

Unexpected Formation of the Cobalt-Formate Coordination Polymer $[\text{Co}_3(\text{HCO}_2)_6]\cdot\text{dmf}$ from $\text{Co}(\text{NO}_3)_2$ and 2,2'-Bipyridine-5,5'-dicarboxylic Acid in $\text{dmf-EtOH-H}_2\text{O}$

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Received October 2, 2008

Under hydro(solvo)thermal conditions, the cobalt-formate coordination polymer $[\text{Co}_3(\text{HCO}_2)_6]\cdot\text{dmf}$ (**1-dmf**) was formed from $\text{Co}(\text{NO}_3)_2$ and 2,2'-bipyridine-5,5'-dicarboxylic acid (bpdcH₂) in a mixed solvent of dmf, EtOH, and H₂O. Polymer **1-dmf** contains a formate ligand (HCO_2^-), which may have been formed by decarboxylation of bpdcH₂ or hydrolysis of dmf. Heating up **1-dmf** at 150 °C removed the dmf guests to give crystalline $[\text{Co}_3(\text{HCO}_2)_6]$ (**1**), a guest-free form of **1-dmf**. By immersing polymer **1** into several solvents (guests), we could obtain the corresponding guest-containing crystals of the formula of **1-guest** (guest = CH₃CN, acetone, or thf). The dimensions of the unit-cell volumes of these crystals depended on the contained guests in increasing order of **1-CH₃CN** < **1** < **1-thf** < **1-acetone** < **1-dmf**.

Key Words : 2,2'-Bipyridine-5,5'-dicarboxylate, Decarboxylation, Formate, Guest molecules, Desorption-resorption

Introduction

Porous coordination polymers, or metal-organic networks, have received much attention, due to their useful properties applicable to various fields, such as size-selective sorption, gas storage, host-guest recognition, and catalysis.¹⁻⁶ For the preparation of these polymers, the selection of appropriate ligands is one of the crucial factors to determine the structures of the resulting polymers.¹⁻¹³ Aromatic multi-carboxylate ligands (some examples in Chart 1) have been employed widely for the preparation of metal-organic networks because of their rigidity and various bonding modes.^{1-6,12-18} For example, Yaghi and co-workers reported a series of remarkable 3-D Zn coordination polymers containing cubic porous channels $[\text{Zn}_4\text{O}(\text{carboxylate})_3]$, which exhibit a high capacity for methane gas storage.² Several coordination polymers based on simple non-aromatic carboxylate ligands such as formate and oxalate, however, were recently constructed.^{19,23} For example, Kim and co-workers reported the microporous 3-D Mn-formate polymer $[\text{Mn}_3(\text{HCO}_2)_6]\cdot(\text{C}_4\text{H}_8\text{O}_2)$, which exhibited high framework stability and selective gas sorption properties.²⁰

We have been continually interested in preparing coordination polymers by using aromatic multi-carboxylate ligands.²⁴⁻³² In particular, our group previously employed 2,2'-bipyridine-5,5'-dicarboxylic acid (bpdcH₂) (Chart 1) to prepare a 2-D cobalt coordination polymer $[\text{Co}(\text{bpdc})(\text{H}_2\text{O})]\cdot(\text{H}_2\text{O})$ under hydrothermal conditions.²⁸ As a continuation of our research, we decided to use this ligand to prepare novel cobalt coordination polymers containing guest molecules within their frameworks. When we carried out the hydro(solvo)thermal reaction of $\text{Co}(\text{NO}_3)_3$ with bpdcH₂ in $\text{dmf-EtOH-H}_2\text{O}$, an unexpected 3-D coordination polymer $[\text{Co}_3(\text{HCO}_2)_6]\cdot\text{dmf}$ (**1-dmf**) was formed. This polymer contains a formate ligand (HCO_2^-), not bpdc^{2-} , which seems to have been formed by decarboxylation of bpdcH₂ or hydrolysis of dmf. We report herein the preparation, structure, and desorption-resorption behavior of $[\text{Co}_3(\text{HCO}_2)_6]\cdot\text{dmf}$ (**1-dmf**).

Experimental Section

$\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, anhydrous $\text{Co}(\text{NO}_3)_3$ (analyzed by TGA), and 2,2'-bipyridine-5,5'-dicarboxylic acid (bpdcH₂) were purchased and purified by recrystallization. Ethanol (EtOH),

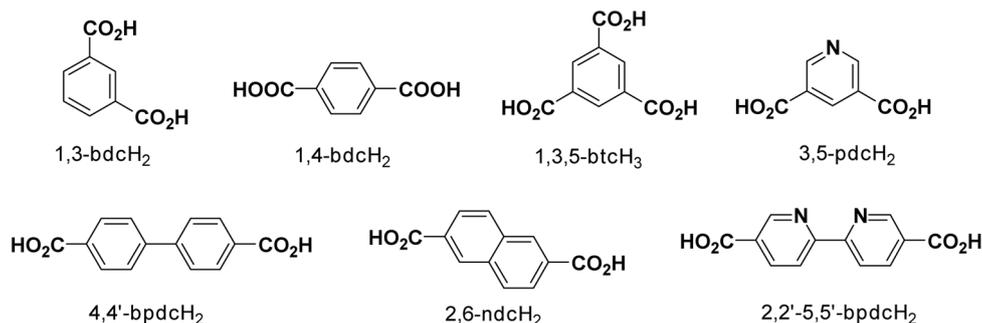


Chart 1

dmf, and guest solvents were distilled and stored over molecular sieves. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) at the Korea Basic Science Institute. TGA analysis was conducted on a TA4000/SDT 2960 instrument at the Cooperative Center for Research Facilities (CCRF) in the Sungkyunkwan University. X-ray powder diffraction (XRPD) data were obtained with a Rigaku D/Max-RC diffractometer.

Preparation of [Co₃(HCO₂)₆]·dmf (1·dmf). A mixture of Co(NO₃)₂ (0.100 g, 0.546 mmol) and bpdcH₂ (0.160 g, 0.655 mmol) in dmf-EtOH-H₂O (1:1:1 by volume, 9 mL) was heated in a Teflon-lined vessel (23 mL) at 120 °C for 48 h, and then air-cooled to room temperature. The resulting pink crystals were filtered, washed with H₂O (2 × 5 mL) and EtOH (2 × 5 mL), and then air-dried to give polymer **1·dmf** (0.068 g, 0.131 mmol, 72% yield). Anal. Calcd. for C₉H₁₃NO₁₃Co₃ (*M_r* = 519.99): C, 20.79; H, 2.52; N, 2.69. Found: C, 20.86; H, 2.39; N, 2.61. IR (KBr, cm⁻¹): 3361 (m), 3072 (m), 1618 (s, CO), 1432 (s, CO), 1373 (s, CO), 1153 (m), 1035 (m), 844 (m), 775 (m), 713 (m).

Preparation of [Co₃(HCO₂)₆] (1). Heating up **1·dmf** in a capped vial at 150 °C for 24 h removed the dmf guest molecules to give [Co₃(HCO₂)₆] (**1**), a guest-free form of **1·dmf**.

Preparation of [Co₃(HCO₂)₆]·guest (1·guest) (guest =

acetonitrile, acetone, or thf). Crystals of polymer **1** were immersed in 2 mL of solvent (acetonitrile, acetone, or tetrahydrofuran) in a capped vial (5 mL), which was kept at 40 °C for 24 h to give guest-containing crystals [Co₃(HCO₂)₆]·guest (**1·guest**). All of the guest-containing products were structurally characterized by X-ray diffraction.

Preparation of [Co(HCO₂)₂(H₂O)₂] (2). A mixture of Co(NO₃)₂ (0.100 g, 0.546 mmol) and excess formic acid (0.1 mL, 2.65 mmol) in dmf-EtOH-H₂O (1:1:1 by volume, 9 mL) was heated at 120 °C for 48 h to give pink crystals of polymer **2** (0.067 g, 0.362 mmol, 66% yield). Anal. Calcd. for C₂H₆O₆Co (*M_r* = 185.00): C, 12.98; H, 3.27. Found: C, 13.10; H, 2.99. IR (KBr, cm⁻¹): 3206 (m), 1573 (s, CO), 1373 (s, CO), 773 (m).

X-ray structure determination. All crystals are pink, and all X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with ψ -scan data. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The C–H hydrogen atoms were generated in idealized positions and refined in a riding model. The O–H hydrogen atoms were located and refined isotropically. All calculations were carried out with the use of SHELXTL programs.³³ Details on crystal data, intensity collection, and refinement details are given in Table 1. Selected bond lengths and angles for **1·dmf** and **2** are

Table 1. X-ray data collection and structure refinement details

	1·dmf	1	2	1·CH₃CN	1·acetone	1·thf
empirical formula	C ₉ H ₁₃ Co ₃ NO ₁₃	C ₆ H ₆ Co ₃ O ₁₂	C ₂ H ₆ CoO ₆	C ₈ H ₉ Co ₃ NO ₁₂	C ₉ H ₁₂ Co ₃ O ₁₃	C ₁₀ H ₁₄ Co ₃ O ₁₃
formula weight	519.99	446.90	185.00	487.95	504.98	519.00
temperature, K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	11.418(3)	11.332(1)	8.727(1)	11.255(2)	11.361(1)	11.323(3)
<i>b</i> , Å	10.076(2)	9.905(1)	7.203(1)	9.826(2)	9.960(1)	9.935(3)
<i>c</i> , Å	14.908(5)	14.503(1)	9.331(1)	14.547(2)	14.800(1)	14.708(4)
β , deg	91.42(2)	91.317(1)	97.47(1)	91.35(1)	91.527(8)	91.17(1)
<i>V</i> , Å ³	1714.6(9)	1627.53(7)	581.6(1)	1608.5(5)	1674.2(2)	1654.3(8)
<i>Z</i>	4	4	4	4	4	4
<i>d</i> _{cal} , g cm ⁻³	2.014	1.824	2.113	2.015	2.003	2.084
μ , mm ⁻¹	2.936	3.070	2.911	3.118	3.002	3.041
<i>F</i> (000)	1036	876	372	964	1004	1036
<i>T</i> _{min}	0.3407	0.6976	0.2367	0.6804	0.7546	0.4450
<i>T</i> _{max}	0.7640	0.9139	0.3014	0.9083	0.9320	0.8168
2 θ range (°)	3.5–50	3.5–50	3.5–50	3.5–50	3.5–50	3.5–50
No. of reflns measured	3136	2947	1084	2975	3078	3058
No. of reflns unique	2977	2802	1016	2824	2921	2904
No. of reflns with <i>I</i> > 2 σ (<i>I</i>)	2784	2517	965	2180	2447	2298
No. of params refined	239	193	102	205	209	214
Max., in $\Delta\rho$ (e Å ⁻³)	1.036	0.674	0.292	0.492	1.181	0.678
Min., in $\Delta\rho$ (e Å ⁻³)	-0.643	-0.308	-0.221	-0.498	-0.576	-0.577
<i>GOF</i> on <i>F</i> ²	1.050	1.054	1.117	1.024	1.050	1.082
<i>R</i> 1 ^a	0.0291	0.0296	0.0195	0.0370	0.0355	0.0466
<i>wR</i> 2 ^b	0.0772	0.0758	0.0531	0.0760	0.0861	0.1078

^a*R*1 = $\Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, ^b*wR*2 = $\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table 2. Selected bond lengths (Å) and bond angles (deg) in **1·dmf**

Co1–O10#1	2.064(2)	Co1–O7	2.065(2)	Co1–O6	2.110(2)
Co1–O11	2.123(2)	Co1–O9	2.127(2)	Co1–O2	2.126(2)
Co2–O4	2.077(2)	Co2–O8#1	2.097(2)	Co2–O6	2.102(2)
Co2–O11#1	2.121(2)	Co2–O2	2.124(2)	Co2–O9#1	2.137(2)
Co3–O3	2.080(2)	Co3–O1	2.089(2)	Co3–O8#1	2.138(2)
Co4–O12#1	2.078(2)	Co4–O5	2.101(2)	Co4–O4	2.150(2)
O7–Co1–O6	89.45(9)	O7–Co1–O11	90.42(9)	O4–Co2–O6	89.81(9)
O4–Co2–O2	97.71(8)	O3–Co3–O1	88.43(10)	O5–Co4–O4	94.81(8)

Symmetry transformations used to generate equivalent atoms: #1 = $-x + 1/2, y - 1/2, -z + 3/2$

Table 3. Selected bond lengths (Å) and bond angles (°) in **2**

Co1–O2	2.079(1)	Co1–O1#2	2.105(1)	Co1–O4	2.150(1)
Co2–O6	2.056(1)	Co2–O5	2.134(1)	Co2–O3	2.154(1)
O2–Co1–O1#2	89.49(4)	O2–Co1–O4	87.24(4)	O1#2–Co1–O4	93.11(4)
O6–Co2–O5	90.87(5)	O6–Co2–O3	89.59(6)	O5–Co2–O3	88.47(4)

Symmetry transformations used to generate equivalent atoms: #2 = $x, -y + 1/2, z + 1/2$

given in Tables 2 and 3, respectively.

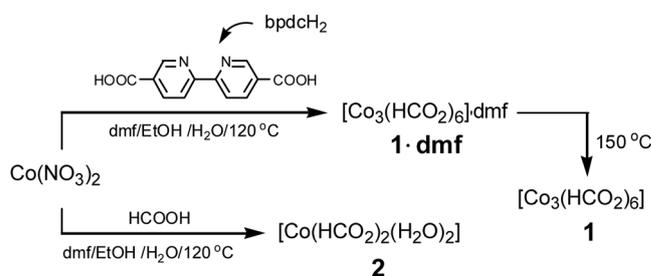
Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: CCDC No. 632701 (**1·dmf**), 632702 (**1**), 632703 (**1·acetone**), 632704 (**1·CH₃CN**), 632705 (**1·thf**), and 633217 (**2**). Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Results and Discussion

Preparation and structure of 1·dmf. The 3-D microporous cobalt-formate coordination polymer $[\text{Co}_3(\text{HCO}_2)_6]\cdot\text{dmf}$ (**1·dmf**) was formed from $\text{Co}(\text{NO}_3)_2$ and bpdcH_2 in $\text{dmf-EtOH-H}_2\text{O}$ under hydro(solvo)thermal conditions (Scheme 1). Polymer **1·dmf** contains a formate ligand (HCO_2^-), not the starting ligand bpdc^{2-} . This crystalline product has been characterized by elemental analysis, IR spectroscopy, TGA, and X-ray crystallography. The IR spectrum of this polymer displays carboxylate stretches at 1618, 1432, and 1373 cm^{-1} .

In preparing certain coordination polymers, several cases of decarboxylation of aromatic carboxylate ligands have recently been reported.^{29,34-37} For example, our group observed that hydrothermal reactions of terbium nitrate and 3,5- or 2,4-pyridinedicarboxylic acid (3,5-pdcH₂ or 2,4-pdcH₂) gave Tb coordination polymers with an empirical formula of $[\text{Tb}_2(3,5\text{-pdc})_2(\text{H}_2\text{O})_4(\text{C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}$ or $[\text{Tb}_2(2,4\text{-pdc})_2(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)]$, in which the oxalato ligand was formed by decarboxylation of pdcH₂.^{29,37} This type of decarboxylation of the aromatic carboxylates was also observed for 1,2,4-benzenetricarboxylic acid,³⁴ 2-pyrazinecarboxylic acid,³⁵ and 3,4-pyridinedicarboxylic acid,^{3,4-pdcH₂}.

It is known that formate can be formed by hydrolysis of dmf under acidic or basic conditions.³⁴ We, however, have several observations that propose a possibility of the formation of the formate ligand in **1·dmf** by the decarboxyl-

**Scheme 1**

ation of bpdcH_2 . We carried out several experiments to investigate this possibility (Table 4). First, when the reaction was carried out with $\text{Co}(\text{NO}_3)_2$ and formic acid (HCOOH), in place of bpdcH_2 , under the same reaction conditions, the essentially different cobalt-formate coordination polymer $[\text{Co}(\text{HCO}_2)_2(\text{H}_2\text{O})_2]$ (**2**) was produced (Scheme 1 and Entry 2 in Table 4). Second, the reaction including a single reactant $\text{Co}(\text{NO}_3)_2$ (that is, in the absence of bpdcH_2) produced only cobalt(II,III) oxide Co_3O_4 , whose identity was confirmed by XRPD (Entry 3). If the formate ligand had been formed by hydrolysis of dmf , the same product (**1·dmf**) should have been obtained in this case; however, such a phenomenon was not observed. Third, reactions in neat dmf (that is, in the absence of EtOH and water) also produced **1·dmf**, regardless of the hydrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, Entry 4) and anhydrous ($\text{Co}(\text{NO}_3)_2$, Entry 5) forms of cobalt nitrate, although its crystal quality is somewhat poor. Consequently, we can exclude the possibility that the formate ligand has come from EtOH . Fourth, in order to further investigate the role of dmf , reactions were carried out in other solvents (guests) such as acetonitrile, acetone, and tetrahydrofuran, in place of dmf , with the remaining experimental parameters unchanged (Entries 7-9). All these reactions produced the same product $[\text{Co}(\text{bpdc})(\text{H}_2\text{O})]\cdot(\text{H}_2\text{O})$, which strongly indicates that dmf is an essential reactant in our reaction system. Finally, we performed the reaction in $\text{dma-EtOH-H}_2\text{O}$, in which dma (dimethylacetamide), like dmf , may decompose

Table 4. Reaction conditions and products

Entry	Reactants	Solvent composition	Product
1	Co(NO ₃) ₂ + bpdcH ₂	dmf–EtOH–H ₂ O	[Co ₃ (HCO ₂) ₆]·dmf (1·dmf)
2	Co(NO ₃) ₂ + HCOOH	dmf–EtOH–H ₂ O	[Co(HCO ₂) ₂ (H ₂ O) ₂] (2)
3	Co(NO ₃) ₂	dmf–EtOH–H ₂ O	Co ₃ O ₄
4	Co(NO ₃) ₂ ·6H ₂ O + bpdcH ₂	dmf	1·dmf
5	Co(NO ₃) ₂ + bpdcH ₂	dmf	1·dmf
6	Co(NO ₃) ₂ ·6H ₂ O + bpdcH ₂	H ₂ O	[Co(bpdc)(H ₂ O)]·(H ₂ O) (A) ²⁸
7	Co(NO ₃) ₂ + bpdcH ₂	CH ₃ CN–EtOH–H ₂ O	A
8	Co(NO ₃) ₂ + bpdcH ₂	acetone–EtOH–H ₂ O	A
9	Co(NO ₃) ₂ + bpdcH ₂	thf–EtOH–H ₂ O	A
10	Co(NO ₃) ₂ + bpdcH ₂	dma–EtOH–H ₂ O	A

by hydrolysis, and we also obtained [Co(bpdc)(H₂O)]·(H₂O) (Entry 10). From the above observations, we speculate that (1) dmf plays an essential role in the reaction system (Entries 1, 4, 5, and 7–10) because **1·dmf** is formed only when both bpdcH₂ and dmf are present, and (2) the formate ligand may be formed by decomposition of bpdcH₂ (Entries 2 and 3). In order to search fragments coming from the decomposition of bpdcH₂ (or, maybe, of the solvent dmf), we took the mass spectra of the mother liquor (direct mass spectrometry). Unfortunately, however, we cannot find peaks assignable to the decomposition products of bpdcH₂, including 2,2'-bipyridine ($m/z = 156.2$) and 2,2'-bipyridyl-COOH ($m/z = 200.1$) in the mass spectra. The GC-mass spectra of a CH₂Cl₂ extract of the mother liquor display only a single peak, but its fragmentations cannot possibly be interpreted as the decomposition products of bpdcH₂. It should be mentioned that bpdcH₂ is practically insoluble in CH₂Cl₂, and this insolubility may hinder us from detecting those decomposition products. Because of lack of a direct and definitive evidence for the bpdcH₂ decomposition, we cannot rule out the possibility of the dmf hydrolysis. We think at this point that the formate ligand may have been formed by the hydrolysis of dmf, decarboxylation of bpdcH₂, or both during the reaction.

The local coordination geometries of Co metals (Co1–Co4) in polymer **1·dmf** with the atom-numbering scheme are shown in Figure 1a, which shows four distinct octahedral cobalt metals. The Co3 and Co4 atoms lie at the crystallographic inversion centers with a site occupation of 0.5. As shown in Figure 1b, Co2 resides at the center of a distorted tetrahedron consisting of Co1, Co3, Co4, and a symmetry-equivalent Co1 (Co2···Co1: 3.224 Å, Co2···Co1A: 3.206 Å, Co2···Co3: 3.555 Å, Co2···Co4: 3.565 Å; Co1···Co2···Co1A 111.1°, Co3···Co2···Co1 112.2°, Co3···Co2···Co1A 110.3°, Co4···Co2···Co1 104.9°). Very recently, Li and co-workers reported the structure and adsorption property of polymer **1·dmf**, whose structure was basically the same as that of our polymer, except for difference in properties related to unit cell parameters such as unit cell volume (1630.9(2) Å³), density (2.118 g/cm³), channel dimensions (~5–6 Å), and the β angle (91.250(1)°).³⁸ They prepared this polymer by heating a mixture of Co(NO₃)₂·6H₂O, formic acid, and dmf at 100 °C. Li and our groups' results demon-

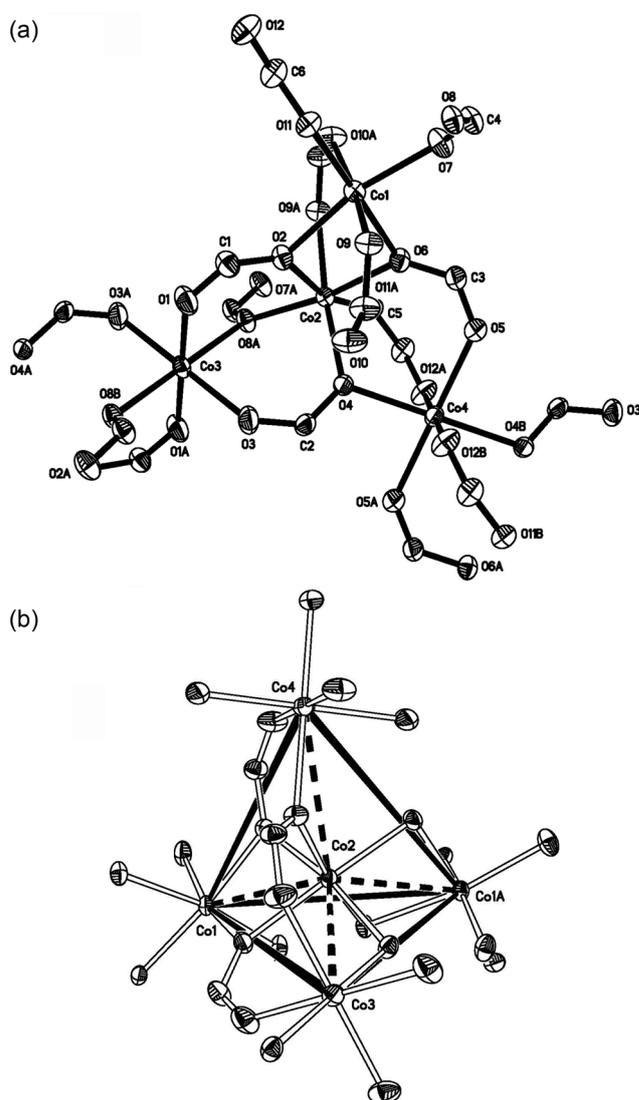


Figure 1. (a) Local coordination environments of Co metals in polymer **1·dmf**. (b) The distorted tetrahedral Co₄ node with Co₂ at its center.

strate that crystal growth is a highly sensitive and essentially unpredictable process. In other words, slight changes to the reaction system (solvent composition and reaction temperature) may cause dramatic changes in the structures of the

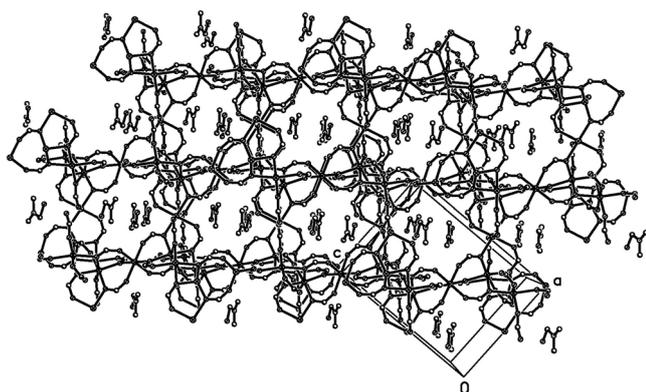


Figure 2. Packing diagram of polymer **1·dmf** along the *b*-axis.

crystals one obtains. Figure 2 shows a packing diagram of polymer **1·dmf** along the *b*-axis and demonstrates a 3-D network structure. The tetrahedral connecting nodes (Figure 1b) are linked by the formate ligands to give a compact 3-D network. This 3-D open framework has channels of approximate dimensions of $4.5 \times 5.5 \text{ \AA}$ (on the basis of covalent radii), which are occupied by the guest dmf molecules.

The local coordination environments of Co metals in polymer **2** are shown in Figure 3, which exhibits two distinct octahedral cobalt ions. Both Co metals (Co1 and Co2) lie at the centers of symmetry. Whereas the Co1 metal is coordinated by six formate ligands, the Co2 metal by two formate and four aqua ligands. Two aqua ligands (O5 and O6) and two COO^- groups of the formate ligands are involved in the hydrogen bonds of the type $\text{O-H} \cdots \text{O}$: one intramolecular ($\text{O5-HO5A} = 0.88 \text{ \AA}$, $\text{HO5A} \cdots \text{O4} = 1.94 \text{ \AA}$, $\text{O5-HO5A} \cdots \text{O4} = 155^\circ$, $\text{O5} \cdots \text{O4} = 2.77 \text{ \AA}$) and three intermolecular ($\text{O5-HO5B} = 0.85 \text{ \AA}$, $\text{HO5B} \cdots \text{O4} = 1.96 \text{ \AA}$, $\text{O5-HO5B} \cdots \text{O4} = 173^\circ$, $\text{O5} \cdots \text{O4} (-x, -y + 1, -z + 1) = 2.80 \text{ \AA}$; $\text{O6-HO6A} = 0.89 \text{ \AA}$, $\text{HO6A} \cdots \text{O1} = 1.90 \text{ \AA}$, $\text{O6-HO6A} \cdots \text{O1} = 174^\circ$, $\text{O6} \cdots \text{O1} (-x, -y + 1, -z + 1) = 2.79 \text{ \AA}$; $\text{O6-HO6B} = 0.89 \text{ \AA}$, $\text{HO6B} \cdots \text{O3} = 1.88 \text{ \AA}$, $\text{O6-HO6B} \cdots \text{O3} = 168^\circ$, $\text{O6} \cdots \text{O3} (-x - 1, y + 1/2, -z + 3/2) = 2.77 \text{ \AA}$) hydrogen bonds. Polymer **2** also has a 3-D structure, and its packing diagram along the *b*-axis is presented in Figure 4. The formate ligands link neighboring Co metals to form an infinite 3-D network. Powell and co-workers recently reported a man-

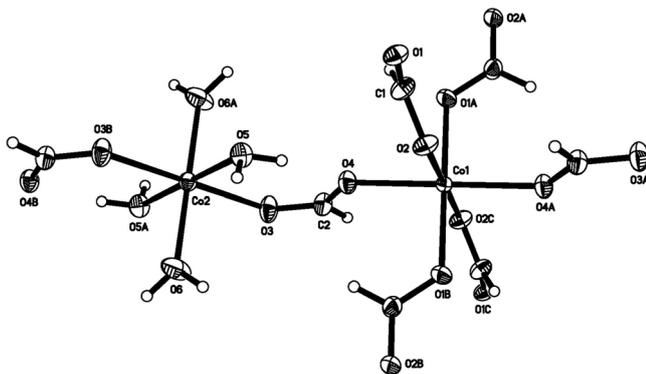


Figure 3. Local coordination environments of Co metals in polymer **2**.

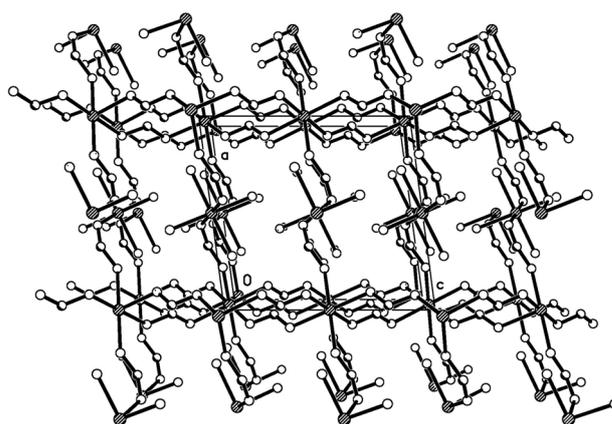


Figure 4. A packing diagram of polymer **2** along the *b*-axis.

ganese analogue $[\text{Mn}(\text{HCO}_2)_2(\text{H}_2\text{O})_2]$, which is isostructural with **2**, and its dehydrated form $[\text{Mn}(\text{HCO}_2)_2]$.¹⁹

Guest-containing coordination polymers. Thermal gravimetric analysis (TGA) shows that polymer **1·dmf** loses the guest dmf molecules in the range of $110\text{--}200 \text{ }^\circ\text{C}$. On the basis of this result, the guest-free form $[\text{Co}_3(\text{HCO}_2)_6]$ (**1**) could be prepared by heating **1·dmf** at $150 \text{ }^\circ\text{C}$ for 24 h. The high crystal quality of **1** allowed us to determine its structure, whose unit-cell volume turned out to be 5.1% smaller than that observed for **1·dmf** (Table 1). The crystal structure of **1** (Figure 5) revealed that its framework is exactly the same as that of **1·dmf**, except for some shrinkage of the unit cell probably due to the absence of the guest dmf molecules.

As mentioned in Introduction, Kim and co-workers prepared the microporous 3-D Mn-formate coordination polymer $[\text{Mn}_3(\text{HCO}_2)_6] \cdot (\text{C}_4\text{H}_8\text{O}_2)$ from $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and HCOOH in diethylformamide/1,4-dioxane by solvothermal reactions.²⁰ When evacuated, this polymer gave its guest-free form $[\text{Mn}_3(\text{HCO}_2)_6]$. The structural relation between $[\text{Mn}_3(\text{HCO}_2)_6] \cdot (\text{C}_4\text{H}_8\text{O}_2)$ and $[\text{Mn}_3(\text{HCO}_2)_6]$ is essentially the same as that between **1·dmf** and **1**. In addition, Wang's group also prepared a couple of 3-D formate coordination polymers, $[\text{M}_3(\text{HCO}_2)_6] \cdot (\text{CH}_3\text{OH})(\text{H}_2\text{O})$ ($\text{M} = \text{Mn}$ or Co), by layering $\text{MCl}_2 \cdot 4\text{H}_2\text{O}$ in methanol onto HCOOH in methanol in the presence of triethylamine (NEt_3).²¹

The successful preparation of polymer **1** urged us to intro-

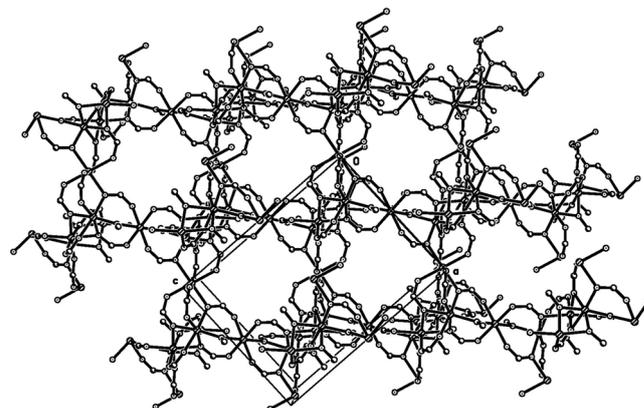


Figure 5. Packing diagram of polymer **1** along the *b*-axis.

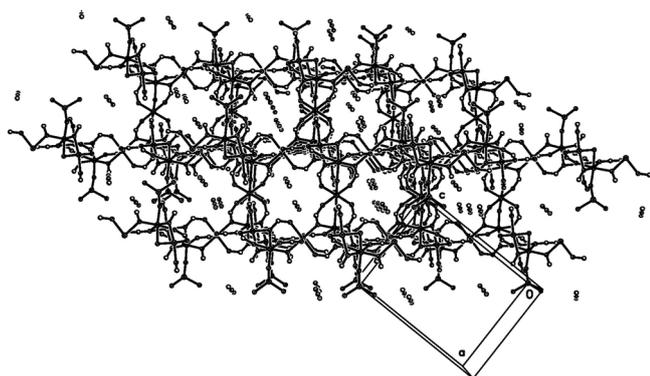


Figure 6. Packing diagram of polymer **1·CH₃CN** along the *b*-axis.

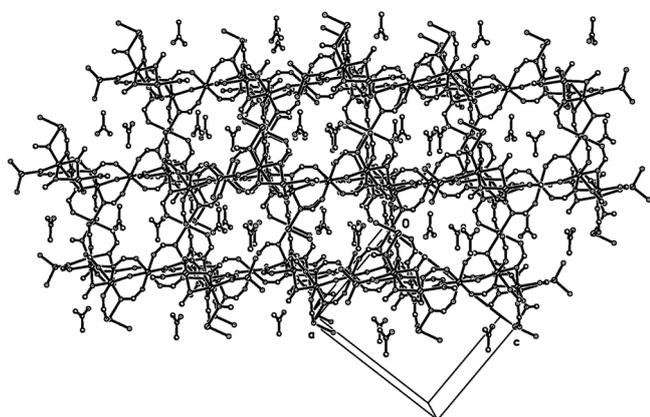


Figure 7. Packing diagram of polymer **1·acetone** along the *b*-axis.

duce other guest molecules such as acetonitrile, acetone, dichloromethane, benzene, and tetrahydrofuran into its empty channels. Immersing the crystals of polymer **1** in the solvent (guest) at 40 °C for 24 h produced the guest-containing crystals [Co₃(HCO₂)₆·guest (**1·guest**)]. The resulting crystals were characterized by both XRPD and single crystal X-ray crystallography. Packing diagrams of these crystals are given in Figures 6–8, which illustrate the same framework as that found for **1·dmf**. Consistent with the fact that **1·acetone**, **1·CH₃CN**, and **1·thf** were prepared from polymer **1** (a dmf-desorbed form of **1·dmf**), all five related polymers crystallized in the same monoclinic space group

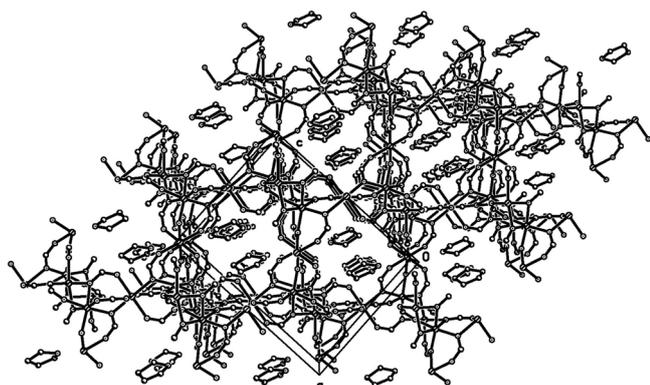


Figure 8. Packing diagram of polymer **1·thf** along the *b*-axis.

$P2_1/n$. In other words, the framework of the **1·dmf** is retained even when resorption is carried out in solvents (guests) other than the original solvent (dmf). Unfortunately, we could not determine the structure of the dichloromethane-containing crystal due to its extremely high structural disorder. Furthermore, benzene was not adsorbed at all, which quite contrasts with the known fact that both Co₃(HCOO)₆³⁸ and the Mn analogue Mn₃(HCOO)₆²² absorb an appreciable amount of benzene.

The unit cell volumes of the guest-containing crystals were observed to depend on the contained guests in increasing order of **1·CH₃CN** < **1** < **1·thf** < **1·acetone** < **1·dmf**. These results do not demonstrate a direct correlation between unit cell volume and guest polarity, and therefore we speculate that several factors including polarity, steric bulk, and kinetic diameters of the guests may collectively influence the unit cell volumes. It should be mentioned that Wang and co-workers previously performed a similar study on [Mn₃(HCO₂)₆], variation in unit cell volume with guest molecules, and observed a tendency in order of thf < dmf < MeOH·H₂O < free < benzene.²² In their study, the guest-free crystal of [Mn₃(HCO₂)₆] turned out to have a larger unit cell volume than its dmf-containing parent crystal, which contrasts with our results (**1** < **1·dmf**).

The XRPD patterns of all crystals in this study are presented in Figure 9. The patterns of the original polymer (**1·dmf**, Figure 9a) and its guest-free (dmf-desorbed) form (**1**, Figure 9b) show an overall agreement in *d*-spacing and peak shape. To examine the reversibility of desorption-resorption of the dmf guest molecules, we took the XRPD spectrum of the dmf-resorbed sample that was prepared by immersing polymer **1** in 5 mL of dmf at 40 °C for 3 days. The XRPD spectrum of the dmf-resorbed crystals of polymer **1** (Figure 9c) demonstrates that the original polymer **1·dmf** is restored, although we observe minor discrepancies

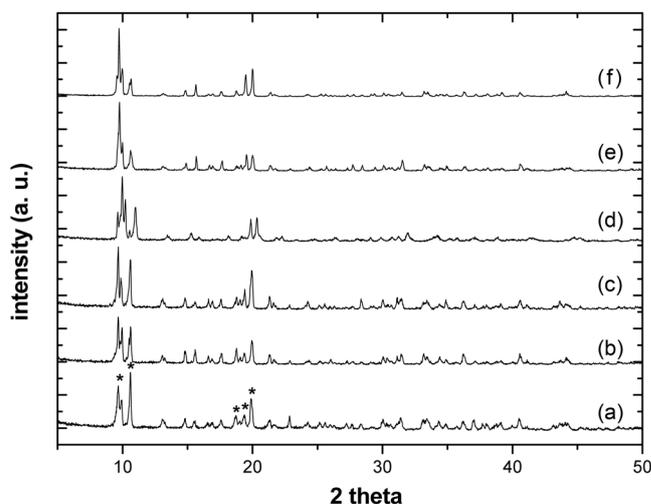


Figure 9. XRPD patterns of polymers: (a) an original form (polymer **1·dmf**); (b) a guest-free form (polymer **1**); (c) a dmf-resorbed form (polymer **1**); (d) a CH₃CN-resorbed form (polymer **1·CH₃CN**); (e) an acetone-resorbed form (polymer **1·acetone**); (f) a thf-resorbed form (polymer **1·thf**).

in relative intensities (the peaks with asterisks in Figure 9a). The XRPD patterns of the remaining samples (Figures. 9d-f), which were prepared by immersing the crystals of polymer **1** in the corresponding guest (solvent), also support facile resorption behavior of this polymer.

In summary, the cobalt-formate coordination polymer $[\text{Co}_3(\text{HCO}_2)_6]\cdot\text{dmf}$ (**1**·**dmf**) was formed from $\text{Co}(\text{NO}_3)_2$ and bpdcH_2 in $\text{dmf-EtOH-H}_2\text{O}$ under hydro(solvo)thermal conditions. By contrast, when the reaction was carried out with formic acid, in place of bpdcH_2 , while all the other experimental variables were kept unchanged, the essentially different cobalt-formate coordination polymer $[\text{Co}(\text{HCO}_2)_2\cdot(\text{H}_2\text{O})_2]$ (**2**) was produced. Polymer **1**·**dmf** contains a formate ligand, which may have been formed by decarboxylation of the starting ligand bpdcH_2 , by hydrolysis of dmf , or by both. This polymer has a highly stable microporous 3-D framework with channels of $4.5 \times 5.5 \text{ \AA}$, which contain dmf guest molecules. Heating up **1**·**dmf** at $150 \text{ }^\circ\text{C}$ for 24 h removed the dmf guest molecules to give crystalline $[\text{Co}_3(\text{HCO}_2)_6]$ (**1**). The guest-free polymer **1** readily took up several guest molecules to give the corresponding guest-containing crystals of the general formula of **1**·**guest** (guest = CH_3CN , acetone, or thf). Structural characterization of crystals of polymer **1** and its guest-containing polymers revealed that the dimensions of the unit-cell volumes of these crystals vary with guests in order of **1**·**CH₃CN** < **1** < **1**·**thf** < **1**·**acetone** < **1**·**dmf**.

Acknowledgments. This paper was supported by Samsung Research Fund, Sungkyunkwan University, 2008.

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