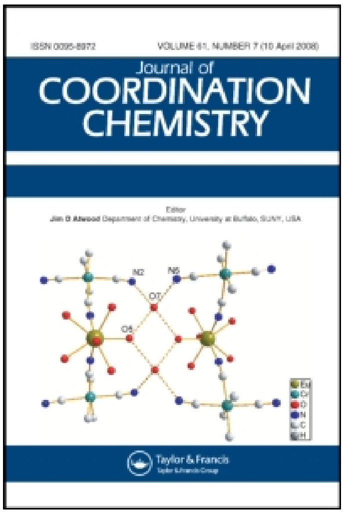

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Two helical coordination polymers constructed from V-shaped and chelate ligands

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Two helical coordination polymers constructed from V-shaped and chelate ligands

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The synthesis and X-ray characterization of two supramolecular isomers, $[Co(oba)(2,2'\text{-bpy})]_n$ (**1** and **2**) (oba = 4,4′-oxybis(benzoate), 2,2′-bpy = 2,2′-bipyridine) are reported. Crystal data for **1**: $a = 12.026(2)$, $b = 15.120(3)$, $c = 11.361(2)$ Å, $\beta = 91.46(3)^\circ$, $Z = 4$, $R_1 = 0.0330$, $wR_2 = 0.0949$. Crystal data for **2**: $a = 16.171(3)$, $b = 19.162(4)$, $c = 22.914(5)$ Å, $\alpha = 107.66(3)$, $\beta = 91.46(3)$, $\gamma = 98.99(3)^\circ$, $Z = 2$, $R_1 = 0.0388$, $wR_2 = 0.0456$. They are conformational supramolecular isomers without solvent molecules in the structures, and exhibit different one-dimensional helical structures that are further assembled into distinct two-dimensional layers *via* π–π stacking interactions. The results indicate that the geometry of ligand is one of the most important factors for the construction of a helical motif.

Keywords: Hydrothermal synthesis; Crystal structure; Supramolecular isomerism; Helical

1. Introduction

The rational design and construction of metal–organic coordination networks have received considerable attention in recent years in the field of supramolecular chemistry and crystal engineering, not only because of their intriguing structural motifs but also their potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics and molecular sensing [1–6]. To date, many metal–organic coordination networks with interesting compositions and topologies have been prepared and characterized using a variety of aromatic polycarboxylate ligands [7–11]. Linear polycarboxylate ligands, such as 1,4-benzenedicarboxylate, and 1,4-biphenyldicarboxylic acid have been widely used [12–17]. In addition to the common linear bridging ligands, it is profitable to explore nonlinear benzene polycarboxylates because they can be assembled around metal centers in diverse arrangements [18–20]. Recently, extensive studies have demonstrated that flexible or V-shaped *exo*-bidentate bridging ligands can be effectively used

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to construct helical structures [21–24]. However, 4,4′-oxybis(benzoate) (oba) is rarely used [25–27] although it has the ability to improve the helicity of polymeric chains. In order to obtain one-dimensional helical chain structures, we use 2,2′-bpy (2,2′-bpy = 2,2′-bipyridine) as co-ligand because chelating bipyridyl-like ligands may provide recognition sites for π–π stacking interactions to form interesting supramolecular structures.

In addition, 'supramolecular isomers' introduced by Zaworotko and coworkers are widely encountered in the field of crystal engineering [28]. Hydrothermal synthesis is an effective method for construction of supramolecular isomers. Very recently, Chen and coworkers have successfully isolated supramolecular isomeric polygons, molecular chains, zippers, zigzag and helical chains based on imidazolate derivatives under hydrothermal conditions [29–31].

In this article, we report two supramolecular isomers under hydrothermal conditions, $[Co(oba)(2,2'\text{-bpy})]_n$ (**1** and **2**) (oba = 4,4′-oxybis(benzoate)). Compounds **1** and **2** exhibit different one-dimensional helical structures that are further extended into interesting two-dimensional grid layer architectures.

2. Experimental

2.1. *Materials and general methods*

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

2.1.1. Synthesis of 1. A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.5 mmol, 0.146 g), H_2oba (0.6 mmol, 0.155 g), 2,2′-bpy (0.6 mmol, 0.094 g), triethylamine (1.2 mmol) and water (10 mL) was stirred for 20 min in air. The mixture was then transferred to a 23 mL Teflon reactor and kept at 160°C for 3 days, and then cooled to room temperature at a rate of $10^\circ C\,h^{-1}$. Brown crystals of **1** were obtained (yield: 83% based on Co). Elemental analysis for **1** Found: C, 61.42%; H, 3.30%; N, 5.71% (Calcd: C, 61.16%; H, 3.42%; N, 5.94%).

2.1.2. Synthesis of 2. A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (1.5 mmol, 0.45 g), H_2oba (2 mmol, 0.516 g), 2,2′-bpy (2 mmol, 0.313) triethylamine (1.5 mmol) and water (10 mL) in a 23 mL Teflon reactor, was kept under autogenous pressure at 140°C for 5 days and then cooled to room temperature at a rate of $10^\circ C\,h^{-1}$. Brown crystals of **2** were obtained (yield: 69% based on Co). Elemental analysis for **2** Found: C, 61.36%; H, 3.27%; N, 5.68% (Calcd: C, 61.16%; H, 3.42%; N, 5.94%).

2.2. *X-ray crystallography*

Single crystals of compounds **1** and **2** with dimensions $0.27 \times 0.17 \times 0.15\,mm^3$ (**1**) and $0.31 \times 0.24 \times 0.22\,mm^3$ (**2**) respectively, were glued on a glass fiber. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo-Kα monochromated radiation ($\lambda = 0.71073$ Å) at 293 K. Empirical absorption correction was applied. The structures were solved by the direct method and refined by full-matrix least-squares

Table 1. Crystal data and structure refinement of **1** and **2.**

	Compound **1**	Compound **2**
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	12.026(2)	16.171(3)
b (Å)	15.120(3)	19.162(4)
c (Å)	11.361(2)	22.914(5)
α (°)		107.66(3)
β (°)	91.46(3)	108.24(3)
γ (°)		98.99(3)
V (Å^3)	2065.2(7)	6173(2)
Z	4	2
D_c (g cm^{-3})	1.516	1.521
$F(000)$	964	2892
Reflections collected/unique	19883/4719	46816/23150
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0330$, $wR_2 = 0.0949$	R_1=0.0388, $wR_2 = 0.0456$

on F^2 using the SHELXTL crystallographic software package [32, 33]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. The crystal data and structure refinement of compounds **1** and **2** are summarized in table 1. Selected bond lengths and angles of compounds **1** and **2** are listed in table 2.

3. Results and discussion

Single-crystal X-ray analysis reveals that **1** and **2** are conformational supramolecular isomers without the presence of any guest component in the structures. In **1**, there are one crystallographic independent cobalt atom, one oba ligand, and one 2,2′-bpy ligand in the asymmetric unit. The fundamental unit is shown in figure 1. The cobalt(II) atom is coordinated by four oxygen atoms from two different oba ligands [Co(1)–O(1) = 2.1197(15), Co(1)–O(2) = 2.1635(15), Co(1)–O(4) = 2.1267(13), Co–O(5) = 2.1607(14) Å] and two nitrogen atoms from a chelate 2,2′-bpy ligand [Co(1)–N(1) = 2.0777(15), Co(1)–N(2) = 2.0869(16) Å], showing a distorted octahedral geometry. The V-shaped oba ligand acts as a bridge to link two adjacent Co(II) ions in a bis(bidentate) mode, resulting in a helical chain running along the *a* axis (figure 2). The helix is generated around the crystallographic 2_1 with a long pitch of 26.337 Å. The two benzene rings of oba ligand are severely bent (the dihedral angle between the benzene rings is ca 80.01°). The twist geometry of oba plays a key role in forming the helical structure because it results in the steric disposition of cobalt atoms. The 2,2′-bpy ligands are attached to both sides of the helical chain and adjacent two 2,2′-bpy ligands are nearly perpendicular each other with the dihedral angle of 87.1°. Two adjacent chains are linked in a zipper fashion into a two-dimensional grid layer (window size ca 13.92 × 25.24 Å) parallel to the *ab* plane through strong π–π stacking interactions of 2,2′-bpy ligands (face-to-face distance ca 3.54 Å) (figure 3).

Different from the structure of **1**, there are six cobalt ions, six oba ligands, and six 2,2′-bpy ligands in the asymmetric unit of **2**. Each cobalt atom is coordinated to four oxygen atoms from two different oba ligands [bond length range from 2.067 (10) to

Table 2. Selected Bond lengths [Å] and angles [°] for **1** and **2**.

*Compound **1***			
Co(1)–N(1)	2.0777(15)	Co(1)–O(2)	2.1635(15)
Co(1)–N(2)	2.0869(16)	Co(1)–O(4)	2.1267(13)
Co(1)–O(1)	2.1197(15)	Co(1)–O(5)	2.1607(14)
N(1)–Co(1)–N(2)	78.77(6)	N(2)–Co(1)–O(5)	154.93(5)
N(1)–Co(1)–O(1)#2	106.24(6)	O(1)#2–Co(1)–O(5)	102.46(6)
N(2)–Co(1)–O(1)#2	102.56(6)	O(4)–Co(1)–O(5)	61.45(5)
N(1)–Co(1)–O(4)	91.58(6)	N(1)–Co(1)–O(2)#2	166.16(6)
N(2)–Co(1)–O(4)	94.94(6)	N(2)–Co(1)–O(2)#2	97.33(6)
O(1)#2–Co(1)–O(4)	157.02(5)	O(1)#2–Co(1)–O(2)#2	61.35(5)
N(1)–Co(1)–O(5)	92.71(6)	O(4)–Co(1)–O(2)#2	102.03(6)
		O(5)–Co(1)–O(2)#2	95.99(6)
*Compound **2***			
Co(1)–N(9)	2.104(13)	Co(2)–N(5)	2.056(14)
Co(1)–O(9)	2.067(10)	Co(2)–O(19)	2.076(10)
Co(1)–O(11)	2.107(10)	Co(2)–O(21)	2.116(10)
Co(1)–N(10)	2.106(11)	Co(2)–N(6)	2.090(11)
Co(1)–O(10)	2.171(13)	Co(2)–O(20)	2.157(12)
Co(1)–O(12)	2.126(10)	Co(2)–O(22)	2.150(9)
Co(3)–N(7)	2.054(12)	Co(4)–N(3)	2.107(11)
Co(3)–O(14)	2.159(12)	Co(4)–O(24)	2.177(13)
Co(3)–O(16)	2.127(10)	Co(4)–O(26)	2.119(10)
Co(3)–N(8)	2.045(15)	Co(4)–N(4)	2.093(13)
Co(3)–O(15)	2.083(10)	Co(4)–O(25)	2.083(10)
Co(3)–O(17)	2.131(9)	Co(4)–O(27)	2.148(10)
Co(5)–N(11)	2.111(12)	Co(6)–N(1)	2.069(12)
Co(5)–O(4)	2.173(12)	Co(6)–O(29)	2.102(10)
Co(5)–O(6)	2.140(10)	Co(6)–O(2)#2	2.116(10)
Co(5)–N(12)	2.086(15)	Co(6)–N(2)	2.061(15)
Co(5)–O(5)	2.090(10)	Co(6)–O(30)	2.169(12)
Co(5)–O(7)	2.109(10)	Co(6)–O(1)#2	2.132(10)
O(9)–Co(1)–O(11)	158.6(4)	O(11)–Co(1)–N(9)	95.1(4)
O(9)–Co(1)–N(10)	99.9(4)	N(10)–Co(1)–N(9)	75.5(5)
O(11)–Co(1)–N(10)	96.6(4)	O(12)–Co(1)–N(9)	96.4(5)
O(9)–Co(1)–O(12)	103.5(4)	O(9)–Co(1)–O(10)	62.7(4)
O(11)–Co(1)–O(12)	61.5(4)	O(11)–Co(1)–O(10)	101.8(4)
N(10)–Co(1)–O(12)	156.3(4)	N(10)–Co(1)–O(10)	97.3(5)
O(9)–Co(1)–N(9)	102.1(4)	O(12)–Co(1)–O(10)	96.1(5)
N(9)–Co(1)–O(10)	162.4(4)	N(5)–Co(2)–O(19)	101.2(5)
N(5)–Co(2)–O(22)	95.0(5)	N(5)–Co(2)–N(6)	80.0(5)
O(19)–Co(2)–O(22)	104.0(4)	O(19)–Co(2)–N(6)	99.7(4)
N(6)–Co(2)–O(22)	156.3(4)	N(5)–Co(2)–O(21)	94.5(5)
O(21)–Co(2)–O(22)	61.4(4)	O(19)–Co(2)–O(21)	159.7(4)
N(5)–Co(2)–O(20)	161.6(4)	N(6)–Co(2)–O(21)	95.7(4)
O(19)–Co(2)–O(20)	61.9(4)	O(21)–Co(2)–O(20)	103.7(4)
N(6)–Co(2)–O(20)	95.2(5)	O(22)–Co(2)–O(20)	96.1(5)
N(7)–Co(3)–N(8)	77.9(5)	N(7)–Co(3)–O(17)	156.9(5)
N(7)–Co(3)–O(15)	99.7(4)	N(8)–Co(3)–O(17)	96.2(5)
N(8)–Co(3)–O(15)	102.3(5)	O(15)–Co(3)–O(17)	103.4(4)
N(7)–Co(3)–O(16)	95.9(4)	O(16)–Co(3)–O(17)	61.9(4)
N(8)–Co(3)–O(16)	94.0(5)	N(7)–Co(3)–O(14)	96.5(5)
O(15)–Co(3)–O(16)	159.4(4)	N(8)–Co(3)–O(14)	161.5(4)
O(16)–Co(3)–O(14)	104.1(4)	O(15)–Co(3)–O(14)	61.0(4)
O(17)–Co(3)–O(14)	95.5(5)	N(4)–Co(4)–O(25)	101.5(5)
O(25)–Co(4)–O(27)	103.5(4)	N(4)–Co(4)–N(3)	78.6(5)
N(3)–Co(4)–O(27)	156.8(4)	O(25)–Co(4)–N(3)	99.6(4)
O(26)–Co(4)–O(27)	61.3(4)	N(4)–Co(4)–O(26)	94.8(5)
N(4)–Co(4)–O(24)	161.7(4)	O(25)–Co(4)–O(26)	158.9(5)
O(25)–Co(4)–O(24)	62.0(4)	N(3)–Co(4)–O(26)	96.6(4)

(*Continued*)

Table 2. Continued.

N(3)–Co(4)–O(24)	95.7(5)	N(4)–Co(4)–O(27)	95.1(5)
O(26)–Co(4)–O(24)	103.1(4)	O(27)–Co(4)–O(24)	96.5(5)
N(12)–Co(5)–O(5)	102.4(5)	O(5)–Co(5)–O(6)	103.2(4)
N(12)–Co(5)–O(7)	93.9(5)	O(7)–Co(5)–O(6)	61.4(4)
O(5)–Co(5)–O(7)	158.7(5)	N(11)–Co(5)–O(6)	155.9(5)
N(12)–Co(5)–N(11)	77.3(5)	N(12)–Co(5)–O(4)	161.6(4)
O(5)–Co(5)–N(11)	100.8(4)	O(5)–Co(5)–O(4)	61.0(4)
O(7)–Co(5)–N(11)	96.0(4)	O(7)–Co(5)–O(4)	104.1(4)
N(12)–Co(5)–O(6)	95.1(5)	N(11)–Co(5)–O(4)	97.1(5)
O(6)–Co(5)–O(4)	96.5(5)		

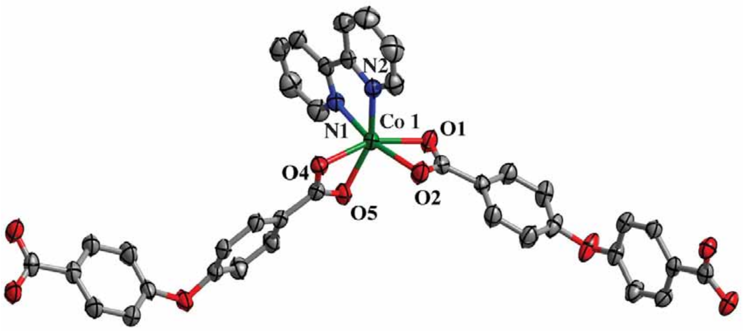

Figure 1. The coordination environment of cobalt atoms in **1**.

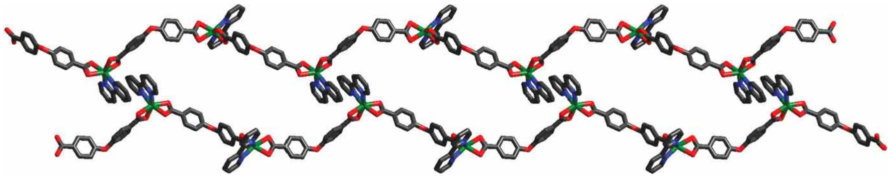

Figure 2. Views of the double-strand helical chains in **1**, showing the strong π–π stacking interactions between them.

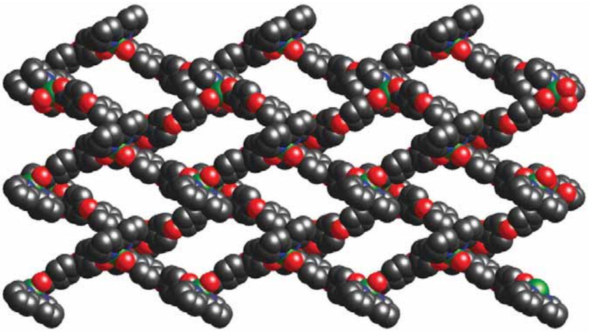

Figure 3. View of the two-dimensional grid layer along the *ab* plane of **1**.

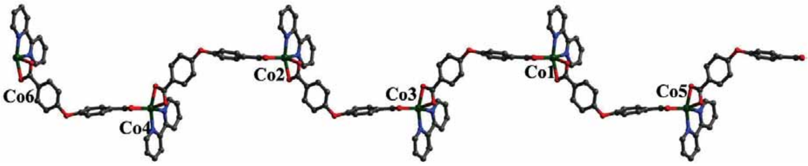

Figure 4. The coordination environments of cobalt atoms in **2**.

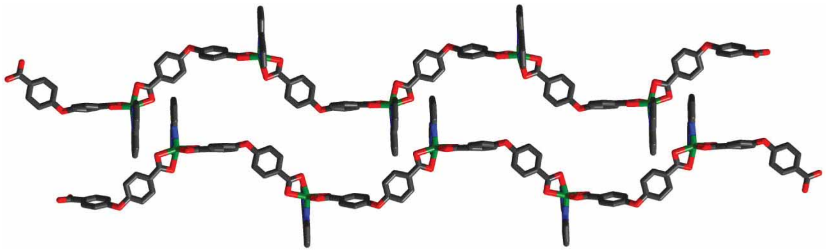

Figure 5. Views of the double-strand helical chains in **2**, highlighting the π–π stacking interactions between them.

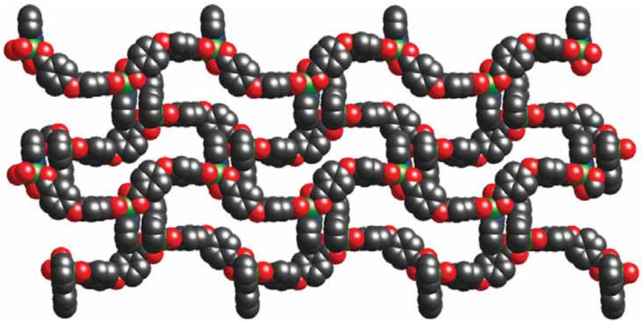

Figure 6. View of the two-dimensional grid layer along the *ab* plane of **2**.

2.177 (13) Å] and two nitrogen atoms from a 2,2′-bpy ligand [bond length range from 2.045(15) (10) to 2.111(12) Å], exhibiting a distorted octahedral geometry (figure 4). The length of an asymmetry unit is about 78 Å. Such a long asymmetric unit, to the best of our knowledge, is the longest in the [M/oba/L] (L = chelate ligands) system. Adjacent Co atoms are interconnected by V-shaped oba ligands in a bis(bidentate) fashion giving a helical chain running along the *a* axis with a pitch of 26.50 Å (figure 5). The dihedral angle between the phenyl rings of oba is ca 81.89°, larger than that in **1**. Different from **1**, lateral 2,2′-bpy ligands are parallel to each other. The π–π stacking interaction of 2,2′-bpy ligands between the adjacent helical chains is 3.81 Å which extends these chains into a two-dimensional grid layer containing a spindly cavity (figure 6). As expected, the crystal densities of these two polymers are rather similar (**1**, 1.516 g cm^{-3}; **2**, 1.521 g cm^{-3}).

In conclusion, combining V-shaped and chelate ligands we synthesized two helical supramolecular isomers $[Co(oba)(2,2'\text{-bpy})]_n$ (**1** and **2**) under hydrothermal conditions. The syntheses demonstrate the ability of V-shaped carboxylate ligands to construct helical structures. The judicious combination of metal atoms and V-shaped ligands enriches the chemistry of metal-based coordination polymers.

Supplementary data

Tables of crystal data and structure refinement details, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for nonhydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre, No. CCDC 261601 and 261602.

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