-crystal X-ray diffraction method. The X-ray structural analysis revealed the formation of single-stranded helical chain structures. Each Co(II) center exhibits a tetrahedral coordination geometry (N1–Co–N2, 105.25°) with two quinolines from L^4 and two bound SCN ligands as anticipated (Figure 5a). The coordinated quinoline rings are

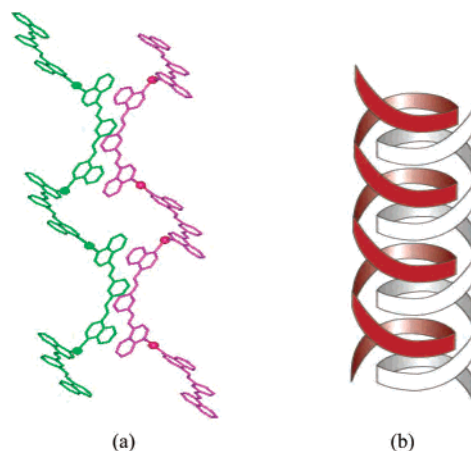


Figure 6. (a) Diagram illustrating the aromatic stacking interactions between neighboring helical coils in **4**. (b) Schematic representation.

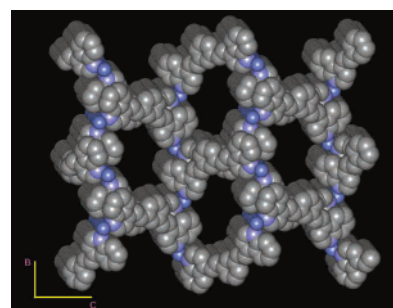


Figure 7. Channels existing within helical coils in **4**. SCN anions and included nitromethane molecules are omitted for clarity.

perpendicularly twisted relative to each other, presumably to minimize the steric hindrance between them. The ligand of L^4 adopts a nearly planar molecular structure and symmetrically bridges two cobalt centers with intermetal distances of 17.353 \AA . Thus, the combination of spacers of L^4 with an angle of 120° and nodes of Co(II) centers with an angle of 105° affords a single-stranded helicate (Figure 5b). Two crystallographic asymmetry units constitute one turn of a helix, and the cylindrical helix structure is extended along the b axis with a pitch of 23.565 \AA , i.e., the b axis length. The helical polymer crystallizes in the centrosymmetric space group of $P2_1/c$, and subsequently both R - and S -helices are present in equal numbers. All the helical chains interact with parallel helicates of opposite handedness through a π - π stacking interaction as illustrated in Figure 6, which may contribute to stabilizing the formation of the helical structure. Through such stacking, 1D channels with approximately $11.0 \times 5.8 \text{ \AA}$ effective dimension are formed along the a axis (Figure 7). These channels are occupied by SCN anions and nitromethane molecules. This structure of **4** represents a basic example of the rational construction of a novel coordination polymer through the alternation of the metal coordination preference for the specific geometry.

Synthesis and Structure of $[\text{Mn}(L^1)(\text{hfac})_2]_\infty$ (5**).** Helical structures such as that found in **4** represent a longstanding synthetic target for the supramolecular chemist due to their intrinsic aesthetic appeal and potentially exploitable properties.²² At this time, our attempts were directed toward the generation of a helical chain through the variation of the

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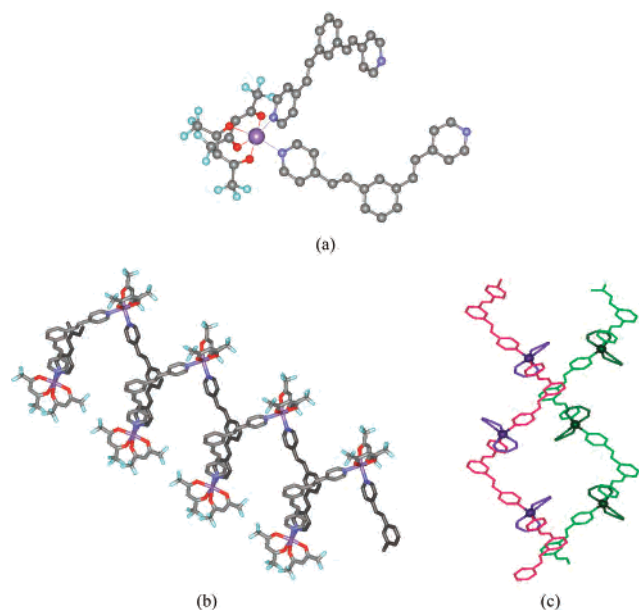


Figure 8. (a) Octahedral coordination geometry around a manganese center in **5**. (b) Single-stranded helical chain structure found in **5**. (c) Diagram for illustrating the aromatic stacking interactions between neighboring helical coils in **5**.

metal ion component while maintaining the ligand structure. It is envisioned that if it is combined with a suitable corner component having a predetermined angular coordination angle, L^1 may also afford a helical chain structure. With this expectation, $Mn(hfac)_2$ was chosen as a corner unit because $Mn(hfac)_2$ had been widely used as a building block for the construction of an extended one-dimensional coordination polymer.²³ In assemblies with dipyrindine-type ligands, two $hfac$ chelate ligands were found to occupy cis positions of the octahedral $Mn(II)$ center and, thus, $Mn(II)$ serves as a right-angled node to afford a coil structure.

In this context, assembly of L^1 with $Mn(hfac)_2$ was carried out. Single crystals of **5**, $[Mn(L^1)(hfac)_2]_\infty$, were grown on the interface between an MeOH solution of L^1 and an acetonitrile solution of $Mn(hfac)_2$. X-ray crystallography analysis shows the generation of a single-stranded helical chain structure. The coordination environment about the manganese center is illustrated in Figure 8a. Two pyridines of L^1 are coordinated with $Mn(II)$ in the cis configuration and afford a distorted octahedral coordination geometry with two bidentate $hfac$ ligands, similar to those found in previously reported structures.^{23a-c} The octahedral $Mn(II)$ center is chiral, and both Λ and Δ configurations coexist in the crystal of **5**. Each metal center perpendicularly ($N1-Mn-N2$ angle, 88.73°) links two L^1 ligands and, consequently, extends the helical coil along the crystallographic

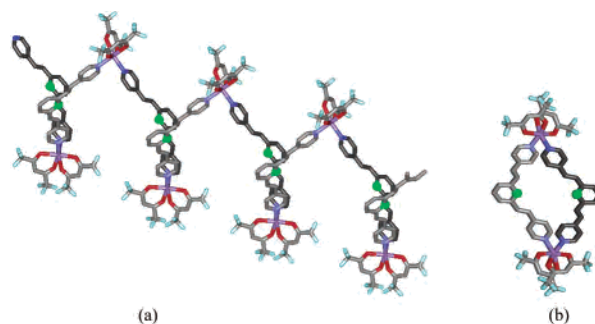


Figure 9. Single-stranded helical structure found in **6**. 2-N atoms on the inner wall were represented as green balls. Key: (a) side view of the helix; (b) top view of the helix.

b axis (Figure 8b). A turn of helicate is composed of two $Mn(II)$ and two L^1 ligands, and the distance between subsequent turns in the helix is $20.676(1)$ Å, the same as the b axis length. The crystal of **5** possesses in the centrosymmetric space group, $P2_1/n$, and there are both right-handed and left-handed helices in equal quantities. The helical polymer **5** has an isotactic nature, such that every metal center with Λ chirality is incorporated into the right-handed helix and, likewise, for the left-handed helix those with Δ chirality. It is quite apparent that the point chirality at the metal center is transmitted to the supramolecular helicity. Each helical coil makes contact with neighboring coils via $\pi-\pi$ interactions in the manner illustrated in Figure 8c.

Synthesis and Structure of $[Mn(L^2)(hfac)_2]_\infty$ (6**).** As a further step in our strategy, we tried to functionalize helical cylinders. On the basis of the same concept adopted for the modification of channels of **2**, the L^2 ligand was again applied to the self-assembly with $Mn(hfac)_2$. The reaction of L^2 with $Mn(hfac)_2$ afforded yellow crystals of **6** with the formulation of $[Mn(L^2)(hfac)_2]_\infty$. The crystallographic structure analysis of **6** shows that the additional 2-N atom in L^2 hardly affects the construction and alignment of helical chains in a crystal and, consequently, it is clearly crystallographically isostructural with **5**. The distinct feature of this structure is the situation of 2-N atoms of L^2 on the inner wall of the helix. The 2-N atoms remain uncoordinated, and their lone pairs are prominent toward the inner channel (Figure 9). Thus, the channel surface of the helical cylinder is regarded to be modified by the potential hydrogen-bonding accepting groups and to be relevant to the selective interaction with guest molecules. This result, along with that of **2**, suggests that the coordination framework can be rationally functionalized through our simple and predictable synthetic strategy including the introduction of additional donating groups in the ligand skeleton.

Magnetic Properties. We have attempted to examine the magnetic behavior of the assemblies in this report through variable-temperature bulk magnetic susceptibility measurements. As a result of their low structural stability, measurements for **1** and **2** could not be carried out. Magnetic susceptibility data for **3–6** were collected in the 5–300 K temperature ranges under a constant magnetic field of 10 kG. The measured magnetic susceptibilities indicate $Co(II)$. Each measured magnetic susceptibilities are found to obey

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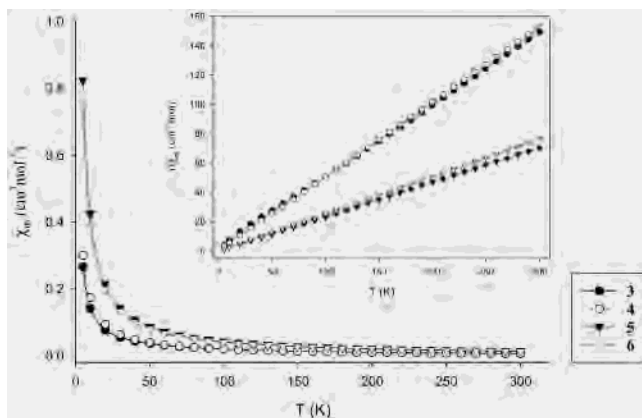


Figure 10. Temperature dependence of molar magnetic susceptibilities of **3–6**.

the Curie law, $\chi_m = C/(T - \Theta)$, such that plots of $\chi^{-1} = f(T)$ give straight lines with almost zero intercept value (Figure 10). The observed values fall into a reasonable range for complexes containing Co(II) and Mn(II) centers in the high-spin state and indicate that Co(II) ions in **3** and **4** and Mn(II) ions in **5** and **6** are not coupled magnetically. The absence of magnetic coupling in **3** is not surprising in view of its discrete crystal structure, which shows no apparent pathway for magnetic exchange. Besides, no magnetic coupling in **4–6** is assumed to be due to the long ligands structure to propagate magnetic interactions.²⁴ From these observations, it is concluded that the ligands of **L**¹, **L**², and **L**⁴ are not pertinent bridges for propagating an exchange interaction between paramagnetic metal centers.

Conclusion

In this report, we demonstrate that rigid angular ligands with a molecular angle of 120° can be exploited in the

(24) (a) Park, S. H.; Kim, K. M.; Lee, S.-G.; Jung, O.-S. *Bull. Korean Chem. Soc.* **1998**, *19*, 79. (b) Haddad, M. S.; Hendrickson, D. N.; Cannady, J. P.; Drago, R. S.; Bieksza, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 898.

context of rational design of coordination polymers. Assemblies of 1,3-bis(*trans*-4-styrylpyridyl)benzene (**L**¹), 2,6-bis(*trans*-4-styrylpyridyl)pyridine (**L**²), 1,3-bis(*trans*-4-styrylpyrimidyl)benzene (**L**³), and 1,3-bis(*trans*-4-styrylquinoly)benzene (**L**⁴) with Co(NCS)₂ lead to novel structures which have not been obtained using normal linear bidentate ligands, such as pyrazine and 4,4'-dipyridine. The coordination environments around a Co(II) center are modulated by simple variation of ligand structures, and consequently, open-framework (**1**, **2**), stairlike hydrogen-bonded chain (**3**), and single-stranded helical coil (**4**) structures are constructed. Moreover, other single-stranded helicates **5** and **6** are rationally generated by combining the angular spacers of **L**¹ and **L**² with the right-angled node of Mn(hfac)₂, respectively. Moreover, through the substitution of 2-pyridine moiety instead of benzene in the ligand skeleton, the inner channels of **2** and **6** are successfully modified by a hydrogen-bonding acceptor while sustaining the network topologies of **1** and **5**. This represents a relevant example of a simple and predictable isomorphous substitution approach for the rational functionalization of coordination frameworks. We believe that the results in this report may be extended to establish a simple strategy for the preparation and modification of novel solid materials with useful properties, and further transferable crystal engineering research efforts will be directed toward this end.

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Supporting Information Available: X-ray crystallographic information files (CIF) for **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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