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Triply interpenetrating coordination polymers based on paddle-wheel type secondary-building units of $M_2(CO_2R)_4$: $[Ni_3(2,6\text{-}NDC)_3(bipy)_{1.5}]$, $[Co_3(2,6\text{-}NDC)_3(bipy)_{1.5}]$, and [Co(1,3-BDC)(bipyen)] (2,6-NDC = 2,6-naphthalenedicarboxylate; 1,3-BDC = 1,3-benzenedicarboxylate; bipy = 4,4′-bipyridine; bipyen = *trans*-1,2-bis(4-pyridyl)ethylene)

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Abstract

Triply interpenetrating 3-dimensional nickel and cobalt coordination polymers, $[M_3(2,6\text{-}NDC)_3(bipy)_{1.5}]$, were prepared from metal nitrate $\{M(NO_3)_2 \cdot 6H_2O\}$, 2,6-naphthalenedicarboxylic acid (2,6-$NDCH_2$), and 4,4′-bipyridine (bipy) under hydrothermal (M = Ni) or water–benzene hydro(solvo)thermal (M = Co) conditions. Both polymers have the same secondary building units (SBUs) of paddle-wheels of the type $[M_2(CO_2R)_4]$, which are composed of two metals and four di(monodentate) bridging carboxylates. On the other hand, the hydrothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ with 1,3-benzenedicarboxylic acid (1,3-$BDCH_2$) and *trans*-1,2-bis(4-pyridyl)ethylene (bipyen) gave a 2-dimensional polymer [Co(1,3-BDC)(bipyen)]. The structures of all products were determined by X-ray diffraction.

Keywords: Triply interpenetrating; Coordination polymers; Paddle wheels; SBU

1. Introduction

Coordination polymers with a variety of cavities or channels are currently under intensive studies because of their useful properties such as chemical separations, sorption, and catalysis, as well as potential applications in functional materials [1–5]. In designing 1-, 2-, and 3-D extended porous coordination polymers, the selection of appropriate ligands is crucial to determining the structural outcome of target polymers. In this context, the concept of 'node-spacer', in which the node corresponds to a metal center and the spacer to a ligand, has become a fundamental tool in the rational design of crystalline architectures (crystal engineering) [6].

Linear spacers such as carboxylates [7,8] and pyridyls [9] frequently provide rigid grid-type frameworks with large voids although the carboxylates tend to form relatively more rigid frameworks due to the potential bidentate coordination of their carboxylate groups. In preparing the frameworks based on those linear spacers, the phenomenon of interpenetration often hinders the formation of useful coordination polymers at least in terms of porosity [10]. Although interpenetration in some cases has been proposed as a means of increasing the dimensionality and structural rigidity of coordination polymers [3,4], it has been a plague to constructing a desired high-dimensional network with large voids. Recently, from the study on M-carboxylate (M = Co, Ni, Cu, Zn; carboxylate = 1,4-benzenedicarboxylate,

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1,4-azidobenzoate, 1,3,5-benzenetricarboxylate, 1,3,5,7-adamantanetetracarboxylate) coordination polymers, Yaghi and co-workers found that the rodlike carboxylate has a great tendency to form interpenetrating frameworks when either large guests or hydrogen-bonded guest aggregates are absent [11]. In addition, longer ligands compared with shorter ones will generally favor the formation of interpenetrating over non-interpenetrating polymers [10,12].

Secondary building units (SBUs) are molecular complexes and clusters, in which ligand coordination modes and metal coordination environments are utilized to transform these fragments into extended networks using multidentate ligands [8]. The SBUs have long been fundamental concepts in zeolite chemistry [13,14], and now draw considerable attention as a firm basis of synthetic strategies for constructing high-dimensional coordination polymers. For example, Yaghi and co-workers used the paddle-wheel cluster of the type $[M_2(OCOR)_4]$ (M = Cu or Zn) as a square-planar SBU to prepare porous polymers with large voids and channels [8]. In addition, there are currently two general synthetic strategies to prepare non-interpenetrating square-grid (or rectangular-grid) coordination polymers and to control the size of their channels: (1) the use of bipyridine-type ligands of different lengths [15,16]; and (2) the modification of the ligand to affect the shape of the grid [17].

We recently prepared several coordination polymers based on carboxylates or bipyridyls by hydrothermal reactions [18–21]. We now become interested in preparing coordination polymers based on a mixed-ligand system possessing dicarboxylates {2,6-naphthalenedicarboxylate (2,6-NDC) and 1,3-benzenedicaboxylates (1,3-BDC)} and linear dipyridyls {*trans*-1,2-bis(4-pyridyl)ethylene (bipyen) and 4,4′-bipyridine (bipy)}. We report here two triply-interpenetrating coordination polymers formed by the bipyridyl linking of square-grid nets based on paddle-wheel type SBUs of $[M_2(CO_2R)_4]$, $[Ni_3(2,6\text{-NDC})_3(bipy)_{1.5}]$ (**1**) and $[Co_3(2,6\text{-NDC})_3(bipy)_{1.5}]\cdot H_2O$ (**2**), which were prepared from metal nitrate, $NDCH_2$, and bipy by hydrothermal or hydro(solvo)thermal reactions. As expected, the variation in the coordination angle of the dicarboxylate led to a fundamental change in the structural outcome of the resulting polymer. When we treated a bent dicarboxylate ($1,3\text{-BDCH}_2$; coordination angle ≈120°) instead of a linear counterpart ($2,6\text{-NDCH}_2$; coordination angle ≈180°) with $Co(NO_3)_2\cdot 6H_2O$ and bipyen, a 2-dimensional polymer [Co(1,3-BDC)(bipyen)] (**3**) was formed. In this paper, we would like to show: (i) square-grid networks based on the paddle-wheel type SBUs linked to triply interpenetrating polymers; and (ii) a coordination-angle dependence of the structural outcome of the resulting polymer.

2. Experimental

$Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $2,6\text{-NDCH}_2$, $1,3\text{-BDCH}_2$, bipy, and bipyen were purchased. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) by the Korea Basic Science Institute. TGA analysis was conducted on a TA4000/SDT 2960 instrument.

2.1. Preparation of $[Ni_3(2,6\text{-NDC})_3(bipy)_{1.5}]$ (1)

A mixture of $Ni(NO_3)_2\cdot 6H_2O$ (0.135 g, 0.403 mmol), $2,6\text{-NDCH}_2$ (0.100 g, 0.403 mmol), bipy (0.072 g, 0.403 mmol), and H_2O (6.0 ml, 0.333 mol) in the mole ratio of 1:1:1: 600 was heated in a 23-ml capacity Teflon-lined reaction vessel at 180 °C for 2 days, and then cooled to room temperature. The green crystalline product was collected by filtration, washed with H_2O (2 × 5 ml), EtOH (3 × 5 ml), and acetone (2 × 5 ml), and then air-dried to give 0.081 g (0.077 mmol, 57%) of $[Ni_3(2,6\text{-BDC})_3(bipy)_{1.5}]$. *Anal*. Calc. for $C_{51}H_{30}N_3Ni_3O_{12}$: C, 58.18; H, 2.87; N, 3.99. Found: C, 57.99; H, 2.84; N, 4.05%. IR (KBr): 1688 (m, C=O), 1618 (s, C=O), 1537 (m, C=O), 1490 (m, C=O), 1421 (s, C=O), 921 (s), 821 (s), 784 (s), 645 (s), 564 (s), 501 (s) cm^{-1}.

2.2. Preparation of $[Co_3(2,6\text{-NDC})_3(bipy)_{1.5}]$ (2)

This polymer was prepared similar to **1**, except that a benzene–water mixture was used as a solvent. $Co(NO_3)_2\cdot 6H_2O$ (0.100 g, 0.344 mmol), $2,6\text{-NDCH}_2$ (0.025 g, 0.115 mmol), bipy (0.054 g, 0.344 mmol), benzene (1.53 ml, 17.18 mmol), and H_2O (6 ml, 0.333 mol) in the mole ratio of 3:1:3:150:2900 was heated at 180 °C for 3 days. The black crystalline product of $[Co_3(2,6\text{-NDC})_3(bipy)_{1.5}]$ along with orange powdery impurity of unknown nature was collected by filtration and air-drying. The desired product was mechanically separated from the impurity. The yield was 52% based on cobalt. *Anal*. Calc. for $C_{51}H_{30}Co_3N_3O_{12}$: C, 59.41; H, 2.26; N, 3.92; Found: C, 58.45; H, 2.83; N, 3.94%. IR (Nujol): 1619 (s, C=O), 1409 (vs, C=O), 921 (m), 818 (m), 782 (vs), 642 (w), 567 (w), 493 (vs) cm^{-1}.

2.3. Preparation of [Co(1,3-BDC)(bipyen)] (3)

A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.10 g, 0.344 mmol), $1,3\text{-BDCH}_2$ (0.10 g, 0.602 mmol), bipyen (0.050 g, 0.274 mmol), and H_2O (6.0 ml, 333 mmol) in the mole ratio of 1:1.75:0.80:968 was heated at 180 °C for 2 days to give 0.074 g (0.183 mmol, 67%) of [Co(1,3-BDC)(bipyen)]. *Anal*. Calc. for $C_{20}H_{14}CoN_2O_4$: C, 59.27; H, 3.48; N, 6.91. Found: C, 59.52; H, 3.27; N, 6.89%. IR (KBr): 3433 (br), 2924 (s), 1611 (s, C=O), 1397 (s, C=O), 1074 (s), 832 (s), 718 (s), 554 (s), 459 (s) cm^{-1}.

2.4. X-ray structure determination

X-ray data were collected with the use of either a Bruker CCD SMART diffractometer (polymer **1**) or a Siemens P4 diffractometer (polymers **2** and **3**) equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with ψ-scan data, except for polymer **1** for which absorption corrections were made with SADABS. All calculations were carried out with use of the SHELXTL programs [22]. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode.

A green crystal of **1**, shaped as a cube of approximate dimensions $0.32 \times 0.30 \times 0.28$ mm^3, was used. The unit-cell parameters suggested a monoclinic unit cell with three possible space groups: *C*2, *C*2/*m* and *Cm*. A statistical analysis of reflection intensities suggested a non-centrosymmetric space group, and the structure analysis converged only in *C*2. A black crystal of **2**, shaped as a block of approximate dimensions $0.41 \times 0.24 \times 0.21$ mm^3, was placed in a sealed glass capillary. The structure analysis of **2** was also successful only in *C*2. A pink crystal of **3**, shaped as a block of approximate dimensions $0.38 \times 0.18 \times 0.12$ mm^3, was used. This crystal belongs to the triclinic system and was solved in the centrosymmetric space group $P\bar{1}$.

Details on crystal data and refinement details are given in Table 1. Selected bond lengths and bond angles are given in Tables 2 and 3.

Table 1
X-ray data collection and structure refinements

	Polymer **1**	Polymer **2**	polymer **3**
Empirical formula	$C_{51}H_{30}N_3O_{12}Ni_3$	$C_{51}H_{30}Co_3N_3O_{12}$	$C_{20}H_{14}CoN_2O_4$
Formula weight	1052.91	1053.57	405.26
Temperature (K)	153(2)	296(2)	296(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C*2	*C*2	$P\bar{1}$
A (Å)	17.159(4)	17.209(4)	9.729(2)
B (Å)	19.747(5)	19.865(5)	10.067(1)
C (Å)	13.709(4)	13.880(11)	10.341(1)
α (°)	90.000(0)	90.000(0)	80.13(1)
β (°)	95.935(4)	95.81(4)	85.98(2)
γ (°)	90.000(0)	90.000(0)	68.59(1)
V (Å^3)	4620(2)	4721(4)	929.0(3)
Z	4	4	2
D_{calc} (g cm^{-3})	1.319	1.449	1.482
μ (mm^{-1})	1.278	1.109	0.951
F(000)	2148	2136	414
T_{min}	0.2608	0.2192	0.7231
T_{max}	0.3013	0.3293	0.9250
2θ Range (°)	3.5–50	3.5–50	3.5–50
Scan type	ω	ω	ω
Scan speed	variable	variable	variable
Reflections measured	9795	4403	3474
Reflections unique	5971	4254	3262
Reflections with $I > 2\sigma(I)$	4066	3189	2471
Parameters refined	556	622	245
Max., in $\Delta\rho$ (e Å^{-3})	0.728	0.900	0.277
Min., in $\Delta\rho$ (e Å^{-3})	−0.432	−0.564	−0.545
Goodness-of-fit on F^2	0.978	1.073	1.023
R	0.0389	0.0532	0.0487
wR_2 [a]	0.0903	0.1307	0.1046

[a] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. Formation of interpenetrating polymers

Triply interpenetrating Ni and Co coordination polymers, $[M_3(2,6\text{-NDC})_3(\text{bipy})_{1.5}]$ (M = Ni (**1**) or Co (**2**)), were prepared from metal nitrate $\{M(NO_3)_2 \cdot 6H_2O\}$, 2,6-NDCH$_2$, and bipy under hydrothermal or hydro(solvo)thermal conditions (Eq. (1)). The crystalline products have been characterized by elemental analysis, IR spectroscopy, thermal gravimetric analysis (TGA), and X-ray crystallography.

$$\begin{aligned} &M(NO_3)_2 \cdot 6H_2O + 2,6\text{-NDCH}_2 + \text{bipy} \\ &\quad \rightarrow [M_3(2,6\text{-NDC})_3(\text{bipy})_{1.5}] \qquad (1) \\ &\quad (M = \text{Ni } (\mathbf{1}) \text{ or Co } (\mathbf{2})) \end{aligned}$$

The preparation of polymer **2** deserves some considerations. Contrary to the successful synthesis of polymer **1** by the hydrothermal reaction, the attempted synthesis of **2**, a cobalt analog of **1**, under the same conditions did not produce single crystals suitable for structure determination although the product appeared to be pure from the looks. We speculated that the poor solubility of bipy in water among many other possible causes was mainly responsible for the poor crystalline state of polymer **2**. Therefore, we decided to add benzene to the reaction mixture in order to facilitate the dissolution of bipy. Later on, we have found that reactions starting with a mixture of a benzene solution of bipy and an aqueous solution of $Co(NO_3)_2 \cdot H_2O$ and 2,6-NDCH$_2$ give the highest yields of **2**. This observation strongly supports our assumption that the low solubility of bipy hinders the formation of high-quality crystals. However, it still remains unclear why the similar reaction for **1** without added benzene produced single crystals. At any rate, because of the immiscibility of benzene and water, the formation of **2** presumably occurs at the interfaces between the two solvents. A

Table 2
Selected bond lengths (Å) and bond angles (°) in **1** and **2**

Bond lengths	
Ni1–O5	1.990(9)
Ni2–O2	2.006(8)
Ni3–N3	2.008(9)
Ni1–O1	2.012(8)
Ni2–O6	2.014(8)
Ni3–O9	2.015(8)
Ni1–Ni2	2.654(2)
Ni2–N1	2.028(9)
Ni3–Ni3#7	2.645(3)
Bond angles	
O5–Ni1–O1	89.0(3)
O6–Ni2–N1	94.6(4)
N1–Ni2–Ni1	175.3(3)
O2–Ni2–O6	90.8(3)
O2–Ni2–Ni1	81.7(3)
N3–Ni3–O9	94.4(4)
O2–Ni2–N1	94.1(4)
O6–Ni2–Ni1	83.5(3)
Bond lengths	
Co1–O5	2.048(11)
Co2–O2	2.054(11)
Co3–N3	2.055(10)
Co1–O1	2.025(10)
Co2–O6	2.029(11)
Co3–O9	2.030(10)
Co1–Co2	2.736(3)
Co2–N1	2.068(10)
Co3–Co3#8	2.725(4)
Bond angles	
O5–Co1–O1	89.5(4)
O6–Co2–N1	96.9(5)
N1–Co2–Co1	175.1(3)
O2–Co2–O6	91.0(3)
O2–Co2–Co1	81.9(4)
N3–Co3–O9	96.0(5)
O2–Co2–N1	93.7(5)
O6–Co2–Co1	81.1(3)

Symmetry transformations used to generate equivalent atoms: #7 = $-x, y, -z$; #8 = $-x-1/2, y-1/2, -z$.

similar approach was previously employed in the synthesis of $Cu_3(C_6H_8O_4)_3(H_2O)_2(C_6H_{11}OH)$, where a cyclohaxanol solution of adipic acid was layered on an aqueous solution of $Cu(OAc)_2 \cdot H_2O$ and heated at 120 °C. In this case, however, the solvent cyclohexanol is incorporated into the product as a ligand, different from the present system in which the benzene functions only as an aid to grow single crystals [23]. In addition, it is worth noting that Williams and co-workers recently carried out the hydro(solvo)thermal reaction of $Cu(NO_3)_2 \cdot H_2O$, $BDCH_2$, and bipy in the 1:1:1 mole ratio in 50% aqueous ethanol at 180 °C for 1 day. Their reaction produced an interpenetrating, 3-D Cu(I)–Cu(II) coordination polymer $[Cu_4(BDC)_3(bipy)_2]$, which has little porosity and consequently contains no guest molecules [24].

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

Bond lengths	
Co1–O2#1	2.014(3)
Co1–N2#3	2.169(3)
Co1–O1	2.039(2)
Co1–N1	2.169(3)
Co1–O4#2	2.141(2)
Co1–O3#2	2.234(3)
Bond angles	
O2#1–Co1–O1	110.8(1)
O2#1–Co1–N1	87.0(1)
N2#3–Co1–N1	176.9(1)
O1–Co1–O4#2	153.0(1)
O1–Co1–N1	88.3(1)
O1–Co1–O3#2	93.0(1)
O1–Co1–N2#3	94.0(1)
O4#2–Co1–N1	89.1(1)
N1–Co1–O3#2	88.4(1)

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

According to the TGA, polymer **1** exhibits no weight loss up to 430 °C, which indicates its thermal stability up to that temperature. An abrupt weight loss (57.7%) occurs between 430 and 480 °C, and above 480 °C the second process occurs to give an ultimate solid residue. Polymer **2** shows practically the same thermal behavior with a single weight loss step between 473 and 517 °C by 72.7% to result in $Co(CO_3)_2$ (calculated: 76.7%), which gradually decomposes into CoO at higher temperatures.

Polymers **1** and **2** are isostructural. We will discuss only polymer **1** in detail. The local coordination environments of the Ni metals (Ni1, Ni2, and Ni3) in polymer **1** with the atom-numbering schemes are shown in Figs. 1 and 2. Fig. 1 illustrates a SUB of a paddle-wheel of the type $[M_2(OOCR)_4]$, which comprises two nickel metals and four di(monodentate) bridging carboxylates. The Ni–O and Ni–N bond lengths lie in the range of 1.990(9)–2.015(8) and 2.005(9)–2.028(9) Å, respectively. In addition, the distances of Ni1–Ni2 and Ni3–Ni3 are 2.654(2) and 2.645(3) Å, respectively, indicating a Ni–Ni single bond. In crystal structure of **2**, the corresponding bond lengths are 1.996(11)–2.062(12) Å for Co–O, 2.055(10)–2.073(11) Å for Co–N, 2.736(3) Å for Co1–Co2, and 2.725(4) Å for Co3–Co3 (Table 2).

Each nickel metal has a pseudo-octahedral geometry, whose equatorial plane consists of four oxygen atoms from four 2,6-NDC carboxylates. In addition, the axial positions are occupied by one nickel atom and one nitrogen atom from the bipy ligand. Two nickel metals (Ni1 and Ni2) and four NDC ligands form the paddle-wheel SBUs, which are linked by 2,6-NDC ligands to give two square-grid nets in the [110] direction that subsequently interpenetrate. The remaining nickel metal (Ni3) and one 2,6-NDC form a half of another paddle-wheel whose partner is generated by the crystallographic

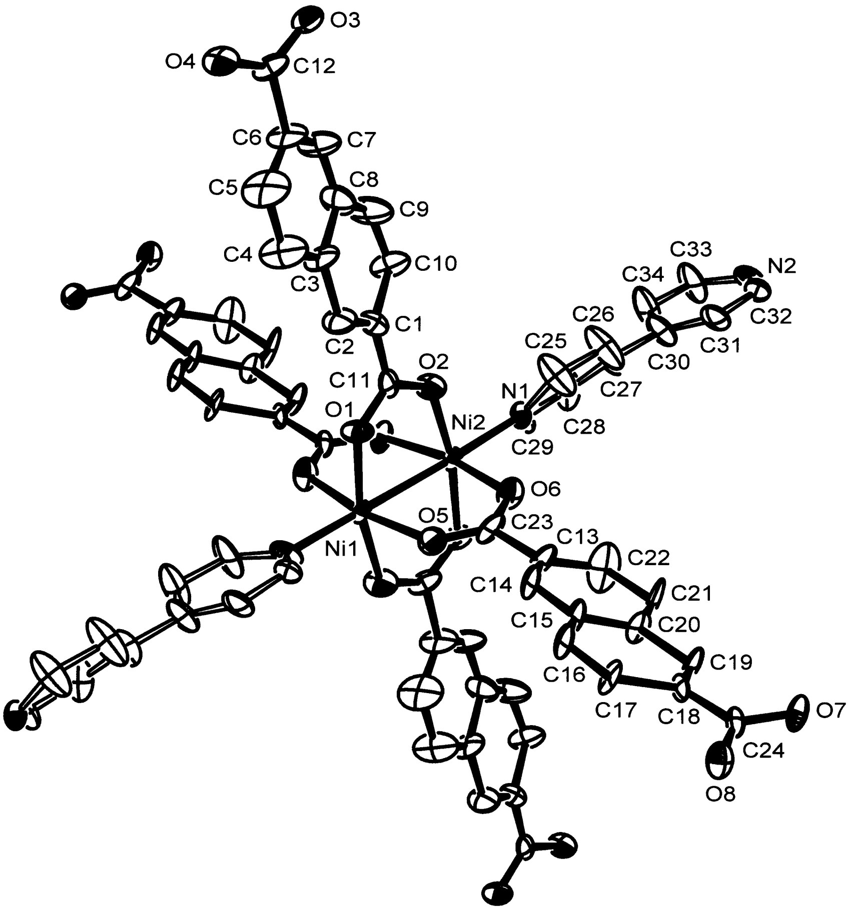

Fig. 1. ORTEP drawing of the local coordination environments of Ni1 and Ni2 in polymer **1**, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

inversion operation. The packing diagram resulting from a combination of the three units is illustrated in Fig. 3, where a light gray unit is a doubly interpenetrating unit and a dark gray unit is a single non-interpenetrating unit. In overall, polymer **1** (and **2**) is a triply interpenetrating 3-D polymer based on three square-grid networks in the [110] direction, which are linked by bipy ligands in the [001] direction. Although the constituent square grid, based on the paddle-wheel units and the 2,6-NDC ligands, has a relatively large dimension of 17.2 × 19.7 Å ($a \times b$) along the c-axis, the triple interpenetration has extremely reduced it to 4.3 × 4.3 Å.

Representing the points of extension of a SBU (that is, the carboxylate carbon atoms in a paddle-wheel

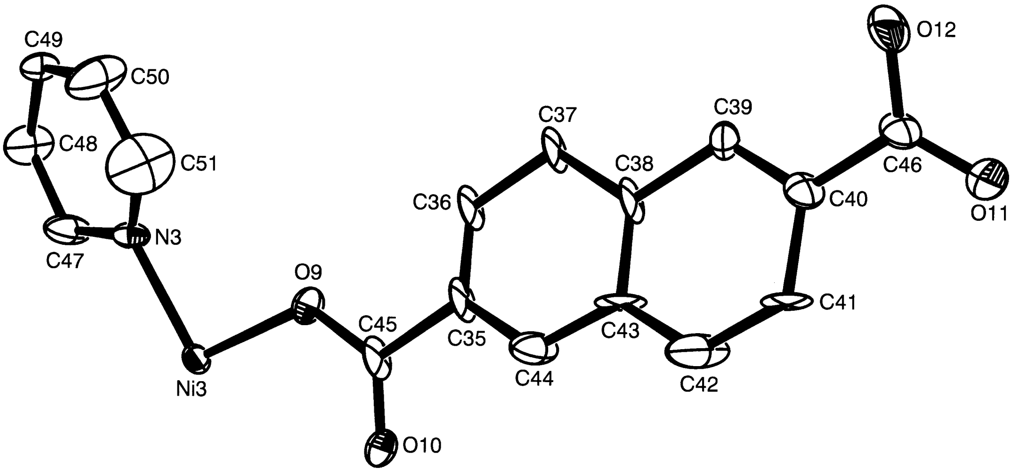

Fig. 2. Local coordination environment of Ni3 in polymer **1**.

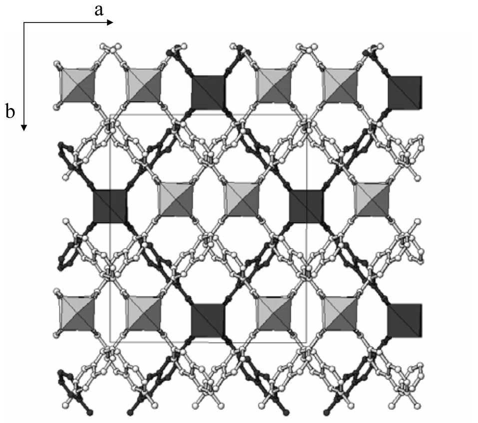

Fig. 3. A perspective view along the *c*-axis for a combination of the two polymers.

SBU) by simple points is frequently useful to describe and predict the topology of coordination polymers constructed by SBUs and organic spacers [25]. The paddle–paddle SBU in polymers **1** and **2** can be represented by a square as shown in Chart 1. The SBUs are linked to form porous 2-dimensional layers in the [110] direction, which are linked by organic spacers (bipyridines) in the [001] direction to give a 3-dimensional basic unit. A related zinc coordination polymer, $[Zn_2(2,6\text{-NDC})_3]\{(HNEt_3)(DEF)\}(ClBz)\}_2$ (DEF = *N*,*N′*-diethylformamide; ClBz = chlorobenzene), was very recently reported, in which the paddle-wheel SBUs ($[Zn_2(CO_2R)_4]$) are linked to form 2-dimensional layers that are spaced by the 2,6-NDC ligands [26]. Although the polymer $[Zn_2(2,6\text{-NDC})_3]\{(HNEt_3)(DEF)\}(ClBz)\}_2$ has the same SBU type as that in our polymers, this polymer does not form an interpenetrating polymer due to the presence of hydrogen-bonded guests that have probably prevented the interpenetration. Whereas 2,6-NDC ligands participate both in the formation of the SBU and in the linking of the SBUs in the polymer $[Zn_2(2,6\text{-NDC})_3]\{(HNEt_3)(DEF)\}(ClBz)\}_2$, the bipy ligands link the SBUs in polymers **1** and **2**. These observations suggest that large guests or hydrogen-bonded guest aggregates play an important role in the formation of non-interpenetrating porous polymers, as suggested by Yaghi and co-workers [11] and that the pyridine-type ligands can act as linear spacers in a mixed ligand system of carboxylates and pyridyls.

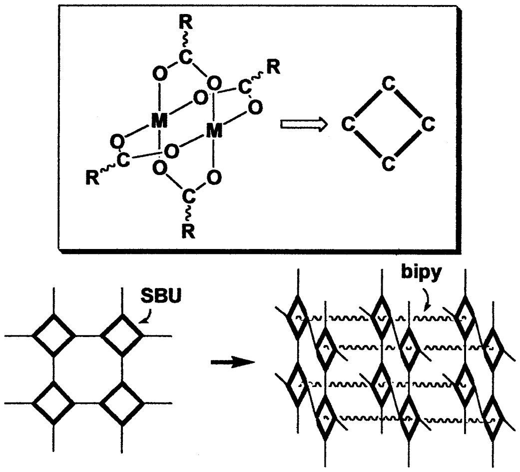

Chart 1.

3.2. Forming a 2-dimensional polymer by employing 1,3-BDCH$_2$

We have decided to employ 1,3-BDCH$_2$ instead of 2,6-NDCH$_2$ to prevent the interpenetration that occurs in the formation of polymers **1** and **2**. Because 1,3-BDCH$_2$ has a coordination angle of 120°, we expected a different topology of the polymer to be formed. As is consistent with our expectation, the different coordination angle of 1,3-BDCH$_2$ led to a totally different structure of the resulting coordination polymer. The hydrothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ with 1,3-BDCH$_2$ and bipyen gave a 2-dimensional coordination polymer with an empirical formula of [Co(1,3-BDC)(bipyen)] (Eq. (2)). Polymer **3** is also thermally stable up to 410 °C, and a drastic weight loss occurs at 410–450 °C, followed by a gradual decomposition at higher temperatures.

$$Co(NO_3)_2 \cdot 6H_2O + 1,3\text{-BDCH}_2 + \text{bipyen} \rightarrow [Co(1,3\text{-BDC})(\text{bipyen})]\ (\mathbf{3}) \tag{2}$$

Polymer **3** has an infinite 2-dimensional structure based on a double layer in which constituent layers are related by inversion. The monomer unit of **3** is shown in Fig. 4. The coordination sphere of cobalt can be described as a pseudo-octahedron, whose equatorial plane consists of two nitrogens from two bipyen ligands and two oxygens from two 1,3-BDC ligands. The axial sites are occupied by two carboxylate oxygens. The Co–N bond length is 2.169(3) Å and Co–O bond lengths are 2.014(3)–2.234(3) Å (Table 3).

Two carboxylate groups of 1,3-BDC ligand are distinct, one of which acts as a bidentate end. The other carboxylate group acts as a bis(monodentatate) bridge that links Co metals in the adjacent layers in the double layer unit. This phenomenon contrasts with that in polymers **1** and **2**, in which all four 1,3-BDC ligands act as a bis(monodentatate) ligand linking metals to form a paddle-wheel SBU. The 1,3-BDC ligands link the double layers in the [010] direction and the bipyen ligands in the [100] direction to complete an infinite 2-dimensional network (Fig. 5). Polymer **3** appears to have a rectangular channel of an approximate dimension of 9.7 × 10.1 Å ($a \times b$) along the *c*-axis.

In summary, two triply interpenetrating coordination polymers of the type $[M_3(2,6\text{-NDC})_3(\text{bipy})_{1.5}]$ (M = Ni;

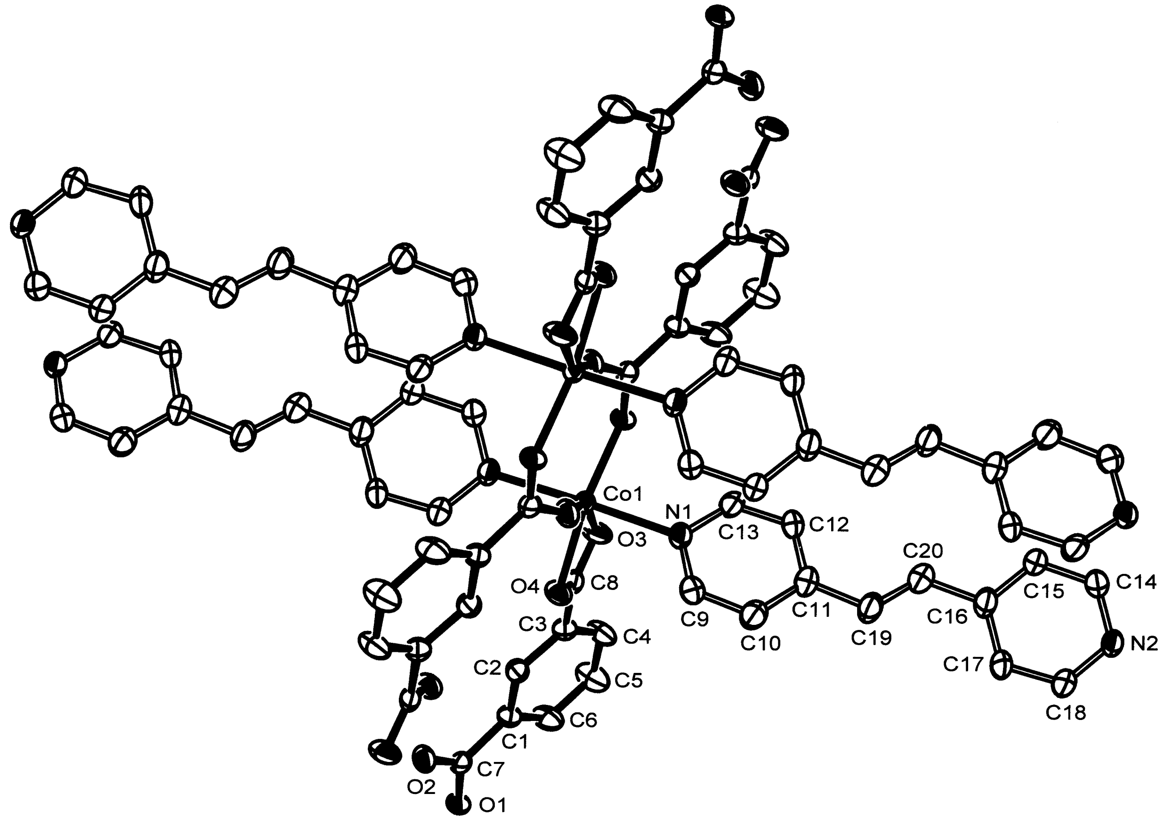

Fig. 4. Local coordination environment of Co in polymer **3**. Unlabeled atoms are related to the labeled atoms by the crystallographic inversion center.

Co) have been synthesized under hydrothermal or hydro(solvo)thermal conditions. Benzene was required to form high-quality crystals of polymer **2**. On the other hand, the hydrothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ with 1,3-$BDCH_2$ and bipyen gave a 2-dimensional coordination polymer with an empirical formula of [Co(1,3-BDC)(bipyen)]. These results indicate that a solvent composition and a coordination angle of a molecular building block can exert a great influence on the structural outcome of the resulting coordination polymer. Studies on the prevention of interpenetration are currently under study.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data

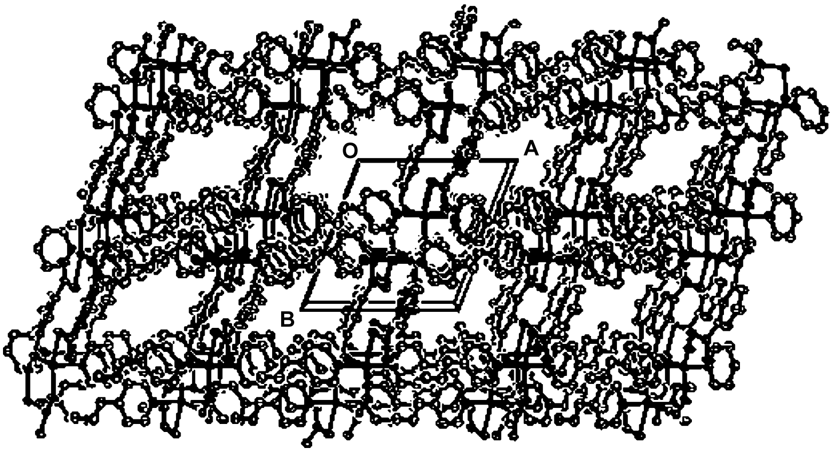

Fig. 5. A perspective view of polymer **3** along the *c*-axis.

Center, CCDC Nos. 197029–31 for polymers **1**, **2** and **3**. 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).

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