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Nano-dimensional square grid, helix chain, interpenetrated double layer, and chain of ring structures in new cobalt(II) metal–organic polymers based on 4,4'-oxybis-(benzoic acid) and 1,*n*-bis(imidazol-1-yl-methyl)benzene (*n* = 2, 3, 4)

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Four cobalt(II) coordination polymers, $[\text{Co}_2(\text{oba})_2(1,2\text{-bix})_2]_n$ (**1**), $[\text{Co}(\text{oba})(1,3\text{-bix})]_n$ (**2**), $\{[\text{Co}_4(\text{oba})_4(1,4\text{-bix})_4] \cdot 6\text{H}_2\text{O}\}_n$ (**3**), and $\{[\text{Co}_6(\text{oba})_6(1,4\text{-bix})_6] \cdot 2\text{H}_2\text{oba} \cdot 3\text{DMF} \cdot 11\text{H}_2\text{O}\}_n$ (**4**), where $\text{H}_2\text{oba} = 4,4'$ -oxybis(benzoic acid), DMF = N,N-Dimethyl formamide, and 1,*n*-bix = 1, *n*-bis(imidazol-1-yl-methyl)benzene (*n* = 2, 3, 4), have been synthesized. These compounds were structurally characterized by single-crystal X-ray crystallography, IR spectroscopy, and thermogravimetric analysis. Compound **1** exhibits a 2-D nano square grid (4,4) network, while **2** features a 2-D structure with two distinct left- and right-handed helical chains. Compound **3** possesses a doubly interpenetrated double-layered framework structure. The structure of **4** is comprised of 1-D chains of rings. The structural differences reveal that the flexible dicarboxylate and neutral bis(imidazole) are effective building blocks in constructing coordination polymers with diverse architectures.

Keywords: Cobalt(II); Metal–organic polymers; 4,4'-Oxybis(benzoic acid); Nano-dimensional square grid

1. Introduction

Much attention has been focused on potential properties of metal–organic polymers as functional materials [1–4], as well as intriguing architectures and topologies. To get desired structures, researchers often introduce N-containing auxiliary ligands into a metal–polycarboxylate system [5–12].

In this work, we have selected 4,4'-oxybis(benzoic acid) (H_2oba) as a linker that bridges metal centers and forms the skeleton of polymers [13–16]. With the aim of understanding the influence of neutral ligands on structural features, 1,*n*-bis(imidazol-1-yl-methyl)benzene (*n* = 2, 3, 4) were introduced [17–23]. The coordination sites are in different positions in the three N-containing ligands; the ligands can adopt different conformations to meet coordination geometry requirements of metal ions to increase dimensionality [24–26].

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We have synthesized four Co(II) metal–organic polymers, $[\text{Co}_2(\text{oba})_2(1,2\text{-bix})_2]_n$ (**1**), $[\text{Co}(\text{oba})(1,3\text{-bix})]_n$ (**2**), $\{[\text{Co}_4(\text{oba})_4(1,4\text{-bix})_4] \cdot 6\text{H}_2\text{O}\}_n$ (**3**), and $\{[\text{Co}_6(\text{oba})_6(1,4\text{-bix})_6] \cdot 2\text{H}_2\text{oba} \cdot 3\text{DMF} \cdot 11\text{H}_2\text{O}\}_n$ (**4**), where $\text{H}_2\text{oba} = 4,4'$ -oxybis(benzoic acid), DMF = N,N-Dimethyl formamide, and 1,n-bix = 1,n-bis(imidazol-1-yl-methyl)benzene ($n = 2, 3, 4$). Thermogravimetric analysis (TGA) and IR spectroscopy for **1–4** are also reported.

2. Experimental

2.1. Materials and measurements

Commercially available chemicals are of reagent grade quality and are used without purification. Ligands 1,n-bis(imidazol-1-ylmethyl)benzene ($n = 2, 3, 4$) were prepared according to the literature [27–29]. IR data were recorded on a Thermo Scientific Nicoletti. TGA were collected on a Perkin-Elmer Pyris1 TGA from room temperature to 800 °C with a heating rate of 20 °C/min under nitrogen. Single-crystal analyses were performed with the Bruker SMART APEXII CCD diffractometer for **1–4** using graphite monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K. Accurate unit cell parameters and orientation matrices for data collection were obtained from least-squares refinement. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 . Crystal data and refinement parameters are given in table 1. Selected bond lengths and angles are given in tables 2–5.

2.2. Preparation of 1–4

2.2.1. Syntheses of $[\text{Co}_2(\text{oba})_2(1,2\text{-bix})_2]_n$ (1**).** $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0421 g, 0.14 mmol), H_2oba (0.0251 g, 0.10 mmol), and 1,2-bix (0.0251 g, 0.11 mmol) were placed in a 15-mL Teflon-lined, stainless-steel Parr bomb with water (10 mL). The bomb was heated at 433 K for four days and cooled slowly to room temperature to furnish red block crystals. Anal. Calcd for $\text{C}_{56}\text{H}_{44}\text{Co}_2\text{N}_8\text{O}_{10}$ (%): C, 60.77; H, 4.01; N, 10.12. Found: C, 60.63; H, 3.95; N, 10.05. FT-IR (KBr pellet, cm^{-1}) selected bands: $\nu = 1597\text{s}, 1498\text{w}, 1383\text{s}, 1378\text{s}, 1237\text{s}, 1156\text{s}, 1106\text{s}, 101\text{m}, 949\text{m}, 879\text{s}, 782\text{m}, 740\text{m}, 656\text{s}$.

2.2.2. Syntheses of $[\text{Co}(\text{oba})(1,3\text{-bix})]_n$ (2**).** $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.0263 g, 0.11 mmol), H_2oba (0.0254 g, 0.098 mmol), and 1,3-bix (0.0261 g, 0.11 mmol) were placed in a 15-mL Teflon-lined, stainless-steel Parr bomb with water (10 mL). The bomb was heated at 433 K for four days and cooled slowly to room temperature to furnish red block crystals. $\text{C}_{28}\text{H}_{22}\text{CoN}_4\text{O}_5$ (%): C, 60.77; H, 4.01; N, 10.12. Found: C, 60.59; H, 3.87; N, 10.03. FT-IR (KBr pellet, cm^{-1}) selected bands: $\nu = 1594\text{s}, 1543\text{m}, 1519\text{m}, 1498\text{w}, 1382\text{s}, 1238\text{s}, 1157\text{m}, 1108\text{m}, 1092\text{m}, 1101\text{w}, 948\text{w}, 879\text{m}, 837\text{w}, 782\text{s}, 729\text{s}, 693\text{w}, 657\text{s}$.

2.2.3. Syntheses of $\{[\text{Co}_4(\text{oba})_4(1,4\text{-bix})_4] \cdot 6\text{H}_2\text{O}\}_n$ (3**).** A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0314 g, 0.11 mmol), H_2oba (0.0259 g, 0.1 mmol), and 1,4-bix (0.0246 g, 0.10 mmol) was dissolved in DMF (10 mL), and water (10 mL). The pale red solution was allowed to stand at room temperature. Good quality red crystals were obtained two weeks later. Anal. Calcd for $\text{C}_{112}\text{H}_{100}\text{Co}_4\text{N}_{16}\text{O}_{26}$ (%): C, 57.94; H, 4.34; N, 9.56. Found: C, 57.85; H, 4.31; N, 9.57. FT-IR (KBr pellet, cm^{-1}) selected bands: $\nu = 1687\text{m}, 1663\text{m}, 1597\text{s}, 1552\text{s}, 1495\text{s}, 1372\text{s}, 1300\text{m}, 1235\text{s}, 1167\text{s}, 1100\text{s}, 949\text{w}, 876\text{s}, 783\text{s}, 736\text{m}, 654\text{s}$.

Table 1. Crystal data and structure refinement for **1–4**.

Identification code	1	2	3	4
Formula	C ₅₆ H ₄₄ Co ₂ N ₈ O ₁₀	C ₂₈ H ₂₂ CoN ₄ O ₅	C ₁₁₂ H ₁₀₀ Co ₄ N ₁₆ O ₂₆	C ₂₀₅ H ₁₉₅ Co ₆ N ₂₇ O ₅₁
fw	1106.85	553.43	2349.77	4255.49
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	Pī	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	Pī
<i>a</i> (Å)	13.0323(9)	6.2784(14)	33.200(3)	13.3231(13)
<i>b</i> (Å)	14.4913(9)	23.605(6)	11.3866(10)	20.788(2)
<i>c</i> (Å)	15.0428(10)	16.862(4)	17.7241(16)	22.187(3)
α (°)	84.817(2)	90	90	113.580(3)
β (°)	65.3960(10)	102.816(8)	120.302(4)	105.255(3)
γ (°)	78.2150(10)	90	90	97.167(2)
<i>Z</i>	2	4	2	1
<i>V</i> (Å ³)	2528.5(3)	2436.7(10)	5784.9(9)	5246.3(10)
<i>D</i> _{calculated} /g cm ⁻³	1.454	1.509	1.349	1.347
<i>T</i> /K	298	298	298	298
μ /mm ⁻¹	0.726	0.753	0.643	0.549
<i>F</i> (000)	1140	1140	2424	2208
Crystal size/mm ³	0.23 × 0.15 × 0.12	0.35 × 0.21 × 0.15	0.25 × 0.22 × 0.15	0.25 × 0.21 × 0.15
θ (°)	1.75–25.10	2.87–25.10	2.13–25.10	1.62–25.10
Index ranges	–15 ≤ <i>h</i> ≤ 15 –17 ≤ <i>k</i> ≤ 17 –17 ≤ <i>l</i> ≤ 17	–7 ≤ <i>h</i> ≤ 7 –28 ≤ <i>k</i> ≤ 28 –17 ≤ <i>l</i> ≤ 20	–39 ≤ <i>h</i> ≤ 39 –12 ≤ <i>k</i> ≤ 13 –21 ≤ <i>l</i> ≤ 15	–15 ≤ <i>h</i> ≤ 15 –24 ≤ <i>k</i> ≤ 24 –26 ≤ <i>l</i> ≤ 26
Max./min. transmission	0.9180/0.8509	0.8954/0.7785	0.9097/0.8557	0.9222/0.8750
Data/restraints/parameters	8909/0/685	4281/72/361	5107/0/372	18,329/85/1380
GOF (<i>F</i> ²)	0.970	1.064	1.093	1.048
<i>R</i> ₁ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0519	0.0906	0.0758	0.0673
<i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.1589	0.2271	0.2205	0.1960
<i>R</i> ₁ ^a (all data)	0.0899	0.1139	0.0842	0.0856
<i>wR</i> ₂ ^b (all data)	0.2223	0.2445	0.2322	0.2126
Largest peak and hole, e·Å ⁻³	1.070, –0.670	1.386, –0.744	0.963, –0.844	1.074, –0.918

$$R_1^a = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2^b = [w(F_o^2 - F_c^2)^2 / w(F_o^2)]^{1/2}.$$

2.2.4. Syntheses of {[Co₆(oba)₆(1,4-bix)₆]·2H₂oba·3DMF·11H₂O}_n (4**).** A mixture of Co(NO₃)₃·6H₂O (0.0316 g, 0.11 mmol), H₂oba (0.0259 g, 0.10 mmol), and 1,4-bix (0.0241 g, 0.10 mmol) was dissolved in DMF (3 mL), then methanol (6 mL) was added. The dark red solution was allowed to stand at room temperature. Good quality red crystals were obtained three weeks later. Anal. Calcd for C₂₀₅H₁₉₄Co₆N₂₅O₅₁ (%): C, 58.71; H, 4.59; N, 9.22. Found: C, 58.56; H, 4.38; N, 9.14. FT-IR (KBr pellet, cm⁻¹) selected bands: ν = 1690m, 1673m, 1595s, 1557m, 1492m, 1378s, 1234s, 1156m, 1091s, 1010w, 950w, 876s, 769s, 669s.

3. Results and discussion

3.1. Crystal structures of **1–4**

3.1.1. Crystal structure of [Co₂(oba)₂(1,2-bix)₂]_n (1**).** Complex **1** crystallizes in the triclinic space group Pī. The asymmetric unit consists of two Co(II), two oba, and two 1,2-bis(imidazol-1-yl-methyl)benzene (1,2-bix). As shown in figure 1, the two crystallographically unique Co ions have almost the same coordination environments. Both adopt distorted tetrahedral geometries coordinated by two oxygens from two different oba and

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

Co(1)–O(1)	1.979(3)	Co(1)–N(1)	2.017(4)
Co(1)–O(5)#1	2.004(4)	Co(2)–O(6)	1.987(3)
Co(1)–N(5)	2.007(4)	Co(2)–N(4)	2.041(4)
O(1)–Co(1)–O(5)#1	97.39(15)	O(6)–Co(2)–O(9)#2	105.88(18)
O(1)–Co(1)–N(5)	109.64(16)	O(6)–Co(2)–N(8)#3	130.96(17)
O(5)#1–Co(1)–N(5)	109.16(15)	O(9)#2–Co(2)–N(8)#3	111.04(17)
O(1)–Co(1)–N(1)	98.91 (14)	O(6)–Co(2)–N(4)	105.46(16)
O(5)#1–Co(1)–N(1)	73.65(9)	O(9)#2–Co(2)–N(4)	93.98(17)
N(5)–Co(1)–N(1)	128.27(16)	N(8)#3–Co(2)–N(4)	103.02(15)

Symmetry transformations used to generate equivalent atoms: #1 $x, y-1, z$; #2 $x, y+1, z$; #3 $x-1, y+1, z-1$; #4 $x+1, y-1, z+1$.

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

Co(1)–O(4)#1	1.976(5)	Co(1)–N(3)#2	2.058(6)
Co(1)–O(2)	2.011(5)	Co(1)–O(1)	2.360(5)
Co(1)–N(1)	2.027(5)	O(4)#1–Co(1)–O(2)	119.5(2)
O(2)–Co(1)–N(3)#2	98.9(2)	O(2)–Co(1)–O(1)	60.10(18)
N(1)–Co(1)–N(3)#2	103.1(2)	N(1)–Co(1)–O(1)	87.8(2)
O(4)#1–Co(1)–O(1)	90.4(2)	N(3)#2–Co(1)–O(1)	158.7(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2, y+1/2, -z+1/2$; #2 $x, -y+1/2, z+1/2$; #3 $-x+2, y-1/2, -z+1/2$; #4 $x, -y+1/2, z-1/2$.

Table 4. Selected bond lengths (Å) and angles (°) for **3**.

Co(1)–O(4)#1	1.994(3)	Co(1)–N(1)	2.037(3)
Co(1)–O(1)	2.002(3)	O(4)–Co(1)#2	1.994(3)
Co(1)–N(3)	2.024(3)	O(4)#1–Co(1)–N(1)	101.85(13)
O(4)#1–Co(1)–O(1)	106.79(13)	O(1)–Co(1)–N(1)	134.17(13)
O(4)#1–Co(1)–N(3)	102.66(13)	N(3)–Co(1)–N(1)	104.41(13)
O(1)–Co(1)–N(3)	103.29(12)		

Symmetry transformations used to generate equivalent atoms: #1 $x+1/2, -y+1/2, z+1/2$; #2 $x-1/2, -y+1/2, z-1/2$; #3 $-x+1/2, -y+3/2, -z+1$; #4 $-x, y, -z+1/2$; #5 $-x+1/2, y+1/2, -z+1/2$.

two nitrogens from two 1,2-bix. Differences exist in the conformation of oba (the dihedral angle of the two benzene rings are *ca.* 63.05° and 79.0°). Like Co(1), Co(2) are also connected by oba into a 1-D [Co(oba)]_n chain. The Co···Co distance spanned by oba with different conformation is 14.4913(12) Å. The T-shaped 1,2-bix ligands (the dihedral angles of 86.40° and 86.81° between the phenyl and each imidazolyl ring) have connectivity with these 1-D [Co(oba)] chains forming a 2-D network structure (figure 2).

Consequently, a 2-D structure with nano square grid (4,4) size of *ca.* 1.4×1.42 nm (figure 2) is achieved by bridging 1,2-bix and oba ligands.

3.1.2. Crystal structure of [Co(oba)(1,3-bix)]_n (2**).** When the bis(imidazole) ligand, 1,3-bix, was introduced into the reaction system, **2** with a different 2-D structure was isolated. Crystallographic analysis reveals that **2** crystallizes in the monoclinic space group *P2₁/c*. The Co(II) in **2** is five-coordinate by two nitrogens from two 1,3-bix and three oxygens from two oba (figure 3). If the connections through 1,3-bix are temporarily

Table 5. Selected bond lengths (Å) and angles (°) for 4.

Co(1)–O(6)	1.971(6)	Co(1)–N(1)	2.028(7)
Co(1)–O(1)	2.003(5)	Co(1)–N(5)	2.005(7)
Co(2)–O(5)#1	1.978(5)	Co(2)–O12	2.008(5)
Co(2)–N(4)	2.019(7)	Co(2)–N(8)	2.022(6)
Co(2)–O(11)	2.384(6)	Co(3)–O(15)#2	1.972(6)
Co(3)–O(10)	1.982(6)	Co(3)–N(11)	2.002(7)
Co(3)–N(9)#2	2.020(7)		
O(6)–Co(1)–O(1)	104.7(2)	O(6)–Co(1)–N(5)	105.5(3)
O(1)–Co(1)–N(5)	129.0(2)	O(6)–Co(1)–N(1)	98.8(3)
O(1)–Co(1)–N(1)	107.6(2)	N(5)–Co(1)–N(1)	107.1(3)
O(5)#1–Co(2)–O(12)	106.4(2)	O(5)#1–Co(2)–N(4)	107.0(3)
O(12)–Co(2)–N(4)	127.8(2)	O(5)#1–Co(2)–N(8)	94.8(2)
O(12)–Co(2)–N(8)	105.7(2)	N(4)–Co(2)–N(8)	110.2(3)
O(5)#1–Co(2)–O(11)	165.0(2)	O(12)–Co(2)–O(11)	59.1(2)
N(4)–Co(2)–O(11)	86.5(2)	N(8)–Co(2)–O(11)	86.4(2)
O(15)#2–Co(3)–O(10)	102.9(3)	O(15)#2–Co(3)–N(11)	111.0(3)
O(10)–Co(3)–N(11)	122.7(2)	O(15)#2–Co(3)–N(9)#2	95.2(3)
O(10)–Co(3)–N(9)#2	113.5(3)	N(11)–Co(3)–N(9)#2	107.9(3)

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

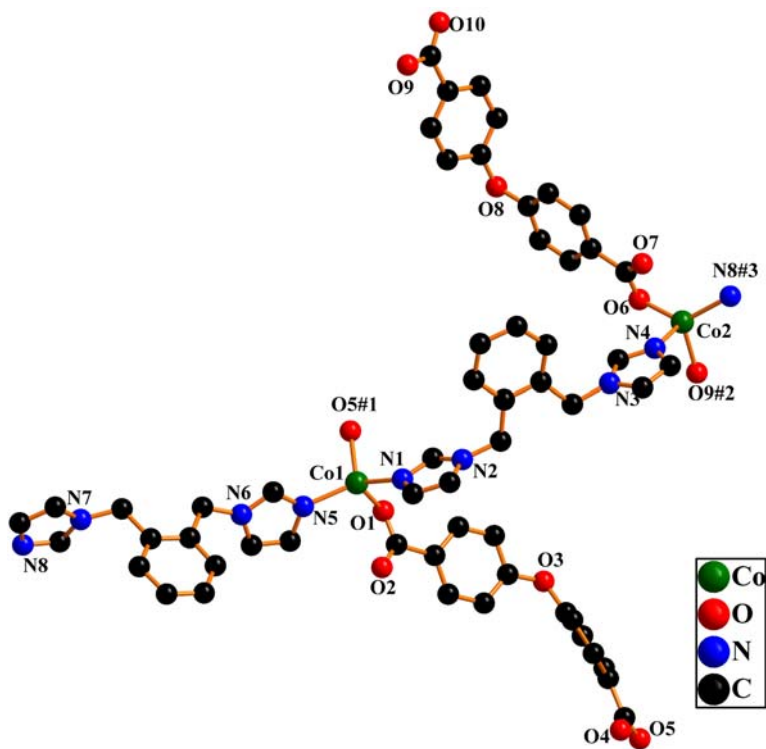


Figure 1. The crystal structure of $[\text{Co}_2(\text{oba})_2(1,2\text{-bix})_2]_n$ (hydrogens are deleted for clarity). Symmetry codes: #1 $x, y-1, z$; #2 $x, y+1, z$; #3 $x-1, y+1, z-1$.

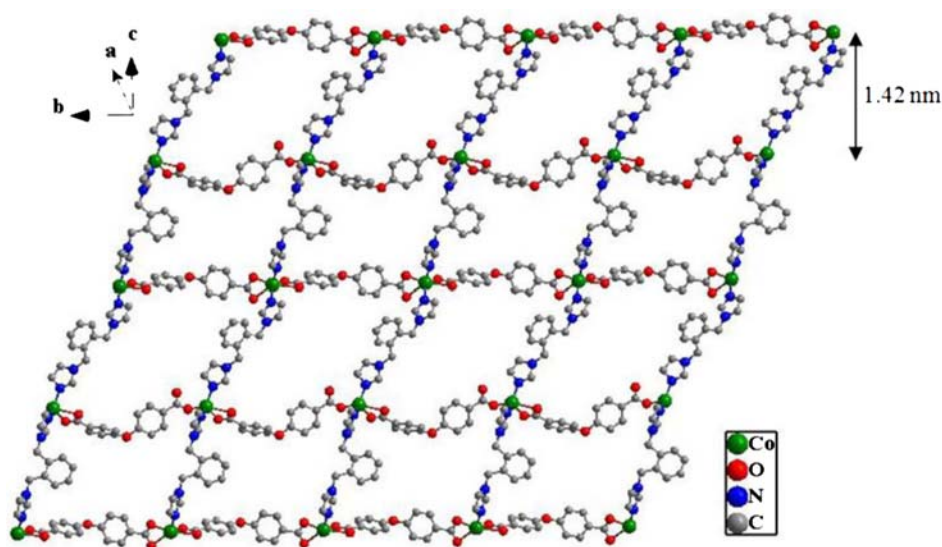


Figure 2. View of the 2-D network in 1.

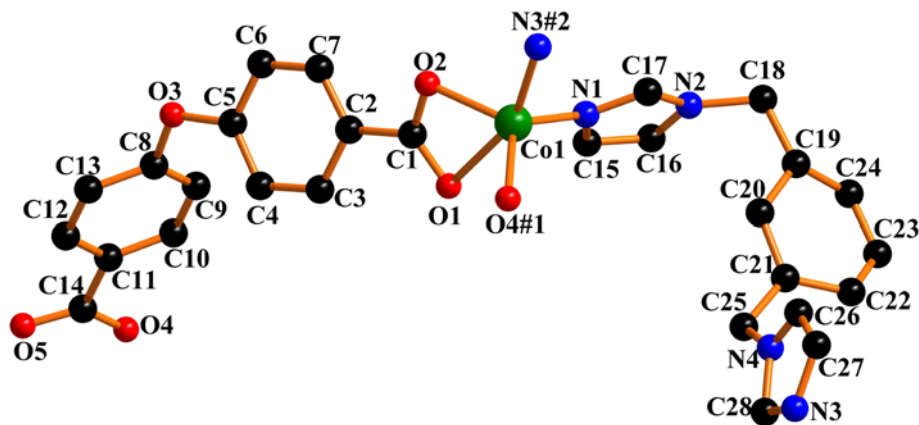


Figure 3. The crystal structure of $[\text{Co}(\text{oba})(1,3\text{-bix})]_n$ (hydrogens are deleted for clarity). Symmetry codes: #1 $-x+2, y+1/2, -z+1/2$; #2 $x, -y+1/2, z+1/2$.

ignored, adjacent Co(II) are bridged by *V*-shaped oba to form a 1-D $[\text{Co}(\text{oba})]$ helical chain [figure 4(b)]. Carboxylates of H_2oba adopt both monodentate and bidentate coordination, and the two benzene rings of oba are severely bent (the dihedral angle of the two benzene rings is *ca.* 69.57°). Compared with the twist of oba, the coordination of oba is more important in forming the helical structure. Two distinct left- and right-handed helical chains are linked by *L*-shaped 1,3-bix forming 2-D networks; *L*-shape arises from one imidazole located above or below the central benzene ring plane and the other imidazole ring being close to the benzene ring plane.

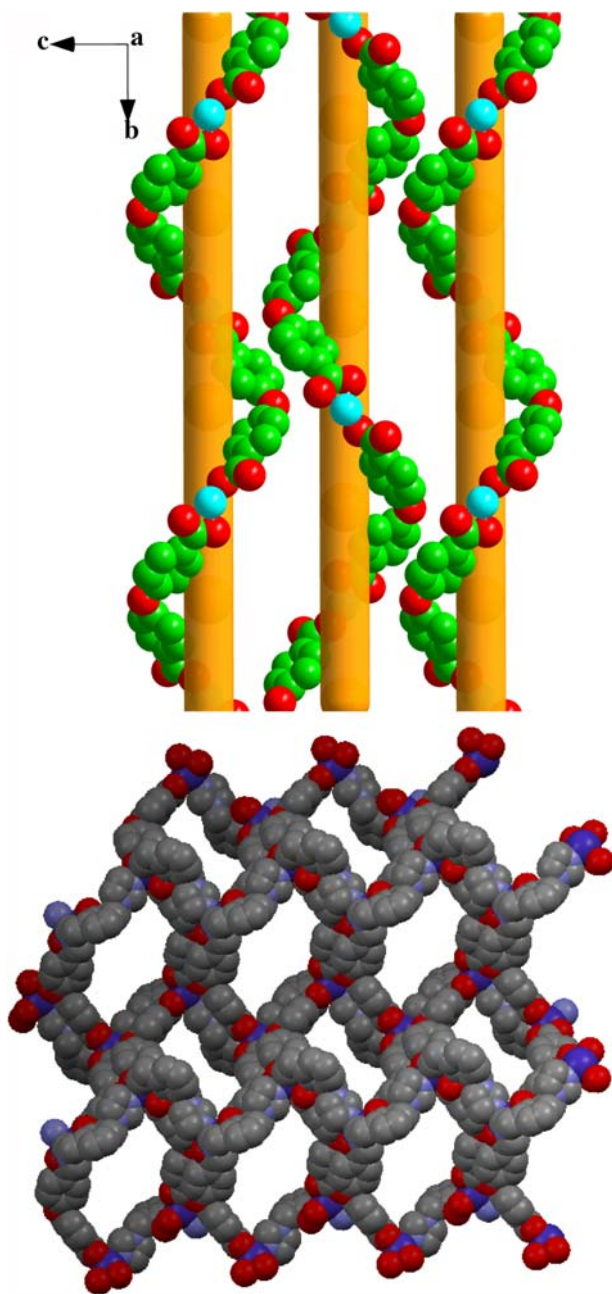


Figure 4. (a) Space-filling diagram of the L- and R-helical chains linked by oba and Co(II) centers and (b) view of the 2-D network in **2**.

3.1.3. Crystal structure of $\{[Co_4(oba)_4(1,4-bix)_4] \cdot 6H_2O\}_n$ (3**).** Complex **3** crystallizes in the monoclinic space group $C2/c$. The asymmetric unit consists of four Co(II), four oba, and four 1,4-bix. Co(II) is a distorted tetrahedron coordinated by two oxygens from two different oba and two nitrogens from two 1,4-bix (figure 5). Carboxylates of H_2oba have

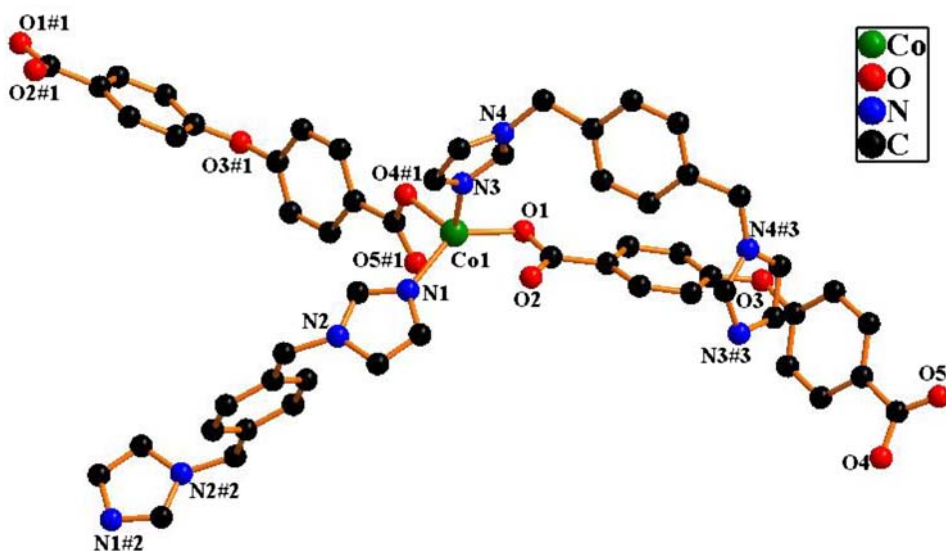


Figure 5. The crystal structure of $\{[\text{Co}_4(\text{oba})_4(1,4\text{-bix})_4]\cdot 6\text{H}_2\text{O}\}_n$ (**3**) (free waters and all hydrogens have been omitted for clarity).

Symmetry codes: #1 $x+1/2, -y+1/2, z+1/2$; #2 $-x+1/2, -y+3/2, -z+1$; #3 $-x, y, -z+1/2$.

monodentate coordination for tetrahedral cobalt, and oba link Co(II) to produce two anti-parallel 1-D wave-like single chains (figure 6). Adjacent Co ions, which belong to different chains of two reverse parallel single chains, are connected by *U*-shaped 1,4-bix from up or down alternately (figure 6). So, two reverse parallel 1-D single chains turn to a double chain. However, the most fascinating structural feature of **3** is that neighboring double chains are connected by 1,4-bix ligands forming a 2-D “sandwich” structure. As shown in

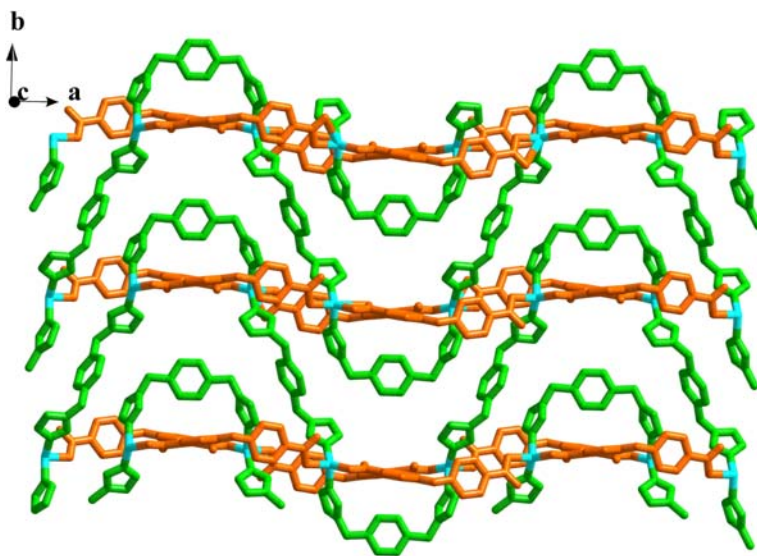


Figure 6. Part of the 2-D “sandwich” structure within **3**: green, 1,4-bix; orange, oba; sky blue, Co. Hydrogens and waters have been deleted for clarity. (see <http://dx.doi.org/10.1080/00206814.2013.779211> for color version.)

figure 6, two adjacent Co(II) ions, which belong to different chains of the equivalent layers, are linked by Z-shaped 1,4-bix like a ladder. The 1,4-bix connected Co(II) giving rise to two distinct wave-like 1-D $[\text{Co}(1,4\text{-bix})]_n$ polymer chains.

3.1.4. Crystal structure of $\{[\text{Co}_6(\text{oba})_6(1,4\text{-bix})_6]\cdot 2\text{H}_2\text{oba}\cdot 3\text{DMF}\cdot 11\text{H}_2\text{O}\}_n$ (4). Complex 4 crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of six Co ions, six oba, and six 1,4-bix. As shown in figure 7(a), Co(1) and Co(3) have almost the same coordination environments, which are different from Co(2). Both have distorted tetrahedral geometries coordinated by two oxygens from two different oba and two nitrogens from two 1,4-bix, but Co(2) is five-coordinate by two nitrogens from two 1,4-bix and three oxygens from two oba. Like 3, Co(II) are also connected by oba generating two reverse parallel 1-D wave-like single chains in 4. However, two U-shaped 1,4-bix link adjacent Co(II) ions of two reverse parallel $[\text{Co}(\text{oba})]$ chains to give a four-membered ring $[\text{Co}_2(1,4\text{-bix})_2]$. The U-shaped 1,4-bix ligands link two reverse parallel 1-D wave-like single chains and convert them to a 1-D cycle.

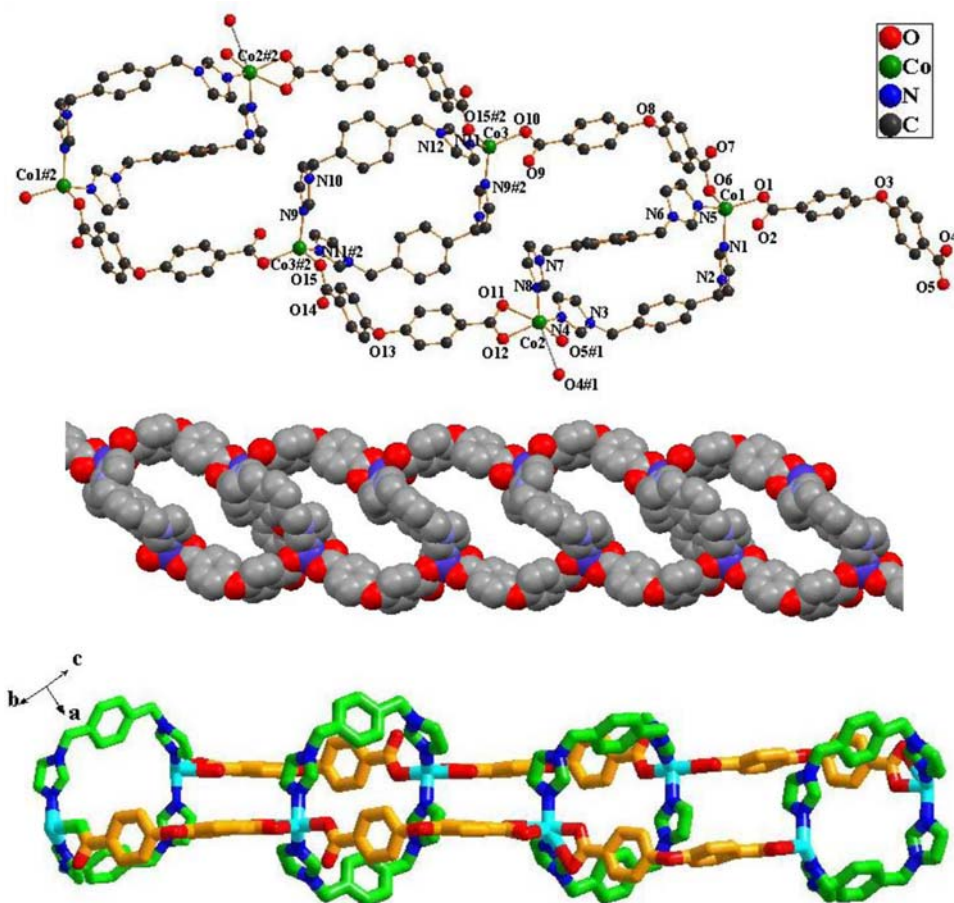


Figure 7. The crystal structure of $\{[\text{Co}_6(\text{oba})_6(1,4\text{-bix})_6]\cdot 2\text{H}_2\text{oba}\cdot 3\text{DMF}\cdot 11\text{H}_2\text{O}\}_n$ (4) (free water, DMF, H_2oba and all hydrogens are deleted for clarity).

Symmetry codes: #1 $-x+3, -y+1, -z+1$; #2 $-x+1, -y+2, -z$.

3.2. Thermal analyses

To examine the thermal stability of **1–4**, TGA were carried out from room temperature to 800 °C under nitrogen (Supplementary material). TGA revealed that **1** is stable up to 375 °C. Decomposition occurs between 375 and 750 °C with a mass loss of 77.8%. Thermal behavior of **1** and **2** is similar. Compound **2** is stable up to 345 °C. Decomposition of **2** occurs between 345 and 633 °C with a mass loss of 71.4% (Calc 72.9%). A mass loss calculation of the end residue shows the formation of CoO. Compound **3** is stable up to 200 °C, then the lattice water begin to be lost. The solid residue formed at around 200 °C is suggested to be $[\text{Co}_4(\text{oba})_4(1,4\text{-bix})_4]_n$. Compound **4** is stable up to 80 °C with decomposition occurring between 80 and 800 °C with a mass loss of 75.2%.

4. Conclusions

Four new coordination polymers with diverse architectures were prepared with three structurally related flexible bis(imidazole) ligands with Co(II) salts and H₂oba. The results show that the V-shaped oba ligands display their characteristic distinct coordination modes, but introduction of N-donor ligands with different positions and conformations plays an important role, which enriches the diversity of structures. All are highly thermally stable.

Supplementary material

Crystallographic data for the structure reported in the article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-865815, 865816, 865814, 865813 for **1–4**, respectively. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax:+44-1223/150 336033; E-mail: deposit@ccdc.cam.ac.uk].

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