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Solvothermal Synthesis, Crystal Structure, and Characterization of Two New 2D Co(II)/Ni(II) Coordination Polymers with Mixed-Organic Tectonics[1]

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Abstract—Two new isomorphous coordination polymers $[Co(4,4'\text{-}Bpda)(Dpa)]_n$ (**I**) and $[Ni(4,4'\text{-}Bpda)(Dpa)]_n \cdot H_2O$ (**II**) ($4,4'\text{-}H_2Bpda$ = benzophenone-4,4'-dicarboxylic acid, Dpa = dipyridin-4-ylamine) were synthesized under solvothermal condition and characterized by elemental analysis, FT-IR and single-crystal X-ray diffraction technique. Compounds **I** and **II** exhibit 2D helical layers resulting from alternating single helical chains and double helical chains, which feature uninodal 4-connected topology with a point symbol of 6^6.

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INTRODUCTION

The rational design and synthesis of new crystalline coordination materials have achieved considerable attraction in synthetic chemistry and crystal engineering, owing to intriguing structural motifs but also for its potential for a variety of applications [1–6]. However, the controllable synthesis of crystalline architectures has been elusive and still remains great challenge in this field due to the fact that the self-assembly process is frequently influenced by various factors, such as the type and spatial disposition of binding sites of organic linkers, the metal-ligand ratio, medium, temperature, pH value, etc. [7–10]. Among them, the tectonic ligands with suitable functional groups (such as carboxylate, pyridyl) and molecular backbones are most pivotal in the structural regulation of the resultant structures [11, 12]. In this context, aromatic carboxylic acid and its derivatives have been extensively utilized as building tectonics to bridge different metal ions to generate diverse crystalline frameworks with interesting topological structures and properties. In our previous attempt to investigate the specific tectons of the ligands on the resulting structures, we obtained a series of new coordination polymers based on semirigid V-shaped aromatic carboxylate building blocks and various N-donor co-ligands [13–15]. To extend our previous research work and fully understand the coordination chemistry of this special tectons, we are interested in the utilization of another semirigid V-shaped phenyl dicarboxylate spacers, benzophenone-4,4'-dicarboxylic acid and investigated the role of this tecton, on constructing coordination crystalline architectures. Herein, we report the synthesis, crystal structure and characterization of two new coordination polymers, namely $[Co(4,4'\text{-}Bpda)(Dpa)]_n$ (**I**) and $[Ni(4,4'\text{-}Bpda)(Dpa)]_n \cdot H_2O$ (**II**), which constructed from mixed-ligands.

EXPERIMENTAL

Materials and instrumentation. All reagents and solvents were analytical grade and commercially available and used as supplied without further purification. Elemental analysis for carbon, hydrogen, and nitrogen were performed on a Vario EL III elemental analyzer. Infrared spectra were recorded using KBr pellets on a Thermo Electron NEXUS FTIR spectrophotometer in the 400–4000 cm^{-1} region. The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å).

Synthesis of compound I. A mixture of $Co(Ac)_2 \cdot 4H_2O$ (0.20 mmol, 0.0498 g), 4,4'-Bpda (0.20 mmol, 0.0540 g), Dpa (0.10 mmol, 0.0181g), 8 mL H_2O–EtOH (3 : 1), and 0.1 mol L^{-1} NaOH (4 mL) solution was stirred under air atmosphere for half an hour. Then the solution was transferred to a 25 mL stainless steel reactor with Teflon liner and heated to 140°C and held at that temperature for 72 h, then the reaction system

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[1] The article is published in the original.

Table 1. Crystal data and structure refinement information for compounds **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	498.35	508.14
Temperature, K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
Unit cell dimensions:		
a, Å	23.5601(7)	23.7102(6)
b, Å	12.1007(4)	12.1250(3)
c, Å	16.9032(5)	16.7934(4)
β, deg	106.732(3)	106.894(2)
Volumen Å^3; Z	4615.0(2); 8	4619.5(2); 8
Crystal size, mm	0.31 × 0.27 × 0.22	0.33 × 0.25 × 0.18
ρ_{calcd}, kg/m^3	1.435	1.461
μ(MoK_α), mm^{-1}	0.785	0.884
F(000)	2040	2096
θ Range, deg	3.13–25.05	2.96–25.04
Limiting indices	$28 \le h \le 27, -14 \le k \le 14, -20 \le l \le 20$	$-28 \le h \le 23, -8 \le k \le 14, -20 \le l \le 19$
Reections collected	9637	8083
Independent reflection, R_{int}	4083 (0.0372)	4076 (0.0263)
Data/restraints/parameters	4083/0/307	4076/3/321
Goodness-of-fit on F^2	1.052	1.026
R_1, wR_2 ($I > 2\sigma(I)$)	0.0537, 0.1427	0.0395, 0.0967
R indices (all data)	0.0741, 0.1565	0.0544, 0.1050
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.649/–0.406	0.546/–0.373

was cooled to room temperature, violet block crystals of compound **I** was obtained in 48% yield based on Co.

For $C_{25}H_{17}N_3O_5Co$

anal. calcd., %:	C, 60.25;	H, 3.44;	N, 8.43.
Found, %:	C, 60.20;	H, 3.45;	N, 8.45.

IR data (KBr; ν, cm^{-1}): 1665 m, 1638 m, 1615 s, 1543 m, 1525 w, 1437 m, 1395 s, 1298 w, 1265 m, 935 w, 825 w, 710 m, 635 m.

Synthesis of compound II. The similar synthetic procedure as that for **I** was used except that $Co(Ac)_2 \cdot 4H_2O$ (0.20 mmol, 0.0498 g) was replaced by $Ni(Ac)_2 \cdot 4H_2O$ (0.20 mmol, 0.0498 g). The green block crystals of **II** were obtained in 55% yield based on Ni.

For $C_{25}H_{19}N_3O_{5.5}Ni$

anal. calcd., %:	C, 59.09;	H, 3.77;	N, 8.27.
Found, %:	C, 60.13;	H, 3.75;	N, 8.35.

IR data (KBr; ν, cm^{-1}): 3430 br, 1657 m, 1635 m, 1620 s, 1545 m, 1520 w, 1434 m, 1385 s, 1280 w, 1247 m, 935 w, 820 w, 705 m, 628 m.

X-ray structure determination. Single crystal X-ray diffraction analyses of compound **I** and **II** were collected on Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using ω–2θ scan technique at room temperature. The structures were solved by direct methods with SHELXS-97 [16]. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [17]. Absorption corrections were applied by using multi-scan program SADABS [18]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. Generally, the positions of C/N-bound H atoms were generated by a riding model on idealized geometries. The H atoms of coordinated water molecules were first located in difference Fourier maps, and then fixed in the calculated sites as riding. The crystallographic data

Table 2. The selected bond lengths (Å) and bond angles (deg) for **I** and **II***

I		**II**	
Bond	*d*, Å	Bond	*d*, Å
Co(1)–O(1)	2.141(3)	Ni(1)–O(1)	2.196(2)
Co(1)–O(2)	2.192(3)	Ni(1)–O(2)	2.063(2)
Co(1)–N(1)	2.074(3)	Ni(1)–O(4*B*)	2.217(2)
Co(1)–O(3*A*)	2.267(3)	Ni(1)–O(5*B*)	2.054(2)
Co(1)–O(4*A*)	2.094(3)	O(4)–Ni(1*C*)	2.217(2)
Co(1)–N(2*B*)	2.103(3)	Ni(1)–N(1)	2.053(2)
N(2)–Co(1*C*)	2.103(3)	Ni(1)–N(2*A*)	2.038(2)
O(3)–Co(1*D*)	2.267(3)	N(2)–Ni(1*D*)	2.038(2)
O(4)–Co(1*D*)	2.094(3)	O(5)–Ni(1*C*)	2.054(2)
Angle	ω, deg	Angle	ω, deg
O(1)Co(1)O(2)	60.12(12)	O(1)Ni(1)O(4*B*)	88.56(8)
O(1)Co(1)O(3*A*)	86.56(12)	O(2)Ni(1)O(1)	61.47(7)
O(2)Co(1)O(3*A*)	113.37(12)	O(2)Ni(1)O(4*B*)	104.07(8)
O(4*A*)Co(1)O(2)	166.93(12)	O((5*B*))Ni(1)O(2)	162.93(8)
O(4*A*)Co(1)O(3*A*)	59.66(10)	O(5*B*)Ni(1)O(4*B*)	61.42(8)
O(4*A*)Co(1)O(1)	107.26(12)	O(5*B*)Ni(1)O(1)	106.96(8)
O(4*A*)Co(1)N(2*B*)	101.05(12)	N(1)Ni(1)O(1)	91.42(9)
N(1)Co(1)O(1)	107.33(13)	N(1)Ni(1)O(2)	97.91(9)
N(1)Co(1)O(2)	92.46(13)	N(1)Ni(1)O(4*B*)	154.89(9)
N(1)Co(1)N(2*B*)	92.84(13)	N(1)Ni(1)O(5*B*)	94.76(9)
N(1)Co(1)O(4*A*)	94.96(11)	N(2*A*)Ni(1)O(5*B*)	96.34(9)
N(1)Co(1)O(3*A*)	154.17(12)	N(2*A*)Ni(1)O(2)	94.68(9)
N(2*B*)Co(1)O(1)	143.23(13)	N(2*A*)Ni(1)N(1)	91.69(9)
N(2*B*)Co(1)O(2)	89.30(12)	N(2*A*)Ni(1)O(1)	156.14(9)
N(2*B*)Co(1)O(3*A*)	87.95(12)	N(2*A*)Ni(1)O(4*B*)	98.39(9)

* Symmetry transformations used to generate equivalent atoms: (*A*) $-x + 2, y - 1, -z + 3/2$; (*B*) $-x + 3/2, y - 1/2, -z + 1/2$; (*C*) $-x + 3/2, y + 1/2, -z + 1/2$; (*D*) $-x + 2, y + 1, -z + 3/2$ (**I**). (*A*) $-x + 3/2, y + 1/2, -z + 1/2$; (*B*) $-x + 2, y + 1, -z + 3/2$; (*C*) $-x + 2, y - 1, -z + 3/2$; (*D*) $-x + 3/2, y - 1/2, -z + 1/2$ (**II**).

for **I** and **II** are given in Table 1 and selected bond lengths and angles are listed and Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 964349 for **I**, 964350 for **II**; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The hydrothermal or solvothermal method has been extensively demonstrated to be a very promising technique for assembling novel and diverse network structures [19, 20]. By fine-tuning the reaction conditions, such as the reaction temperature, pH values, and the metal-to-ligand ratio, in this work, two new isomorphous coordination compounds were isolated in good crystalline forms under the similar synthetic strategy. Parallel experiments showed that appropriate volume ratio of H_2O–EtOH were crucial for the formation of resultant compounds. When the volume ratio of H_2O–EtOH was 3 : 1, good crystalline samples were obtained. If the volume ratio was set 1 : 1, 2 : 1 or other ratio, no crystalline samples were observed.

The compounds **I** and **II** are air stable and are insoluble in common organic solvents and water. The IR spectra of the two compounds were performed by KBr pellets in the range of 4000–400 cm^{-1}. The spectra show characteristic absorption bands mainly attributable to the carboxylate groups stretching vibrations. Two compounds display a strong absorption in the range of ~1600 to 1550 cm^{-1}, which may be assigned to the asymmetric stretching vibrations, and the strong bands at about ~1430 to 1390 cm^{-1} are attributed to the symmetric stretching vibrations.

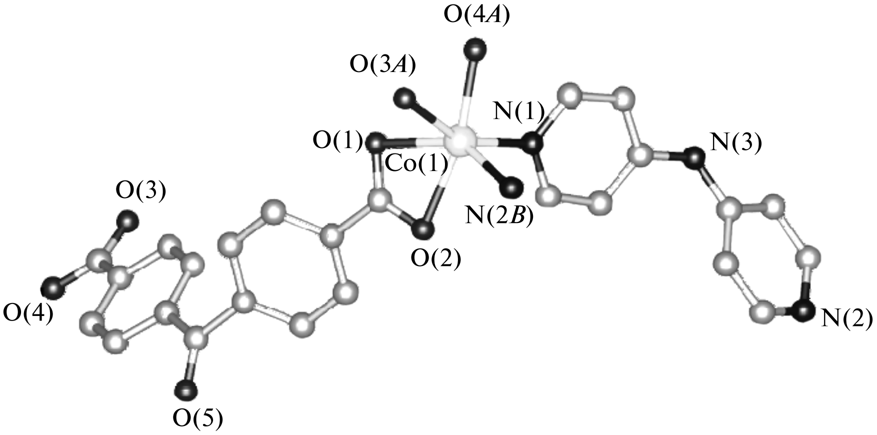

Fig. 1. Coordination environment of Co^{2+} ion of **I**.

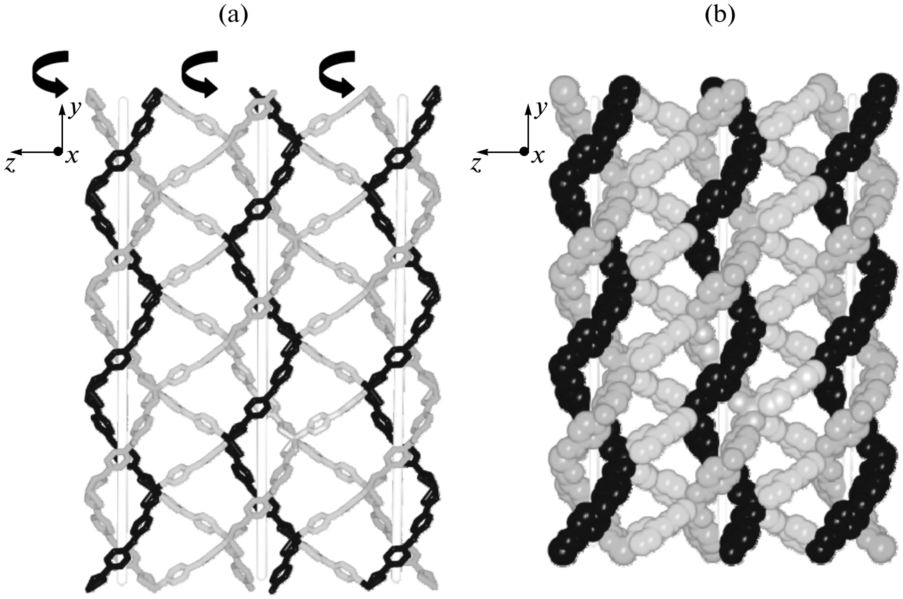

Fig. 2. View of the 2D right-handed helical layers directed by alternate single right-handed helical chains double right-handed helical chains (a); view of the space-filling model of 2D right-handed helical layers directed by Co(1) and mixed-ligands (b).

Single-crystal X-ray diffraction analysis reveals that compounds **I** and **II** are isostructural and feature similar 2D layer structures; herein, only the structure of **I** will be discussed in detailed as a representation. The asymmetric unit of **I** contains one crystallographic Co^{2+} ion, one 4,4'-Bpda ligands, and one Dpa molecule. As shown in Fig. 1, the Co(1) ion is coordinated by four oxygen atoms of two different 4,4'-$Bpda^{2-}$ anions, two nitrogen atoms of two different Dpa molecules, thus representing an obviously distorted octahedral geometry $\{Co[O_4N_2]\}$. The bond lengths of Co–N are 2.074(3) and 2.103(3) Å, and the Co–O lengths are in the range of 2.094(3)–2.267(3) Å, which are in good agreement with those found in other Co(II)-containing coordination complexes [21]. In **I**, the 4,4'-$Bpda^{2-}$ anions bridge Co^{2+} ion to form helical chain in bidentate chelate bridging mode, which are interconnected to each other through μ_2-Dpa ligands forming the 2D network (Fig. 2a). One noteworthy structural feature of **I** is the occurrence of single helical and double helical motif in the 2D net, constructed by dpa and 4,4'-Bpda ligands, respectively (Fig. 2a).

A close inspection of the crystal structure reveals that adjacent 2D helical layers have opposite handedness. One 2D layer composed of single right-handed helical chain and double right-handed helical chain (Fig. 2), the other in the neighboring layer fused single

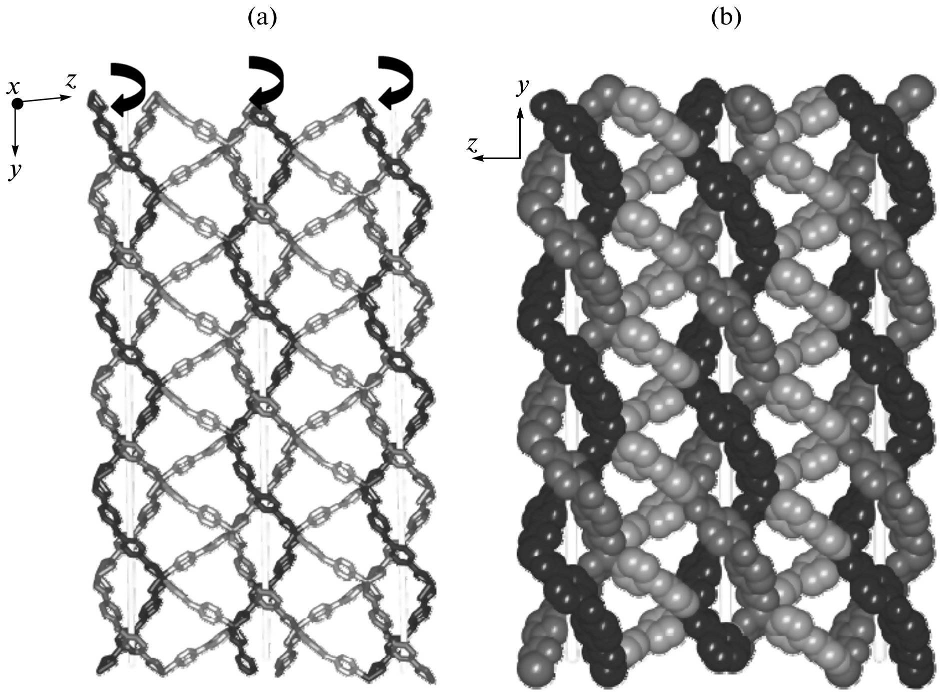

Fig. 3. View of the 2D left-handed helical layers directed by alternate single left-handed helical chains and doubleleft-handed helical chains (a); view of the space-filling model of 2D left-handed helical layers directed by Co(1) and mixed-ligands (b).

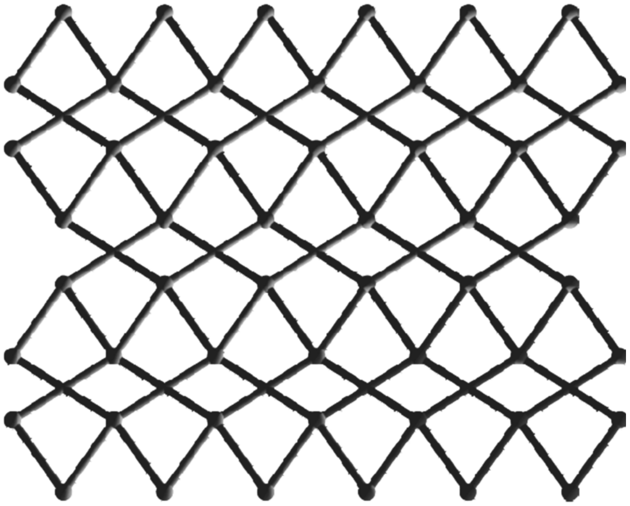

Fig. 4. Schematic description of the uninodal 4-connected topology with a point symbol of 6^6 of **I**.

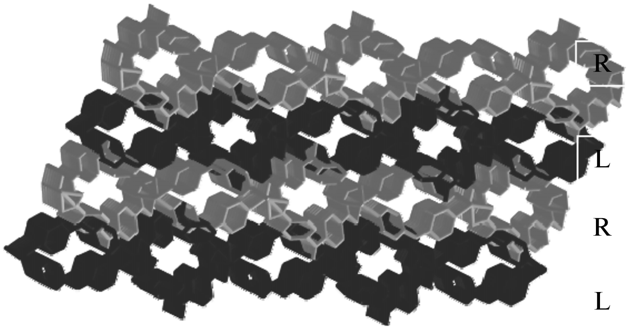

Fig. 5. The 3D packing diagram showing the RLRL pattern in **I**.

left-handed helical chain and double left-handed helical chain (Fig. 3). Topologically, this 2D net can be defined as a uninodal 4-connected topology with a point symbol of 6^6 (Fig. 4). Finally, the adjacent 2D layered structures stack in an –RLRL– pattern along the *x* axis and are packing a 3D mesomeric supramolecular framework (Fig. 5). To the best of our knowledge, few examples in which a mono-helical layer is constructed by mixed ligands have been found to exist in a stable crystalline solid [22, 23].

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